Homolytic Organometallic Reactions. Part IX.[1] An Electron Spin Resonance Study of the Mechanism of β-Scission of Tetra-alkoxyphosphoranyl Radicals. Formation of Trialkoxy(methyl)phosphoranyl Radicals

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The rate of β-scission of the tetra-alkoxyphosphoranyl radicals $(RO)_4P\cdot$, where the alkyl groups may be the same or different, is determined by configurational, steric, electronic, and solvent effects. The rate of C–O cleavage increases along the series $R^p < R^s < R^t < PhCH_2$. In the distorted trigonal bipyramidal radical $(RO)_4P\cdot$, alkyl groups in apical or equatorial positions are not lost at the same rate, probably those in the equatorial position undergoing more rapid β-scission. As a result of this configurational selectivity, bulky alkyl groups are retained preferentially when $(RO)_4P\cdot$ decomposes. The rate of scission of $(EtO)_3\dot{P}OBu^t$ increases somewhat with the solvent polarity, but there appears to be little steric acceleration when $(RO)_4P\cdot$ contains bulky alkyl groups. Methyl radicals react with trialkyl phosphites to give the radicals $(RO)_3\dot{P}Me$ at a rate which is governed primarily by steric effects. $PhCH_2O\dot{P}(OEt)_2Me$ undergoes rapid β-scission to give a benzyl radical.

COMPOUNDS of trivalent phosphorus can react with free radicals to produce phosphoranyl radicals which may undergo subsequent α- or β-scission.[2]

$$A{-}B\cdot + PX_3 \rightleftharpoons A{-}B{-}\dot{P}X_3 \qquad (1)$$

$$A{-}B{-}\dot{P}X_3 \left\{ \begin{array}{l} \xrightarrow{\alpha\text{-scission}} A{-}B{-}PX_2 + X\cdot \\ \xrightarrow[\beta\text{-scission}]{} A\cdot + B{=}PX_3 \end{array} \right. \qquad (2)$$

U.v. irradiation of solutions containing dialkyl peroxides and trialkyl phosphites has been used to produce tetra-alkoxyphosphoranyl radicals for study by e.s.r.

$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO\cdot \qquad (3)$$

$$Bu^tO\cdot + P(OEt)_3 \longrightarrow Bu^tO\dot{P}(OEt)_3 \qquad (4)$$

$$Bu^tO\dot{P}(OEt)_3 \longrightarrow Bu^t\cdot + OP(OEt)_3 \qquad (5)$$

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[1] Part VIII, preceding paper.

[2] A. G. Davies and B. P. Roberts, *Nature Physical Sciences*, 1971, **229**, 221; K. U. Ingold and B. P. Roberts, 'Free Radical Substitution Reactions,' Wiley-Interscience, New York, 1971, ch. 6.

spectroscopy.[3,4] Using e.s.r. to monitor the concentrations of the phosphoranyl and t-butyl radicals we have determined k_5 which is given by,[4] $\log (k_5/\mathrm{s}^{-1}) = 12{\cdot}94 - 10{\cdot}34$ kcal mol^{-1}/θ where $\theta = 2{\cdot}303RT$ kcal mol^{-1}, and $k_5\,(-60°) = 2{\cdot}1 \times 10^2\ \mathrm{s}^{-1}$.

In this kinetic analysis, however, the possibility that different configurations of the distorted trigonal bipyramidal triethoxy-t-butoxyphosphoranyl radical might have different reactivities was not explored. We have now undertaken a systematic study of the constitutional and environmental effects which govern the rates of formation and subsequent decomposition of phosphoranyl radicals in solution. In this paper we discuss the identification by e.s.r. spectroscopy, and the β-scission, of a series of tetra-alkoxyphosphoranyl radicals produced by reaction of alkoxy radicals (generated photolytically from dialkyl peroxides, dialkyl hyponitrites, or alkyl nitrites) with trialkyl phosphites.

RESULTS

(a) *Trialkyl Phosphites and Ethoxyl Radicals from Diethyl Peroxide.*—Using diethyl peroxide as a photolytic source of ethoxyl radicals we have examined a series of trialkoxyethoxyphosphoranyl radicals, $\mathrm{EtO\dot{P}(OR)_3}$. The radicals and their spectroscopic parameters are listed in Table 1.

The phosphite was added to a solution containing diethyl peroxide just prior to insertion into the spectrometer cavity in order to avoid any slow thermal reaction to give penta-alkoxyphosphorane.[5,*]

In general the e.s.r. lines of the phosphoranyl doublet were of unequal width, especially at low temperature and in solvents of relatively high viscosity when tumbling of the radical in solution was inhibited. Normally the high field line was broader than that at low field, typically 2 G and 1·5 G respectively for $\mathrm{(EtO)_4P\cdot}$ in cyclopentane at −70°. As the temperature was increased the concentration of the phosphoranyl radicals decreased whilst that of the alkyl radicals produced by their β-scission increased. There was a general increase in the phosphorus hyperfine splitting as the bulk or electronegativity of the attached alkoxy-groups increased.[4] In general the phosphoranyl radicals showed a decrease in the phosphorus hyperfine splitting as the temperature was decreased.

Triethyl phosphite. The kinetics of β-scission of the tetraethoxyphosphoranyl radical in cyclopentane were examined in the temperature range −38 to +10°.

$$\mathrm{(EtO)_4P} \longrightarrow \mathrm{Et\cdot} + \mathrm{OP(OEt)_3} \qquad (6)$$

$$\left.\begin{array}{r} 2\mathrm{Et\cdot} \longrightarrow \\ \mathrm{Et\cdot} + \mathrm{(EtO)_4P\cdot} \longrightarrow \end{array}\right\} \text{non-radical products} \qquad \begin{array}{c}(7)\\(8)\end{array}$$

Using the method which we have described previously [4,6] $(2k_7/k_8)$ was given by $\log (2k_7/k_8/1\ \mathrm{mol}^{-1}) = -2{\cdot}12 + 10{\cdot}95$ kcal mol^{-1}/θ. Between −9 and −38° the ratio $2k_7/k_8$ increases from 5·1 to 6·4 such that $\log (2k_7/k_8) = -0{\cdot}16 + 1{\cdot}05$ kcal mol^{-1}/θ although the accuracy of the Arrhenius parameters is probably poor.

TABLE 1

Trialkoxyethoxyphosphoranyl radicals $\mathrm{EtO\dot{P}(OR)_3}$ obtained from the interaction of ethoxyl radicals with trialkyl phosphites

Phosphite	Solvent [a]	t/°C	a(P)/G [b]	g [b]
$\mathrm{(MeO)_3P}$	C	−70	884·0	2·003
$\mathrm{(EtO)_3P}$	C	−70	884·5	2·003
	H	−70	884·7	2·003
	H	−20	886·2	2·003
$\mathrm{(ClCH_2CH_2O)_3P}$	C	−70	912·1	2·002
$\mathrm{(CF_3CH_2O)_3P}$	H–THF	−70	954·4	2·003
	H–THF	−20	953·8	2·003
$\mathrm{(Pr^iO)_3P}$	C	−70	889·5	2·003
$\mathrm{(Bu^nO)_3P}$	C	−70	887·9	2·003
$\mathrm{(Bu^tO)_3P}$	C	−90	907·4	2·004
	C	−70	908·6	2·004
$\mathrm{(neo\text{-}C_5H_{11}O)_3P}$	C	−70	899·2	2·003
$\mathrm{(c\text{-}C_5H_9O)_3P}$	C	−70	892·9	2·003
	H	−70	892·5	2·003
	H	−20	893·5	2·003
$\mathrm{(n\text{-}C_{12}H_{25}O)_3P}$	C	−70	889·3	2·003
$\mathrm{c\text{-}C_5H_9OP(OMe)_2}$	H	−70	885·7	2·003
	H	−20	885·8	2·003
$\mathrm{c\text{-}C_5H_9OP(OEt)_2}$	H	−70	886·8	2·003
	H	−20	888·0	2·003
$\mathrm{(CH_2O)_2POEt(II)}$	H	−70	906·3	2·004
	H	−20	908·4	2·004
$\mathrm{CH_2(CH_2O)_2POEt(I)}$	H	−70	921·0	2·003
	H	−20	930·2	2·003

[a] C = Cyclopentane; H = hexane; H–THF = hexane–tetrahydrofuran mixture. [b] Accuracy of a(P) and g estimated to be ±1 G and ±0·001 respectively.

