Site Selectivity in the β-Scission of Alkoxyphosphoranyl Radicals. A Reinterpretation

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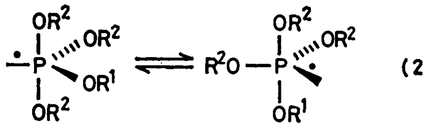
The rate constants for β-scission of cyclic and acyclic trigonal bipyramidal (TBP) phosphoranyl radicals $\overline{OCH_2CH_2O}\dot{P}(OBu^t)X$ (A) and $(EtO)_2\dot{P}(OBu^t)X$ (B) [X = EtO or $(Me_3Si)_2N$] to give t-butyl radicals have been measured by kinetic e.s.r. spectroscopy. The phosphoranyl radicals exist as equilibrium mixtures of isomers which differ in the occupancy of apical and equatorial sites and which interconvert much more rapidly than they undergo β-scission. Radicals for which access of the Bu^{t}O group to an equatorial site is restricted undergo β-scission relatively slowly. The relative rates of t-butyl radical-forming β-scission at 233 K in hydrocarbon solution are shown to be approximately proportional to the equilibrium mole fraction of the isomer in which the Bu^{t}O group occupies an equatorial site, provided that allowance is made for the retarding effect of the five-membered ring. β-Scission of TBP alkoxyphosphoranyl radicals thus involves equatorial site selectivity. Previous results for phosphoranyl radicals (A) and (B) (X = Me_3SiO) are reinterpreted in terms of equatorial site selectivity rather than the apical site selectivity originally proposed. The apicophilicity of Me_3SiO is almost certainly lower than that of Bu^{t}O, whilst in the previous work the reverse order of apicophilicity was assumed.

β-SCISSION of trigonal bipyramidal (TBP) tetra-alkoxyphosphoranyl radicals [equation (1)] would be expected to be site selective, that is the R^1–O bond in (1) will undergo cleavage at different rates depending on whether this alkoxy group occupies an apical or equatorial site [equation (2)].[1,2]

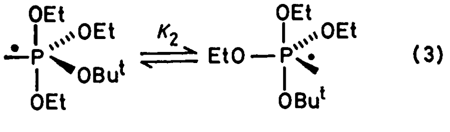
E.s.r. spectroscopic evidence indicates that the two isomers of (1) generally interconvert much more rapidly than they undergo β-scission.[3,4] In an earlier paper [4] we reported rate constants (determined using kinetic e.s.r. spectroscopy) for β-scission of the phosphoranyl radicals (2)—(5) † and, *by assuming* $K_5 \ll 1$, we interpreted the relatively slow fragmentation of (5) in terms of *apical site selectivity in β-scission*. However, recent results [5] strongly suggest that $K_5 \gg 1$ and hence that the earlier work [4] should be reinterpreted in terms of *equatorial site selectivity in β-scission.*

$$R^1O\dot{P}(OR^2)_3 \longrightarrow R^{1\bullet} + O{=}P(OR^2)_3 \quad (1)$$

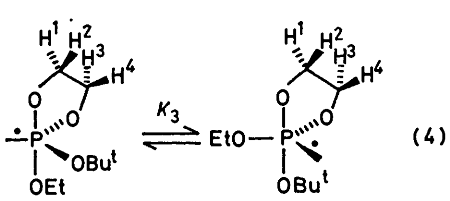
(1)



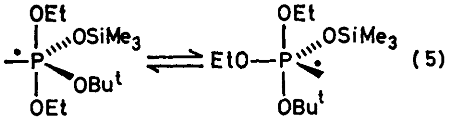
(1a) (1b)



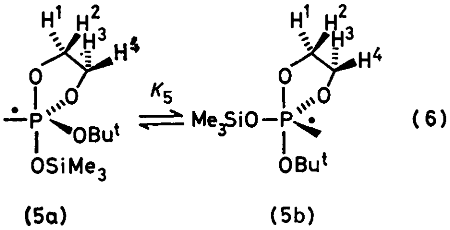
(2a) (2b)



(3a) (3b)



(4a) (4b)



(5a) (5b)

The object of the present work was to confirm this reinterpretation by making use of the bis(trimethylsilyl)amino group as a configuration indicating ligand, because the magnitude of the nitrogen splitting shown by the e.s.r. spectrum of a phosphoranyl radical $(Me_3Si)_2N\dot{P}X_3$ allows the site of attachment of the silylamino group to be established.

RESULTS

(a) *E.s.r. Spectra and Structures of Phosphoranyl Radicals.*—Spectra of TBP phosphoranyl radicals of the type (7) were observed during continuous u.v. irradiation of hydrocarbon solutions containing (6) and $(Me_3Si)_2NN(SiMe_3)_2$ [6] [R = Et, Bu^t, Me_3Si, or Bu^{t}C(O)] or (8) and ROOR (R = Et, Bu^t, or Me_3Si). When both routes to (7) were used the spectra were identical from either source.