Taking [4,7] $2k_7$ as $2 \times 10^9\ \mathrm{l\ mol^{-1}\ s^{-1}}$ at 30° and E_7 as 2 ± 1 kcal mol^{-1} we obtain $\log (k_6/\mathrm{s}^{-1}) = 12{\cdot}86 - 12{\cdot}95$ kcal mol^{-1}/θ and $k_6\,(-60°) = 0{\cdot}36\ \mathrm{s}^{-1}$.

Tri-n-butyl phosphite. At −78° only the radical $\mathrm{(BuO)_3\dot{P}OEt}$ was detected by e.s.r. At higher temperatures, as the phosphoranyl radical concentration decreased, the spectra of ethyl and n-butyl radicals became apparent. At +25° the phosphoranyl radical could no longer be detected and the ratio $[\mathrm{Bu^n\cdot}] : [\mathrm{Et\cdot}]$ was 3·0.

Tridodecyl phosphite. This behaved similarly to tri-n-butyl phosphite and at +25° $[\mathrm{n\text{-}C_{12}H_{25}\cdot}] : [\mathrm{Et\cdot}]$ was 4·8.

Tris-(2-chloroethyl) phosphite. Between −20 and +25° the signal intensity in the alkyl radical region was very poor. However, the spectrum of the ethyl radical was absent and the major species present was probably the 2-chloroethyl radical.

Tri-t-butyl phosphite. A strong spectrum of the t-butyl radical was detected even at −100° and at +25° only t-butyl and no ethyl radicals could be detected.

Trineopentyl phosphite. At −78° the high-field line of the phosphoranyl radical was considerably broader than that at low field, presumably a consequence of the large size

[*] Although this reaction is thought [5] to proceed by ' biphyllic ' attack of the phosphite on the peroxide it is conceivable that a radical chain process might be involved. We consider the

$$\mathrm{EtO\cdot} + \mathrm{(RO)_3P} \longrightarrow \mathrm{EtO\dot{P}(OR)_3} \xrightarrow{\mathrm{EtOOEt}} \mathrm{(EtO)_2P(OR)_3} + \mathrm{EtO\cdot}$$

latter mechanism is unlikely since the e.s.r. spectra persisted for a considerable length of time and in many cases the phosphoranyl radicals involved in this reaction (and in similar ones between dialkyl peroxides and triorganophosphines) could not have sufficiently long lifetimes at room temperature to allow them to react with the peroxide.

[3] A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem. Internat. Edn.*, 1971, **10**, 738.

[4] A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 993.

[5] D. B. Denney, D. Z. Denney, C. D. Hall, and K. L. Marsi, *J. Amer. Chem. Soc.*, 1972, **94**, 245 and earlier papers.

[6] D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1972, 747.

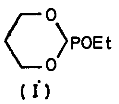
[7] G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 491.

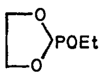
of the radical and incomplete averaging of anisotropic effects. At +25° [neo-C_5H_{11}•] : [Et•] was 1·0 in hexane solution.

Tricyclopentyl phosphite. This was examined in hexane solution to avoid any complication of hydrogen abstraction from cyclopentane solvent. At +25° the ratio [Et•] : [C_5H_9•] was 0·10 and no phosphoranyl radical could be detected at this temperature.

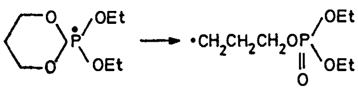
Cyclopentyl diethyl phosphite. At +25° the ratio [Et•] : [C_5H_9•] was 0·90.

Tris-(2,2,2-*trifluoroethyl*)*phosphite.* Tetrahydrofuran was added to the mixture of phosphite, diethyl peroxide, and hexane to maintain a single phase at low temperatures. An extremely strong spectrum of the phosphoranyl radical (peak–peak line width *ca.* 7 G for both lines) was detected at −78° with nothing in the alkyl radical region. Even at +25° no signals from the ethyl or trifluoroethyl radicals could be detected, although a weak spectrum due to the 2-tetrahydrofuryl radical was apparent. This latter result implies that the fluorinated phosphite is less reactive towards ethoxyl radicals than triethyl phosphite, perhaps as a result of the electrophilicity of alkoxyl radicals. At temperatures above −30° each line of the phosphoranyl doublet was further split into an even number of lines, probably ten. This probably results from equal coupling from nine fluorine atoms [*a*(F) 1·8 G]. The effect of increasing temperature on resolution appears to be simply one of decreasing solvent viscosity and increasing rate of tumbling of the radical. Since the nine fluorine atoms will probably not all be magnetically equivalent in the trigonal bipyramidal phosphoranyl radical, their equal coupling constants imply either that positional exchange is rapid on the e.s.r. time scale or that the coupling constants from configurationally different fluorines are the same (within the line width).


(I)

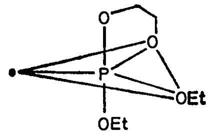

(II)

2-*Ethoxy*-1,3,2-*dioxaphosphorinan* (I). The phosphoranyl radical from this phosphite showed a high field line which was less broad than that at low field, in contrast to most other phosphoranyl radicals which we have detected. At −50° and above the only alkyl radical detected was (III) formed by cleavage of the ring.

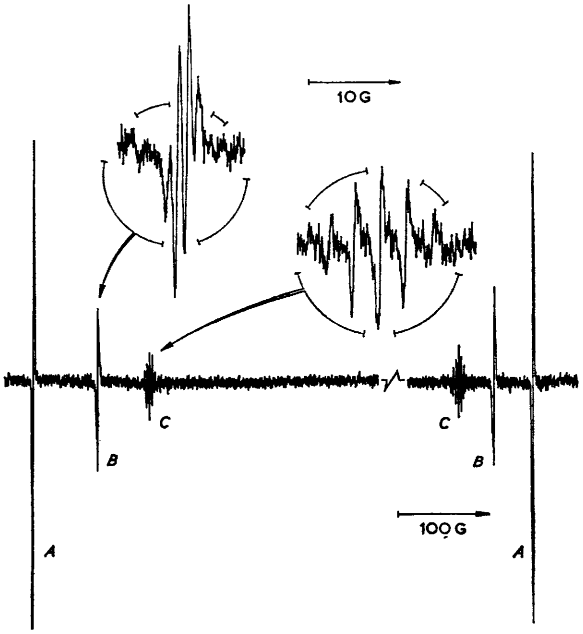

(III) (9)

$a(\alpha H)$ 21·9 G, $a(\beta H)$ 27·2 G } in hexane at −40°.

2-*Ethoxy*-1,3,2-*dioxaphospholan* (II). More than one phosphoranyl radical was apparent at −70°. The species present in largest concentration at all temperatures studied is probably the radical (IV) in which the ring bridges apical and equatorial positions.* Each line of the doublet assigned to (IV) was further split into a 1 : 2 : 1 triplet [*a*(H) = 1·8 G], possibly due to coupling with a pair of ring methyleneoxy hydrogens which are *cis* (or *trans*) to the unpaired electron. The two *cis* (or *trans*) hydrogens may be rendered equivalent by pseudo-rotation of (IV) which is rapid on the e.s.r. time scale,† or their splitting constants may be too similar to be distinguished.


(IV)

At +25° the e.s.r. spectra of both the ethyl radical and of the species $\cdot CH_2CH_2OP(O)(OEt)_2$ [*a*(αH) 22·0, *a*(βH) 26·2 G] in the concentration ratio 3 : 4 could be detected. A third unidentified minor spectrum was also present. It is surprising that the five-membered ring in (IV) seems to cleave less readily than the six-membered ring in phosphoranyl radicals derived from (I) (see the results for t-butoxyl radical adducts with these phosphites).



E.s.r. spectrum obtained by photolysing a solution of diethyl peroxide and trimethyl phosphite in cyclopentane at −2°. The spectra are (*A*), $(MeO)_3\dot{P}OEt$; (*B*), $(MeO)_3\dot{P}Me$; (*C*), $(RO)_2\dot{P}Me_2$

Benzyl diethyl phosphite. Even at −130° in isopentane no phosphoranyl radical could be detected. At this and higher temperatures a strong spectrum of the benzyl radical was observed.

Trimethyl phosphite. At −78° a strong spectrum (*A*) of the radical $(MeO)_3\dot{P}OEt$ was observed. As the temperature was increased, two new phosphoranyl radicals with smaller phosphorus splittings appeared. The spectrum at −2° is shown in the Figure.

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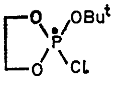
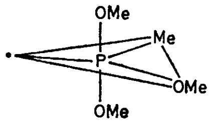
* The identity of the two phosphoranyl radicals present in minor concentration is not known, but further studies of such cyclic phosphorus compounds are in progress.

† Reaction of t-butoxyl radicals with 2-chloro-1,3,2-dioxaphospholan gave the radical A [*a*(P) 1033, $a(^{35}Cl)$ 42·8, $a(^{37}Cl)$ 35·8 G; *g* 2·011 in cyclopentane at −30°] which showed a similar triplet splitting [*a*(H) 1·4 G]. This phosphoranyl radical did not undergo β-scission in the temperature range studied (+27 to −60°).

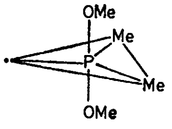

(A)

Spectrum (*B*) has *a*(P) 778·9 G at −2° and each line is further split into a 1 : 3 : 3 : 1 quartet by *a*(H) 1·0 G. Spectrum (*B*) is assigned to the trimethoxymethylphosphoranyl radical (V).[4] Spectrum (*C*) is probably from the dimethoxydimethylphosphoranyl radical (VI) on the basis of the phosphorus hyperfine splitting (687·2 G at −2°) and the further binomial septet splitting (2·9 G at −2°) detected on each line.*

The spectrum (*C*) of radical (VI) was strongest at about −2° and nearly undetectable at +15°, when (*A*) and (*B*) were still present. All changes in spectra were reversible with temperature. Spectra (*B*) and (*C*) were present immediately irradiation was begun and their concentrations did not change with time of irradiation (at a given temperature). Spectra (*A*)—(*C*) decayed immediately the irradiation ceased. At −3° both methyl and ethyl radicals were detected with [Me•] : [Et•] = 1·1.



(V)



(VI)

Cyclopentyl dimethyl phosphite. This phosphite behaved in a similar way to trimethyl phosphite. At low temperatures (−70°) only the radical $C_5H_9O\dot{P}(OMe)_2OEt$ was detected. At −20° a signal assigned to the radical $C_5H_9O\dot{P}(OMe)_2Me$ was observed [*a*(P) 781·6 G]; proton hyperfine splitting of about 1 G was detected but the quartets were less well resolved than those of $(MeO)_3\dot{P}Me$. At −20° there was some suggestion of the spectrum of a species of the type $Me_2\dot{P}(OR)_2$, but the signal intensity was too low to allow positive identification. At +25° three alkyl radicals were present in the concentration ratios [Me•] : [Et•] : [cyclo-C_5H_9•] = 1 : 1 : 2.

(b) *Trialkyl Phosphites and t-Butoxyl Radicals from Di-t-butyl Peroxide.*—These results are an extension of those presented in our earlier paper.[4] The spectroscopic parameters for the previously unreported phosphoranyl radicals are given in Table 2.

TABLE 2

Trialkoxy-t-butoxyphosphoranyl radicals, Bu-$O\dot{P}(OR)_3$ obtained from the interaction of t-butoxyl radicals with trialkyl phosphites

Phosphite	Solvent	*t*/°C	*a*(P)/G [a]
$(CF_3CH_2O)_3P$	H–THF	−70	940·2
	H–THF	−20	943·1
$(CH_2O)_2POEt$(II)	C	−70	906·5
	C	−20	909·6
$CH_2(CH_2O)_2POEt$(I)	C	−70	947·0
$(EtO)_3P$ [b]	C	−70	890·3
	C	−20	893·1

[a] *g* = 2·003 for all radicals. [b] Data from ref. 4. *g* = 2·003.

Tri-t-butyl phosphite. The rate of β-scission of the tetra-t-butoxyphosphoranyl radical [equation (10)] was determined in the usual way[4] in cyclopentane solvent. Taking[4] $2k_{11} = 2 \times 10^9$ l mol^{-1} s^{-1} at 30° and $E_{11} = 2 \pm 1$ kcal mol^{-1} we obtain k_{10} (−60°) = 5·1 × 10^2 s^{-1}.

$$(Bu^tO)_4P\cdot \longrightarrow Bu^t\cdot + OP(OBu^t)_3 \qquad (10)$$

$$2Bu^t\cdot \longrightarrow \text{non-radical products} \qquad (11)$$

Benzyl diethyl phosphite. In pentane solution at −130° no phosphoranyl radical could be detected although a strong spectrum of the benzyl radical was observed. Up to room temperature only benzyl and no t-butyl radicals could be detected by e.s.r. spectroscopy.

Trimethyl phosphite. At low temperatures the trimethoxy-t-butoxyphosphoranyl radical[4] was present and this underwent β-scission[8] at higher temperatures to give a t-butyl radical. At *ca.* −20°, however, the spectrum of the trimethoxymethylphosphoranyl radical (V) was also observed [*a*(P) 779·5, *a*(H) 1·0 G]. There is thus probably a small amount of competing β-scission to give methyl radicals. At no temperature was the spectrum of the dimethoxydimethylphosphoranyl radical (VI) observed, but this may be simply because of the poor signal strength.

Tris-(2,2,2-*trifluoroethyl*) *phosphite.* In contrast to the radical $EtO\dot{P}(OCH_2CF_3)_3$ the fluorine hyperfine splitting in $Bu^tO\dot{P}(OCH_2CF_3)_3$ was barely detectable, probably because of the increased size of this radical. Although $Bu^tO\dot{P}(OCH_2CF_3)_3$ is more sterically congested than $EtO\dot{P}(OCH_2CF_3)_3$, the phosphorus coupling in the former is less than that in the latter [compare $(EtO)_4P\cdot$ and $(EtO)_3\dot{P}OBu^t$]. This could be connected with the different electronegativities of the t-butoxy- and ethoxy-groups.

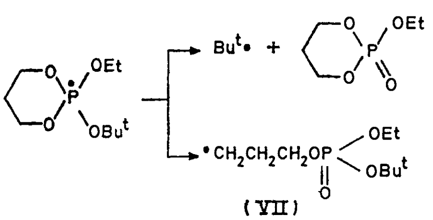
In cyclopentane solvent at −20° both the t-butyl and 2,2,2-trifluoroethyl radicals were present with [CF_3CH_2•] : [Bu^t•] *ca.* 0·5. The signal from the phosphoranyl radical was also present at −20°, and was, in fact, still detectable at +40°. At higher phosphite concentrations and in the presence of tetrahydrofuran to maintain miscibility at low temperatures, the concentration of trifluoroethyl radicals was reduced selectively (possibly by a polar solvent effect) such that in the temperature range −15 to −49° the t-butyl radical and the phosphoranyl radical were the only species detectable. In this temperature range the rate of β-scission of the phosphoranyl radical was measured.

$$Bu^tO\dot{P}(OCH_2CF_3)_3 \longrightarrow Bu^t\cdot + OP(OCH_2CF_3)_3 \qquad (12)$$

$$Bu^t\cdot + Bu^tO\dot{P}(OCH_2CF_3)_3 \longrightarrow \text{non-radical products} \qquad (13)$$

Making the assumption that all of the tris(trifluoroethoxy)-t-butoxyphosphoranyl radicals detected by e.s.r. spectroscopy decompose at the same rate (see Discussion section) we find log ($2k_{11}/k_{12}$/l mol^{-1}) = 2·50 + 5·44 kcal mol^{-1}/θ whence log (k_{12}/s^{-1}) = 8·25 − 7·4 kcal mol^{-1}/θ and k_{12} (−60°) = 4·5 s^{-1}. In the temperature range −27 to −49° the ratio ($2k_{11}/k_{13}$) is *ca.* 6.

2-*Ethoxy*-1,3,2-*dioxaphosphorinan* (I). The phosphoranyl radical from this phosphite underwent competing β-scission with ring cleavage, and loss of a t-butyl radical.



(VII)

(14)

The ratio [Bu^t•] : [(VII)] was 0·9 at +25°, when no phosphoranyl radical was detectable, although it did not

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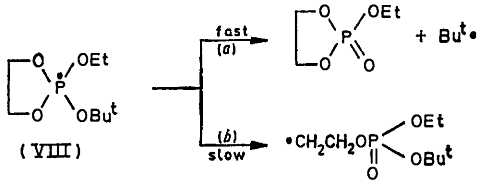
* There is steady decrease in the magnitude of the phosphorus hyperfine splitting as *n* decreases along the series $(RO)_n\dot{P}R_{4-n}$.[4]

[8] G. B. Watts, D. Griller, and K. U. Ingold, *J. Amer. Chem. Soc.*, submitted for publication.

vary appreciably at lower temperatures when all three radicals were present.*

2-*Ethoxy*-1,3,2-*dioxaphospholan* (II). The only alkyl radical detected from the β-scission of the phosphoranyl radical (VIII) derived from this phosphite was t-butyl.