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† The Me_3SiO group is shown in an equatorial site in (4), whereas in ref. 4 it was thought to prefer an apical site. This difference is justified herein.

Apart from a small variation in the value of a(P), the spectrum of [7; R = Bu^{t}C(O)] (see Figure 1) was independent of temperature between 153 and 300 K, and only one isomer was detected. On the basis of the small, temperature-independent nitrogen splitting (5.4 G),[7,8] the coupling of *ca.* 4 G to *one* ring proton,[8] and the absence of lineshape effects[5] we assign this spectrum to the isomer (7b), in which the silylamino ligand occupies an equatorial site. The high apicophilicity of acyloxy ligands in phosphoranyl radicals has been noted previously.[8] The e.s.r. parameters for (7) are given in Table 1.

$$(Me_3Si)_2NN(SiMe_3)_2 \xrightarrow{h\nu} 2(Me_3Si)_2N\bullet \qquad (7)$$

$$RO_2R \xrightarrow{h\nu} 2RO\bullet \qquad (8)$$

$$\overline{OCH_2CH_2OP}OR \xrightarrow{(Me_2Si)_2N^\bullet} \overline{OCH_2CH_2OP}^{\bullet}(OR)N(SiMe_3)_2 \xleftarrow{RO^\bullet} \overline{OCH_2CH_2OP}N(SiMe_3)_2 \qquad (9)$$

(6) (7) (8)

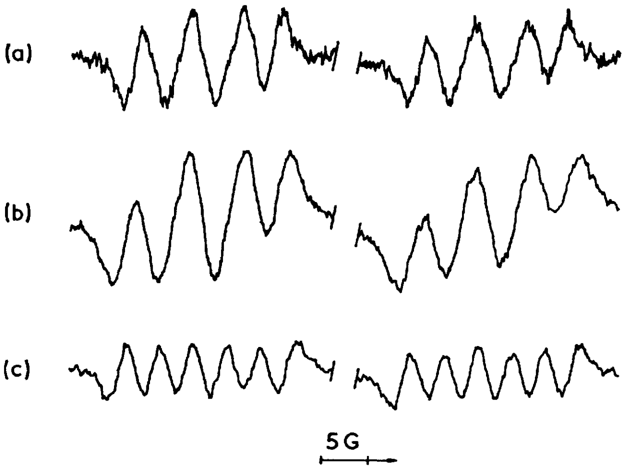
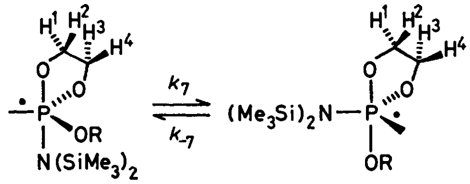


FIGURE 1 E.s.r. spectra of phosphoranyl radicals (7); (a) [7; R = Bu^{t}C(O)] in cyclopropane at 241 K; (b) (7; R = Et) in ethylene at 152 K; (c) (7; R = Et) in cyclopropane at 233 K

When R = Me$_3$Si, separate spectra of both isomers (7a and b) were observed at low temperatures (154 K) in ethylene solvent. The assignments were made on the basis of the values of a(N) which are typical[7,8] for an apical (24.9 G) and an equatorial (6.2 G) sp^2-hybridised ligand nitrogen atom. A preliminary communication discussing the e.s.r. spectrum of (7; R = Me$_3$Si) has appeared.[9] The equilibrium constant K_7 (= k_7/k_{-7}) was measured directly by double integration of the spectra at 154 K and found to be 2.1. As the temperature was increased, differential line broadening and shifts in line position became apparent (see Figure in ref. 9) and we attribute these effects to rapid exchange between the (a) and (b) isomers of (7; R = Me$_3$Si). At the highest accessible temperature (235 K) the spectrum corresponds (apart from the phosphorus splitting) to a nitrogen triplet (15.0 G) of apparent 1 : 2 : 1 triplets resulting from nearly equal coupling to two ring protons (*ca.* 3 G). Thus, at 235 K exchange is rapid on the e.s.r. time scale and (apart from some residual differential broadening) the average of the spectra of (7a and b) is observed, with K_7 now *ca.* 1.* These lineshape effects have been computer



(7a) (7b) (10)

TABLE 1

E.s.r. parameters for phosphoranyl radicals (7)