(15)

The kinetics of β-scission of (VIII) were determined, again making the assumption that all the phosphoranyl radicals detected decomposed at the same rate, whence k_{15a} (−60°) = 43·6 s^{-1} in cyclopentane.

Triethyl phosphite. The rate of β-scission of the radical $Bu^tO\dot{P}(OEt)_3$ has been determined previously [4] (see Introduction) but we wished to examine the effect of change of medium on the reaction. The rate of scission was measured in cyclopentane and in a mixture of cyclopentane and tetrahydrofuran (2 : 1 v/v). In the temperature range −52 to −91° the ratio $k_5(C_5H_{10}\text{–THF}) : k_5(C_5H_{10})$ increased from 1·6 to 2·5.

(c) *Trialkyl Phosphites and Alkoxyl Radicals from Alkyl Nitrites.*—After a few seconds irradiation of a cyclopentane solution containing triethyl phosphite and t-butyl nitrite at −20°, a strong spectrum of di-t-butyl nitroxide [*a*(N) 15·1 G] was visible. In addition there was a nitroxide species with a larger nitrogen splitting, possibly t-butoxy t-butyl nitroxide. During continuous irradiation a large steady concentration of di-t-butyl nitroxide was built-up and this was the only nitroxide detectable. At low temperatures (−70°) the e.s.r. spectrum of $Bu^tO\dot{P}(OEt)_3$ was observed.

$$Bu^tONO \xrightarrow{h\nu} Bu^tO\cdot + NO \tag{16}$$

$$Bu^tO\cdot + P(OEt)_3 \longrightarrow Bu^tO\dot{P}(OEt)_3 \tag{4}$$

$$Bu^tO\dot{P}(OEt)_3 \longrightarrow Bu^t\cdot + OP(OEt)_3 \tag{5}$$

$$Bu^t\cdot + NO \longrightarrow Bu^tNO \tag{17}$$

$$Bu^t\cdot + Bu^tNO \longrightarrow Bu^t_2NO\cdot \tag{18}$$

At high temperatures (+33°) the sample was depleted quite rapidly, possibly because of the incursion of reaction (19) [2] giving rise to a chain process.

$$Bu^t\cdot + Bu^tONO \longrightarrow Bu^tNO + Bu^tO\cdot \tag{19}$$

When the above experiment was repeated with trimethyl phosphite the only phosphoranyl radical detected was $(MeO)_3\dot{P}OBu^t$, presumably because any methyl radicals in the system were trapped by nitroxides, nitroso compounds, or the nitrite in preference to the phosphite.

When s-butyl nitrite was photolysed in the presence of triethyl phosphite the phosphoranyl radical $Bu^sO\dot{P}(OEt)_3$ was detected [*a*(P) 889 G at −70° in cyclopentane]. Nitroxides were also present and at −20° the major species was di-s-butyl nitroxide, although other unidentified species were detected after more prolonged irradiation.

(d) *Trialkyl Phosphites with Alkoxyl Radicals derived from Other Sources.*—Irradiation of a cyclopentane solution containing di-t-butyl hyponitrite and triethyl phosphite at −70° gave rise to the e.s.r. spectrum of the radical $Bu^tO\dot{P}(OEt)_3$, which underwent β-scission in a quantitatively similar manner as when the radical was generated from a di-t-butyl peroxide–phosphite mixture.

Photolysis of cumyl t-butyl peroxide in the presence of triethyl phosphite at −100° gave rise to only one phosphoranyl doublet and the spectrum of the cumyl radical,† but no t-butyl radicals were detected at this temperature. Although the radicals $Bu^tO\dot{P}(OEt)_3$ and $PhC(Me)_2O\dot{P}(OEt)_3$ should have similar phosphorus hyperfine splittings and *g* values, it is probable that the cumyloxyphosphoranyl radical was too unstable to be detected [*cf.* the radical $PhCH_2O\dot{P}(OEt)_3$ above]. At higher temperatures (> −50°) t-butyl radicals were also detected.

(e) *Trialkyl Phosphites and Methyl Radicals from Azomethane.*—U.v. irradiation of solutions containing trialkyl phosphites and azomethane gave rise to the e.s.r. spectra of methyltrialkoxyphosphoranyl radicals.

$$MeN{=}NMe \xrightarrow{h\nu} 2Me\cdot + N_2 \tag{20}$$

$$Me\cdot + P(OR)_3 \rightleftharpoons Me\dot{P}(OR)_3 \tag{21}$$

In no case were any other phosphoranyl radicals detected. In general the phosphorus hyperfine splitting in the radicals $Me\dot{P}(OR)_3$ *increased* with *decreasing* temperature, the opposite behaviour from that generally observed with the tetra-alkoxyphosphoranyl radicals. The phosphorus splitting in $Me\dot{P}(OR)_3$ was *ca.* 100 G less than for $(RO)_4P\cdot$, but showed the same tendency to increase with the bulk of the alkoxy-groups. The smaller phosphorus splitting is presumably a consequence of the lower electronegativity of methyl compared with alkoxy and is probably accompanied by increased distortion from trigonal bipyramidal geometry.[4] Only for the radicals $Me\dot{P}(OMe)_3$ and $Me\dot{P}(OMe)_2(OC_5H_9\text{-cyclo})$ was proton hyperfine splitting also detected. The spectroscopic parameters are listed in Table 3.

Photolysis of hydrocarbon solutions of azomethane (1—2M) gave rise to the e.s.r. spectrum of the methyl radical and no other species. The signal became progressively more intense as the temperature was decreased from +20 to −100°, the change being more than would be expected from the change in spin state populations and in the rate of diffusion together of the radicals. When a trialkyl phosphite (0·5—1M) was added the methyl radical spectrum was quenched to a varying degree depending on the particular phosphite, and the spectrum of the trialkoxymethylphosphoranyl radical appeared.

With trimethyl- and triethyl-phosphites at −70° the spectrum of the methyl radical was completely quenched. At −20°, however, a small signal from methyl was detectable and that due to the phosphoranyl radical had decreased dramatically. Since in the absence of phosphite the methyl signal *decreases* as the temperature is *increased*, this observation may be taken as evidence that reaction (21) is reversible. Similar results were obtained with the other phosphites although as the bulk of the alkoxy-groups increased a methyl signal was detectable even at low temperature. With tricyclopentyl phosphite or tri-t-butyl

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* 2-Methoxy-1,3,2-dioxaphosphorinan behaved in a similar way to the ethyl ester in reactions with ethoxyl and t-butoxyl radicals.

† For the cumyl radical at −28°: *a*(Me) 16·0; *a*(*o*-H) 4·8; *a*(*m*-H) 1·6; *a*(*p*-H) 5·6 G.

phosphite no cyclopentyl or t-butyl radicals respectively were detected in the temperature range −20 to −70°. Addition of tri-t-butyl phosphite to the azomethane solution in fact had little effect on the methyl radical concentration and the spectrum of $Me\dot{P}(OBu^t)_3$ was so weak as to make identification uncertain in view of its apparently large phosphorus hyperfine splitting. Qualitatively, it appears that the acceptor power of the trialkyl phosphites towards methyl radicals is $(MeO)_3P > (EtO)_3P$, $(Bu^nO)_3P > (Pr^iO)_3P$, $(cyclo\text{-}C_5H_9O)_3P$, $(neo\text{-}C_5H_{11}O)_3P \gg (Bu^tO)_3P$.

TABLE 3

Trialkoxymethylphosphoranyl radicals obtained from the interaction of methyl radicals derived from azomethane with trialkyl phosphites

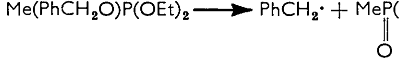
Phosphite	Solvent	t/°C	a(P)/G	g
$(MeO)_3P$	C	−70	783·1	2·003
	C	−20	779·6	2·004
	H	−70	784·3	2·003
$(MeO)_3P$ [a]	C	−2	778·9	2·003
$(MeO)_3P$ [b]	C	−20	779·5	2·003
$(EtO)_3P$	C	−70	786·7	2·004
	C	−20	782·5	2·004
$(Pr^iO)_3P$	C	−70	787·4	2·004
	C	−20	780·6	2·004
$(Bu^nO)_3P$	C	−70	789·2	2·004
	C	−20	784·2	2·004
$(Bu^tO)_3P$ [c]	H	−70	884·0	2·004
$(neo\text{-}C_5H_{11}O)_3P$	H	−70	803·1	2·003
	H	−20	795·9	2·003
$(cyclo\text{-}C_5H_9O)_3P$	H	−70	795·8	2·004
	H	−20	788·6	2·004
$cyclo\text{-}C_5H_9OP(OMe)_2$	H	−70	785·3	2·003
	H	−20	781·8	2·003
$cyclo\text{-}C_5H_9OP(OMe)_2$ [a]	H	−20	781·6	2·003
$cyclo\text{-}C_5H_9OP(OEt)_2$	H	−70	789·9	2·003
	H	−20	783·8	2·003
$PhCH_2OP(OEt)_2$	H	−100	791·2	2·003

[a] From diethyl peroxide and the trialkyl phosphite. [b] From di-t-butyl peroxide and the trialkyl phosphite. [c] Very weak spectrum (see text), assignment possibly incorrect.

The affinity of methyl radicals for trialkyl phosphites is much higher than that of the larger alkyl radicals. For example, no $(EtO)_3\dot{P}Et$ could be detected under conditions of maximum spectrometer gain during photolysis of diethyl peroxide and triethyl phosphite in the temperature range 0 to −20° when the concentration of ethyl radicals is quite high.

Benzyl diethyl phosphite behaved somewhat differently. At −100° the methyl radical spectrum was quenched upon addition of the phosphite and replaced by that of the benzyl radical. The doublet of the phosphoranyl radical $Me(PhCH_2O)P(OEt)_2$ was also detected, although the spectrum was weak.

$$Me\cdot + PhCH_2OP(OEt)_2 \longrightarrow Me(PhCH_2O)\dot{P}(OEt)_2 \qquad (22)$$

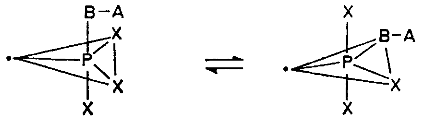


$$Me(PhCH_2O)\dot{P}(OEt)_2 \longrightarrow PhCH_2\cdot + Me\underset{\underset{O}{\|}}{P}(OEt)_2 \qquad (23)$$

Benzyl diethyl phosphite presents little steric hindrance to the incoming methyl radical and once formed the phosphoranyl radical can undergo rapid β-scission to yield the resonance stabilised benzyl radical.*

DISCUSSION

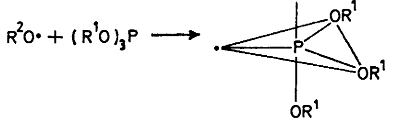
The available data suggest that tetra-alkoxyphosphoranyl radicals possess a distorted trigonal bipyramidal structure in which the unpaired electron occupies an equatorial position in the most stable configuration.[4] Substituents of higher electronegativity prefer to occupy apical positions whilst those of lower electronegativity preferentially take up equatorial positions.[10] Different configurations such as (IX) and (X) interconvert by pseudo-rotation.[11]



(IX) (X) (24)

The important question arises as to whether apical and equatorial groups are equally readily involved in α- or β-scission of the phosphoranyl radicals. The results presented here, as well as others, are interpretable only on the basis of non-equivalence of reactivity of apical and equatorial substituents.

The apical bonds in trigonal bipyramidal phosphoranes, PX_5, are generally longer and weaker than the equatorial bonds. In heterolytic reactions involving phosphorane intermediates cleavage of a group from phosphorus is believed to take place from an apical position.[12] In forming the phosphorane intermediate the incoming group also takes up an apical position.[12] It is reasonable that α-scission of a phosphoranyl radical should involve the loss of an apical group, and that in reaction (25) the incoming group should take up an apical position.



(25)

There is really no compelling evidence for a configurational preference for β-scission. Intuitively it might be thought that β-scission of the radical $AB\dot{P}X_3$ will occur most readily when AB is in the equatorial position and the B–P bond is shorter and stronger.† However, the

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* $Me(PhCH_2O)\dot{P}(OEt)_2$ can be detected by e.s.r. whilst $PhCH_2O\dot{P}(OEt)_3$ cannot. This is probably due to the shorter lifetime of the latter towards β-scission. Further work on such reactivity trends is in progress.[9]

† Recent MO calculations [10] suggest that equatorial positions offer the possibility of the greatest interaction between the ligand and the phosphorus *d* orbitals.

[9] A. G. Davies, R. W. Dennis, B. Griller, and B. P. Roberts, *J. Organometallic Chem.*, 1972, **40**, C33; and unpublished results.

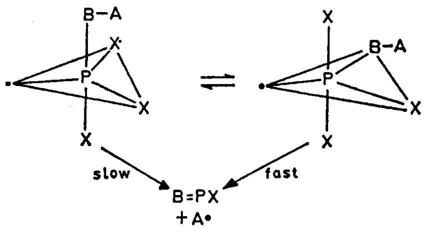
[10] (*a*) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 1963, **2**, 613; (*b*) E. L. Muetterties, W. Mahler, J. K. Packer, and R. Schmutzler, *ibid.*, 1964, **3**, 498; (*c*) P. Gillespie, P. Hoffman, H. Khusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Isolis, and I. Ugi, *Angew. Chem. Internat. Edn.*, 1971, **10**, 687.

[11] (*a*) S. R. Berry, *J. Chem. Phys.*, 1960, **32**, 933; (*b*) G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, 1969, **91**, 5384; (*c*) For a review of ' turnstile rotation ' as an alternative mechanism for ligand permutation see I. Ugi and F. Ramirez, *Chem. in Brit.*, 1972, 918.

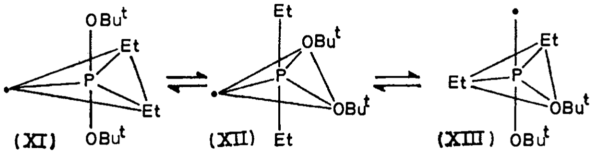
[12] See for example, F. H. Westheimer, *Accounts Chem. Res.*, 1968, **1**, 70; K. Mislow, *Accounts Chem. Res.*, 1970, **3**, 321.

converse configurational preference has recently been suggested.[13]

The relative stability[9] towards unimolecular scission of the radical $Et_2\dot{P}(OBu^t)_2$ [compared with $(EtO)_3\dot{P}OBu^t$, $Et\dot{P}(OEt)_2OBu^t$, and $Et_3\dot{P}OBu^t$] may be partly ascribed to configurational effects.* The most stable structure will be (XI) because of the different electronegativities of the ligands. Because of this the ethyl groups and the t-butoxy-groups are not in the correct positions for ready α- and β-scission respectively. Pseudo-rotation to give (XII) or (XIII) is expected to involve an appreciable barrier because of the unfavourable placing of the ligands.



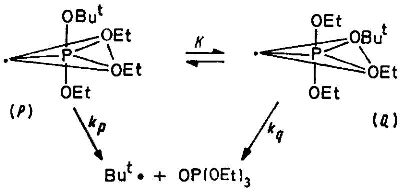
(26)



(27)

At −60° $(Bu^tO)_4P\cdot$ undergoes β-scission to give a t-butyl radical much more rapidly than $(EtO)_4P\cdot$ gives ethyl by the same mechanism. The greater part of the difference is clearly due to the difference in the strengths of the C–O bonds being broken. Bentrude and Wielesek[14] have shown that the phosphate produced by decomposing ^{14}C-labelled di-t-butyl hyponitrite at 65° in the presence of tri-t-butyl phosphite is *ca.* 75% labelled with ^{14}C. If the t-butoxyl radical enters stereospecifically (probably into an apical position) and if the groups have non-equivalent reactivity then the rate of positional scrambling in $(Bu^tO)_4P\cdot$ must be fast compared to its β-scission.[13,14] In the radicals $(R^1O)_3\dot{P}OR^2$ ($R^2 = Bu^t$, Et; R^1 = simple alkyl) it seems likely that the exchange of apical and equatorial alkoxy groups by pseudo-rotation is *rapid* with respect to their β-scission in the range of temperatures discussed in our present work.

The radicals $(Bu^tO)_4P\cdot$ and $(EtO)_4P\cdot$ always have an alkoxy group correctly positioned to allow ready β-scission, and, if the unpaired electron always remains equatorial, pseudo-rotation has no effect on configuration and the phosphoranyl radical detected by e.s.r. is a single species. This is probably not so with the tetra-alkoxyphosphoranyl radicals which have different alkoxy-groups.