R	Isomer [a]	Solvent [b]	T/K	g Factor [c]	Hyperfine splittings (G) a(P) [c]	a(N)	a(H) [d]	K_7 [e]
Bu^{t}C(O)	(b)	C	210	2.0022	996.8	5.4 [f]	4.6	Large [g]
Me$_3$Si	(a)	E	154	2.0024	885.6	24.9	6.8	2.1 [h]
Me$_3$Si	(b)	E	154	2.0020	909.2	6.2	5.2	
Me$_3$Si	(a) + (b)	E	235	2.0022	895.2	15.0	2.9 [i]	1.1
Bu^t	(b)	E	142	2.0025	874.4	5.2	4.6	Large [g]
Bu^t	(a) + (b)	C	269	2.0024	874.9	7.0	3.8	9.9 [j]
Bu^t	(a) + (b)	C	241	2.0024	874.8	6.5	4.0	14.2 [j]
Et	(a) + (b)	E	173	2.0022	868.2	6.1	4.3	20.9 [k]
Et	(a) + (b)	C	200	2.0024	868.9	6.5	4.1	14.2 [k]
Et	(a) + (b)	C	233	2.0022	868.2	7.3	3.9	8.4 [k]

[a] (a) + (b) indicates an average spectrum. [b] C = Cyclopropane, E = ethylene. [c] Obtained using the Breit–Rabi equation. [d] A measured doublet splitting unless otherwise noted. [e] Obtained from equation (11) unless otherwise noted. [f] Independent of temperature between 200 and 300 K. [g] Other isomer not detectable. [h] Obtained by measurement of the concentrations of (7a and b). [i] Apparent triplet splitting, equal to $[\bar{a}(H^1) + \bar{a}(H^2)]/2$. [j] Measurements between 240 and 269 K yield ΔH_7 — 7.5 kJ mol^{-1}, ΔS_7 — 8.7 J mol^{-1} K^{-1}. [k] Measurements between 173 and 253 K yield ΔH_7 — 6.0 kJ mol^{-1}, ΔS_7 — 8.2 J mol^{-1} K^{-1}.

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* The mode of exchange shown in equation (9) was confirmed[4,8,9] by generating deuterium-labelled phosphoranyl radicals by addition of (Me$_2$Si)$_2$N· to $\overline{OCH_2CD_2OP}OSiMe_3$.[4] Apart from ^{31}P and ^{14}N splittings, the averaged spectrum at 232 K showed a 1 : 6 : 1 splitting of 3.0 G confirming[4,8] rapid exchange of H with H (and D with D) rather than of H with D.

simulated on the basis of the following assumptions. (i) Only one ring proton [H^1 in (7a) and H^2 in (7b)] [8] gives rise to non-zero splitting and this splitting is independent of temperature. (ii) The nitrogen splittings for (7a and b), which must have the same sign, are independent of temperature. Hence, K_7 may be calculated from the average nitrogen splitting (obtained from the high temperature

$$K_7 = [a(N_{ap}) - \bar{a}(N)]/[\bar{a}(N) - a(N_{eq})] \qquad (11)$$

$$2.303 \log_{10}K_7 = \Delta S_7/R - \Delta H_7/RT \qquad (12)$$

spectrum) using equation (11).[5,*] The directly measured value of K_7 (2.1 at 154 K) and the value (1.1 at 235 K) obtained from equation (11) combine to yield ΔH_7 — 2.4 kJ mol^{-1} and ΔS_7 — 9.4 J K^{-1} mol^{-1} when substituted into equation (12). (iii) The difference in the phosphorus splittings of (a) and (b) isomers of (7; R = Me_3Si) increases linearly with temperature by 8 G between 154 and 235 K.

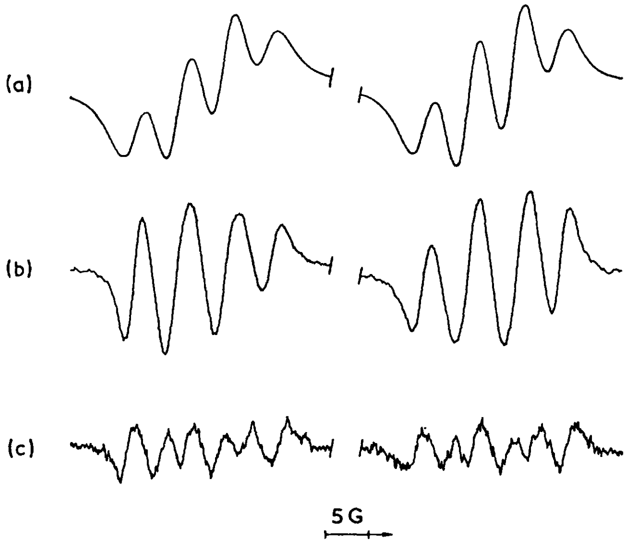


FIGURE 2 E.s.r. spectra of the phosphoranyl radical (7; R = Bu^t); (a) in ethylene at 139 K; (b) in cyclopropane at 217 K; (c) in cyclopropane at 260 K