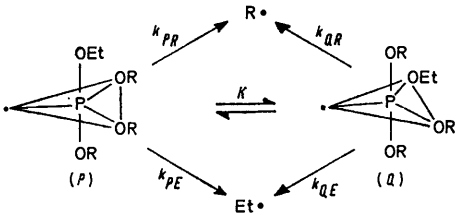


(28)

The e.s.r. spectroscopic parameters of (*P*) and (*Q*) are expected to be similar and thus the concentration of phosphoranyl radicals detected by e.s.r. will be [(*P*)] + [(*Q*)].† If (*P*) and (*Q*) interconvert more rapidly than they decompose by β-scission, then it may be shown that equation (29) holds, where *K* is an equilibrium constant, k_P and k_Q are the rate constants for β-scission of (*P*) and (*Q*) respectively, and k_{obs} is the observed rate constant[4] obtained by assuming all of the phosphoranyl radicals detected react at the same rate.‡

$$k_{obs} = (k_P + k_QK)/(1 + K) \qquad (29)$$

When a tertiary alkyl (or benzylic) radical is lost by β-scission the configurational preference may be quite small[13] and although *K* may be different from unity, k_{obs} will be reasonably close to k_P and k_Q, and our earlier result[4] may not be much affected. When a primary or secondary alkyl radical is lost configurational selectivity may be much greater.



(30)

The β-scission of the radical $EtO\dot{P}(OR)_3$ is described in equation (30) when either Et• or R• may be lost. At temperatures when [(*P*)] and [(*Q*)] are both very small it may be shown that equation (31) holds where $2k_{EE}$, $2k_{RR}$, and k_{ER} are the rate constants for the reaction of Et• with Et•, R• with R•, and Et• with R•, respectively.

$$\frac{[Et\cdot]}{[R\cdot]} = \left(\frac{k_{PE} + k_{QE}K}{k_{PR} + k_{QR}K}\right)\left[\frac{2k_{RR} + k_{ER}\dfrac{[Et\cdot]}{[R\cdot]}}{2k_{EE}\dfrac{[Et\cdot]}{[R\cdot]} + k_{ER}}\right] \qquad (31)$$

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* It appears that β-scission of the radical is also retarded [relative to $(EtO)_3\dot{P}\,OBu^t$] by the presence of the alkyl groups on phosphorus. However slow β-scission of $Et_2\dot{P}(OBu^t)_2$ may not be due entirely to a configurational effect, electronic effects may also be important.

† It is also possible that interconversion of (*P*) and (*Q*) is rapid on the e.s.r. time scale.

‡ It is assumed that both (*P*) and (*Q*) react equally rapidly with t-butyl radicals. The decay of the phosphoranyl radical signal when the light is shuttered may be first order with respect to the observed radical concentration even if k_P and k_Q are different.

[13] W. G. Bentrude and T. B. Min, *J. Amer. Chem. Soc.*, 1972, **94**, 1025.

[14] W. G. Bentrude and R. A. Wielesek, *J. Amer. Chem. Soc.*, 1969, **91**, 2406.

If [7,15] $2k_{EE} = 2k_{RR} = k_{ER}$ then equation (32) holds.

$$[\mathrm{Et}\cdot]/[\mathrm{R}\cdot] = (k_{PE} + k_{QE}K)/(k_{PR} + k_{QR}K) \quad (32)$$

Let us suppose that equatorial alkoxy-groups participate in β-scission more readily than apical groups, that is in equations (31) and (32) $k_{QE} > k_{PE}$ and $k_{PR} > k_{QR}$. Further let us assume that $k_{PR} = 2k_{QR}$. For the radical $(\mathrm{Bu^nO})_3\dot{\mathrm{P}}\mathrm{OEt}$ it is reasonable to assume that $K = 1$ (since the steric requirements of n-butyl and ethyl groups will be similar) and that equation (32) holds. The observed value of $[\mathrm{Et}\cdot] : [\mathrm{Bu^n}\cdot]$ at 25° was 0·33 hence, $0{\cdot}33 = k_{QE}/3k_{QR}$, *i.e.* $k_{QE} = k_{QR}$.

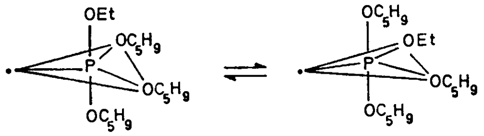
This result is expected because both butyl and ethyl are simple primary alkyl radicals. A similar result is obtained for the radical $(\text{n-C}_{12}\mathrm{H}_{25}\mathrm{O})_3\dot{\mathrm{P}}\mathrm{OEt}$ when due account is taken of the lower value of the rate constant for the self-reaction of dodecyl radicals compared with that for ethyl radicals.[7,16]

The rate constants for the self-reactions of ethyl and neopentyl radicals must be very similar.[7] Thus the ratio $[\mathrm{Et}\cdot] : [\text{neo-C}_5\mathrm{H}_{11}\cdot]$ observed in the β-scission of $(\text{neo-C}_5\mathrm{H}_{11}\mathrm{O})_3\dot{\mathrm{P}}\mathrm{OEt}$ at 25° might be expected to be close to 0·33, since neopentyl and ethyl are both primary alkyl radicals; the observed value is 1·0. We believe that for this phosphoranyl radical $k_{QE} = k_{QR}$, but now K is not equal to unity. The bulky neopentyl group preferentially occupies the apical position and as a result $K > 1$. To a first approximation the results imply that the radical (Q) equation (30), R = neopentyl] is the only source of alkyl radicals since the rates of production of neopentyl radicals and of ethyl radicals are similar. These steric effects are reflected in the hyperfine splitting from phosphorus in the phosphoranyl radicals (see Table 1); $(\mathrm{EtO})_4\mathrm{P}\cdot$, $(\mathrm{Bu^nO})_3\dot{\mathrm{P}}\mathrm{OEt}$, and $(\text{n-C}_{12}\mathrm{H}_{25}\mathrm{O})_3\dot{\mathrm{P}}\mathrm{OEt}$ all have similar values (885—889 G) whilst $(\text{neo-C}_5\mathrm{H}_{11}\mathrm{O})_3\dot{\mathrm{P}}\mathrm{OEt}$ has a higher value (899 G).

There is some evidence that bulky groups prefer to occupy *equatorial* positions in trigonal bipyramidal phosphoranes.[17,18] If this were true also of phosphoranyl radicals our results could be accommodated on similar arguments to those used here if β-scission selectively involved groups in the *apical* position. It should be pointed out, however, that results from phosphorane chemistry are not transferable directly to phosphoranyl radicals. In particular, if the equatorial preference for bulky groups in a phosphorane is because the increased length of the apical bond is outweighed by the presence of *three* bonds at 90° to the apical substituent,[19] then a distorted trigonal bipyramidal phosphoranyl radical may well still prefer to place bulky groups in an apical position, since one of the 'ligands' is now an unpaired electron. Our analysis is not unique but it supplies a convenient rationale of the experimental results from which further development can take place.

Such configurational and steric effects can explain some of the recent results of Barton and his co-workers.[20] These authors found that bulky groups were preferentially retained when tetra-alkoxyphosphoranyl radicals underwent β-scission. Alkoxyl radicals were generated, by photolysis of alkyl nitrites, in the presence of trialkyl phosphites and a mechanism involving the formation and β-scission of phosphoranyl radicals was suggested. Our results substantiate this mechanism since tetra-alkoxyphosphoranyl radicals have now been detected by e.s.r. during photolysis of alkyl nitrites in the presence of trialkyl phosphites. It is possible, however, that the role played by nitroso-compounds, nitroxides, and related species in this system may have been underestimated, although the stationary radical concentrations in their preparative experiments must have been much lower than in our work.

The radical $(\text{cyclo-C}_5\mathrm{H}_9\mathrm{O})_3\dot{\mathrm{P}}\mathrm{OEt}$ underwent β-scission to give a ratio $[\mathrm{Et}\cdot] : [\text{cyclo-C}_5\mathrm{H}_9\cdot]$ of 0·1 at 25°. If equation (32) is assumed to hold in this case, this concentration ratio is readily understood in terms of the more ready loss of a secondary cyclopentyl radical, *i.e.* $k_{QR} \approx 3k_{QE}$. It is consistent with this that the radical $\text{cyclo-C}_5\mathrm{H}_9\mathrm{O}\dot{\mathrm{P}}(\mathrm{OEt})_3$ gives a ratio $[\mathrm{Et}\cdot] : [\text{cyclo-C}_5\mathrm{H}_9]$ of 0·9 at 25°. If the equilibrium constant is *ca.* 1 for reaction (33) then, since the ratio of ethyl to cyclopentyl groups in $\text{cyclo-C}_5\mathrm{H}_9\mathrm{O}\dot{\mathrm{P}}(\mathrm{OEt})_3$ is nine times that in $(\text{cyclo-C}_5\mathrm{H}_9\mathrm{O})_3\dot{\mathrm{P}}\mathrm{OEt}$, the radical concentration ratio should be nine times greater.



(33)

With trimethyl phosphite the situation is more complex. When diethyl peroxide was photolysed in the presence of this phosphite at −3° the ratio $[\mathrm{Et}\cdot] : [\mathrm{Me}\cdot]$ was 0·9, but at this and higher temperatures phosphoranyl radicals were also present. To a first approximation it appears that ethyl radicals are lost only 1—2 times as readily as methyl radicals from a tetra-alkoxyphosphoranyl radical. Methyl radicals react further with the trimethyl phosphite to give methyltrimethoxyphosphoranyl radicals [reaction (34)].

$$\mathrm{Me}\cdot + (\mathrm{MeO})_3\mathrm{P} \rightleftharpoons \mathrm{Me}\dot{\mathrm{P}}(\mathrm{OMe})_3 \quad (34)$$

The origin of the radical $\mathrm{Me}_2\dot{\mathrm{P}}(\mathrm{OMe})_2$ in this system is not clear. It is probably not formed by loss of a methoxyl radical from $\mathrm{Me}\dot{\mathrm{P}}(\mathrm{OMe})_3$ followed by addition of a methyl radical to the product, since this $S_{\mathrm{H}}2$ process should be very endothermic. It is noteworthy that

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[15] A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc.* (*B*), 1971, 1823.

[16] R. D. Burkhart, R. F. Boynton, and J. C. Merrill, *J. Amer. Chem. Soc.*, 1971, **93**, 5013.

[17] K. E. DeBruin and K. Mislow, *J. Amer. Chem. Soc.*, 1969, **91**, 7393.

[18] D. Gorenstein, *J. Amer. Chem. Soc.*, 1970, **92**, 644.

[19] L. S. Bartell, *Inorg. Chem.*, 1970, **9**, 1594.

[20] D. H. R. Barton, T. J. Bentley, R. H. Hesse, F. Mutterer, and M. M. Pechet, *Chem. Comm.*, 1971, 912.

$\mathrm{Me_2\dot{P}(OR)_2}$ species were never detected when azomethane was photolysed in the presence of trialkyl phosphites.

Similar arguments apply to the radical cyclo-$\mathrm{C_5H_9O\dot{P}(OMe)_2OEt}$, the secondary cyclopentyl radical being lost more readily than the primary ethyl radical.

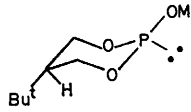
The phosphoranyl radical formed by addition of an ethoxyl radical to 2-ethoxy-1,3,2-dioxaphosphorinan (I) undergoes β-scission exclusively to give the ring opened radical (III). This result may be attributed in part to ring strain in the phosphate formed by loss of ethyl but this should be a very small effect in such an exothermic reaction[12] and should be much less than in the five-membered cyclic phosphate derived from the radical $\mathrm{(CH_2O)_2\dot{P}(OEt)_2}$ which undergoes ring opening less readily.

The phosphoranyl radical formed by addition of a t-butoxyl radical to (I) undergoes competitive scission reactions to give a t-butyl radical and ring cleavage. At 25° the ratio [$\mathrm{Bu^t\cdot}$] : [(VII)] was 0·9, although (VII) is expected to be removed by radical–radical reactions somewhat more slowly than t-butyl because of its greater size.[7] The phosphoranyl radicals from (II) and t-butoxyl radicals undergo β-scission to give exclusively t-butyl radicals. The different behaviour of these tetra-alkoxyphosphoranyl radicals in which the phosphorus atom is part of a five- or six-membered ring is reflected by their phosphorus hyperfine splittings (see Tables 1 and 2). In fact, these parameters may be taken to suggest that there is greater distortion of the bond angles at phosphorus [compared with ($\mathrm{RO_4P\cdot}$] in the radical containing the six-membered ring than in that with the five-membered ring.[4]

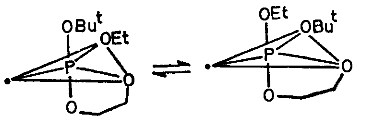
It is possible that the most stable configuration of the phosphoranyl radical derived from 2-ethoxy-1,3,2-dioxaphosphorinan possesses a diequatorial six-membered ring.[10c, 11c] If β-scission is more rapid when an equatorial group departs this would explain the difference in behaviour of the phosphoranyl radicals containing five- or six-membered rings. If a sizeable barrier exists to the apical placement of the unpaired electron, a low energy form with a diequatorial six-membered ring would imply a fairly large barrier to any ligand interchange process, since pseudo-rotation about the unpaired electron as pivot would place the ring in a diapical configuration.

Bentrude *et al.*[21] have shown that reaction of t-butoxyl radicals at 65° with (XIV) (or its *trans*-isomer) gave cyclic phosphate in which the geometric configuration was retained. Their result may imply that pseudo-rotation of the intermediate phosphoranyl radical is slow with respect to β-scission in this case.

The dioxaphospholan (II) was studied with a view to examining the effect of ring size on the rate of β-scission. Ring strain would be expected to be greater in the cyclic phosphate than in the phosphoranyl radical by analogy with the phosphorane systems.[12] With t-butoxyl radicals the major scission process gave t-butyl radicals without ring cleavage. The observed rate constant (at −60°) was less than for $\mathrm{(EtO)_3\dot{P}OBu^t}$ providing some evidence for the effect of ring strain, since the equilibrium constant for reaction (35) should be close to that for reaction (28) at the same temperature.



(XIV)

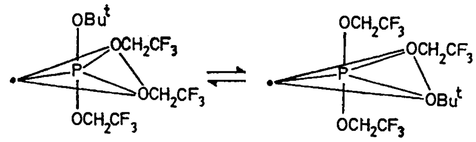


(35)

Stabilisation [relative to $\mathrm{(EtO)_3\dot{P}OBu^t}$] of the phosphoranyl radical due to a reduction of non-bonded interactions brought about by the presence of the five-membered ring could also be partly responsible for the decreased rate of β-scission.

The radical $\mathrm{(CF_3CH_2O)_3\dot{P}OBu^t}$ is interesting because it apparently loses a t-butyl radical much more slowly than $\mathrm{(EtO)_3\dot{P}OBu^t}$.* It seems unlikely that there will be any appreciable difference in the P=O bond energies in the product phosphates.[22]

On electronegativity grounds the radical (XVI) is expected to be more stable than (XV) compared with the similar configurations of $\mathrm{(EtO)_3\dot{P}OBu^t}$. If β-scission occurs from the equatorial position this result implies a large polar effect on the cleavage process. We do not consider that the Arrhenius parameters for this scission are particularly reliable, although they do indicate that the effect is on the *A* factor rather than the activation energy.



(XV) (XVI) (36)

The accelerating effect on the rate of β-scission of $\mathrm{Bu^tO\dot{P}(OEt)_3}$ produced by addition of tetrahydrofuran is surprisingly small. The phosphorus–oxygen bond in the product phosphate is highly polar, but the transition state should lie only a short distance along the reaction co-ordinate in the very exothermic cleavage reaction.

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* Photolysis of di-t-butyl peroxide in the presence of diethyl chlorophosphite gave the radical $\mathrm{(EtO)_2\dot{P}(Cl)OBu^t}$ [*a*(P) 1037, *a*(^{35}Cl) 47·2, *a*(^{37}Cl) 39·3 G in pentane at −50°]. No t-butyl radicals were detected at low temperatures but at +25 to +60°, when the phosphoranyl radical could still be detected, the spectrum of this radical was observed. The substitution of alkoxy-groups in $\mathrm{(RO)_4P\cdot}$ by either relatively electronegative chlorine or electropositive alkyl groups appears to cause a decrease in the rate of β-scission of the resulting phosphoranyl radical.

[21] W. G. Bentrude, J. H. Hargis, and P. E. Rusek, jun., *Chem. Comm.*, 1969, 296.

[22] R. F. Hudson, 'Structure and Mechanism in Organo-Phosphorus Chemistry,' Academic Press, London, 1965.

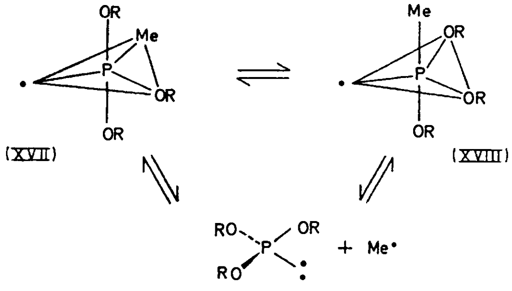
Reactant and transition state may be solvated to similar degrees.

The radical $(\mathrm{Bu^tO})_4\mathrm{P}\cdot$ has a rate constant for β-scission which is only 2·4 times greater than k_{obs} for scission of $\mathrm{Bu^tO\dot{P}(OEt)_3}$ at −60°. As pointed out earlier, the selectivity between loss of a t-alkyl radical from the apical or equatorial position may be quite small, and if there were no selectivity, $(\mathrm{Bu^tO})_4\mathrm{P}\cdot$ should be four times as reactive as $\mathrm{Bu^tO\dot{P}(OEt)_3}$ (neglecting other effects). The relative reactivities of the two phosphoranyl radicals exclude the possibility that for $\mathrm{(EtO)_3\dot{P}OBu^t}$ k_P and k_Q [equation (28)] are very different and K is far removed from unity, such that the t-butoxy-group is preferentially held in the position unfavourable to loss of $\mathrm{Bu^t\cdot}$. For example, if $K \gg 1$ then k_P cannot be much less than k_Q, although it can be greater or much greater than k_Q. These results show that there is probably little steric acceleration for loss of a t-butyl radical from the congested $(\mathrm{Bu^t\Theta})_4\mathrm{P}\cdot$ compared with $\mathrm{Bu^tO\dot{P}(OEt)_3}$.

Even at low temperatures benzyl diethyl phosphite did not give a phosphoranyl radical detectable by e.s.r. when it was treated with either t-butoxyl or ethoxyl radicals. The short lifetime of the phosphoranyl radical in both cases is a consequence of its rapid β-scission to give a resonance stabilised benzyl radical. Similarly, no phosphoranyl radical could be detected when triallyl phosphite was treated with t-butoxyl radicals.[4,23]

Bentrude and Min [13] have recently reported some configurational selectivity in the β-scission of dibenzyloxydiethoxyphosphoranyl radicals, implying that positional exchange by pseudo-rotation in these radicals is slow compared to their scission. They interpreted their results by assuming that the entering alkoxyl radical took up an apical position and that β-scission occurred more readily when the departing group was in the apical position. However, as they pointed out, the analysis was not unique and it is possible that β-scission in fact occurs more readily when the leaving group is in an equatorial position, the *quantitative* result being due to the different polar and radical stability effects brought about by labelling one benzyl group with a *para*-methyl substituent. However, the qualitative result remains that for dibenzyloxydiethoxyphosphoranyl radicals at 65° pseudo-rotation is slow compared to β-scission. A similar conclusion probably holds for the radicals $\mathrm{PhCH_2O\dot{P}(OEt)_3}$, $\mathrm{PhCH_2O\dot{P}(OEt)_2OBu^t}$, and $\mathrm{(CH_2{=}CHCH_2O)_3O\dot{P}Bu^t}$.

The phosphoranyl radicals $\mathrm{(MeO)_3\dot{P}OEt}$, $\mathrm{(MeO)_3\dot{P}OBu^t}$, and $\mathrm{(MeO)_2(cyclo\text{-}C_5H_9O)\dot{P}OEt}$ undergo β-scission to give some methyl radicals which react with the trialkyl phosphite present to give trialkoxymethylphosphoranyl radicals. These radicals are also produced when azomethane is photolysed in the presence of trialkyl phosphites. The affinity of a trialkyl phosphite for methyl radicals seems to be governed mainly by steric effects.* Tri-t-butyl phosphite forms a trialkoxymethylphosphoranyl radical least readily because of an increase in repulsive interaction between the t-butoxy-groups in going from the phosphite to the (distorted) trigonal bipyramidal phosphoranyl radical [equation (37); R = Bu^t].



(37)

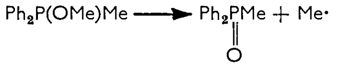
Methyl radical attack on the trialkyl phosphite will probably lead to the most stable phosphoranyl radical (XVII). The most favourable path for loss of methyl may involve pseudo-rotation of (XVII) to give (XVIII) which undergoes subsequent rapid α-scission.[9] The polar effect of the t-butyl groups in $\mathrm{(Bu^tO)_3\dot{P}Me}$ may also be responsible for its low stability, since by increasing the electron density at phosphorus they make valence shell expansion less favourable.

At the temperatures discussed in this work, β-scission of the methyltri-n-alkoxyphosphoranyl radicals was not important in limiting their lifetimes, whereas a benzyl radical was readily lost from the benzyloxydiethoxymethylphosphoranyl radical [equation (38)].

$$\mathrm{PhCH_2O\dot{P}(OEt)_2Me} \longrightarrow \mathrm{PhCH_2\cdot} + \mathrm{O{=}P(OEt)_2Me} \qquad (38)$$

Davidson [24] has shown that at higher temperatures methyl (and other alkyl) radicals will induce the chain oxidation of alkyl diphenylphosphinites.

$$\mathrm{Ph_2POMe} + \mathrm{Me\cdot} \longrightarrow \mathrm{Ph_2\dot{P}(OMe)Me} \qquad (39)$$



$$\mathrm{Ph_2\dot{P}(OMe)Me} \longrightarrow \mathrm{Ph_2\underset{\underset{\displaystyle O}{\|}}{P}Me} + \mathrm{Me\cdot} \qquad (40)$$

The radical $\mathrm{(Bu^tO)_3\dot{P}Me}$ may also readily undergo β-scission to give a t-butyl radical but the latter was not observed by e.s.r. since the formation of the phosphoranyl radical was slow and its steady-state concentration was low at the temperatures examined.

EXPERIMENTAL

The e.s.r. and u.v. irradiation apparatus have been described previously.[4,6,15] Spectroscopic parameters of phosphoranyl radicals were calculated using the Breit–Rabi equation.[4] The procedure for determining rate constants for unimolecular β-scission processes has also been described.[4,6]

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* α-Scission of phosphoranyl radicals appears to be more sensitive than β-scission to steric congestion around the phosphorus.[9]

[23] J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 1969, **91**, 3944.

[24] R. S. Davidson, *Tetrahedron*, 1969, **25**, 3383.

Diethyl peroxide [25] and azomethane [26] were prepared by standard methods and stored in hydrocarbon solution in a freezer. t-Butyl and s-butyl nitrites were prepared by the method used for n-butyl nitrite.[27]

Trialkyl phosphites were either obtained commercially and purified by standard procedures or prepared by standard methods. The following are new compounds. *Cyclopentyl dimethyl phosphite* (from cyclopentanol and trimethyl phosphite [28]) had b.p. 44° at 0·5 mmHg (Found: C, 47·0; H, 8·2; P, 17·2. $C_7H_{15}O_3P$ requires C, 47·2; H, 8·5; P, 17·4%). *Cyclopentyl diethyl phosphite* (from diethyl chlorophosphite and cyclopentanol in the presence of triethylamine [29]) had b.p. 42° at 0·1 mmHg (Found: C, 52·3; H, 9·3; P, 14·8. $C_9H_{19}O_3P$ requires C, 52·4; H, 9·3; P, 15·0%).

Diethyl Peroxide.—The trialkyl phosphite (to give a final concentration of 0·5—1M) was added to a solution of diethyl peroxide (2M) in cyclopentane, hexane, or pentane contained in an e.s.r. tube just prior to insertion into the spectrometer.

Di-t-butyl Peroxide.—The methods used were those described previously.[4,15]

Azomethane.—The trialkyl phosphite (to give a final concentration of 0·6M) was added to a solution of azomethane (10% w/w) in cyclopentane, hexane, or pentane at 0°, just prior to insertion of the sample into the spectrometer cavity.

Alkyl Nitrites.—Neat alkyl nitrite (50 μl) was added to a solution of the trialkyl phosphite (0·5—1M) in cyclopentane just prior to insertion into the spectrometer.

Kinetic Experiments.—The general technique was that described previously.[4,6,15] Radical concentrations were determined by reference to a solution of standardised diphenylpicrylhydrazyl in benzene at 20° using a ruby as internal standard.[4] Corrections to radical concentrations determined at different temperatures were made by assuming that the difference in spin populations was proportional to T^{-1}/K^{-1}. The Arrhenius parameters in the Results section are quoted to two decimal places; this does not imply that they are accurate to this degree, merely that they describe best the experimental results.

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[26] R. Benaud and L. C. Leitch, *Canad. J. Chem.*, 1954, **32**, 545.

[27] W. A. Noyes, 'Organic Syntheses, Coll. Vol. II, Wiley, New York, 1943, p. 108.

[28] M. Imaev, *Zhur. obshchei Khim.*, 1961, **31**, 1770.

[29] A. H. Ford-Moore and B. J. Perry, 'Organic Syntheses, Coll. Vol. IV, Wiley, New York, 1963, p. 955.