The values of k_7 (R = Me_3Si) obtained by simulation gave a good fit to equation (13), and at 233 K k_7 is 4.2×10^8 s^{-1}.

$$\log_{10}(k_7/s^{-1}) = 12.7 - 18.2/2.303RT \text{ kJ mol}^{-1} \qquad (13)$$

In general, when radicals are detected during continuous photolysis of samples it is important to verify that the thermal equilibrium concentrations are being measured and not concentrations corresponding to a photostationary state, a situation which could arise if the radicals exhibit appreciable optical absorption above 250 nm. However, at 150 K [(7b)]/[(7a)] remained constant for at least 20 s during the decay of both radicals after interrupting photolysis, confirming that photolysis did not perturb the relative concentrations from the thermal equilibrium value when R = Me_3Si.

When R in (7) was Et or Bu^t, the e.s.r. spectra at high temperatures appeared (apart from phosphorus splitting) as 1 : 1 : 1 triplets of 1 : 1 doublets (see Figures 1 and 2). As the temperature was decreased, the nitrogen splitting also decreased and the doublet splitting increased. At 217 K the spectrum of (7; R = Bu^t) appeared as a distorted quartet [$a(N) \simeq a(1H)$] of unequally spaced lines (see Figure 2b), indicating that exchange of (7a and b) was becoming slow on the e.s.r. time scale. At very low temperature (139 K in liquid ethylene) the spectrum of (7; R = Bu^t) became a 1 : 2 : 2 : 1 quartet of equally spaced lines and probably corresponds to the isomer (7b) with no contribution from (7a) (see Figure 2a).[†] Separate spectra from (a) and (b) isomers of (7; R = Et) could not be obtained at low temperatures and the spectrum appeared to be the average from the two isomers, even at 152 K (see Figure 1b). Values of K_7 (R = Et or Bu^t), obtained from $\bar{a}(N)$ using equation (11) and assuming $a(N_{ap})$ 24.9 G [the value for (7a; R = Me_3Si)] and $a(N_{eq})$ 5.2 G [the value for (7b; R = Bu^t)], are included in Table 1.

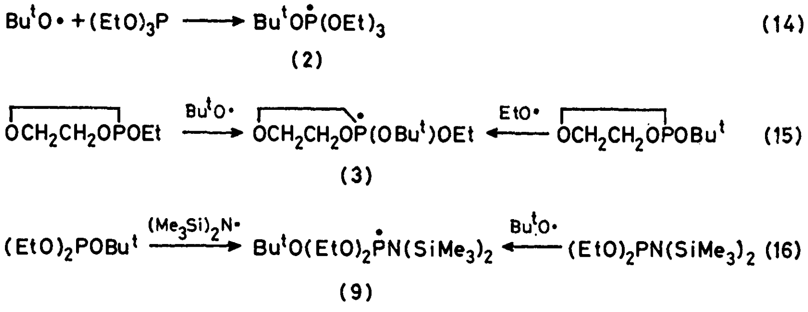
TABLE 2

E.s.r. parameters for phosphoranyl radicals other than (7)

Radical	Solvent [a]	T/K	g Factor [b]	Hyperfine splittings (G) a(P) [b]	 Others
(2)	C	208	2.0021	889.9	
(3)	E	233	2.0021	909.3	c
(9)	E	199	2.0023	849.5	a(N) ca. 2
$(MeO)_3\dot{P}N(SiMe_3)_2$	C	171	2.0021	844.0	a(N) 2.1
(11)	C	183	2.0024	981.8	a(N) 32.0 [d]

[a] C = Cyclopropane, E = ethylene. [b] Obtained using the Breit–Rabi equation. [c] Poorly resolved doublet (spacing ca. 2.9 G) due to ring proton splitting (see Figure 4). [d] Independent of temperature between 161 and 203 K.

For the kinetic studies described in the next section the phosphoranyl radicals (2), (3), and (9) were also generated, as shown in equations (14)—(16). The e.s.r. parameters are given in Table 2.



$$Bu^tO\cdot + (EtO)_3P \longrightarrow Bu^tO\dot{P}(OEt)_3 \qquad (14)$$

(2)

$$OCH_2CH_2OPOEt \xrightarrow{Bu^tO\cdot} OCH_2CH_2O\dot{P}(OBu^t)OEt \xleftarrow{EtO\cdot} OCH_2CH_2OPOBu^t \qquad (15)$$

(3)

$$(EtO)_2POBu^t \xrightarrow{(Me_3Si)_2N\cdot} Bu^tO(EtO)_2\dot{P}N(SiMe_3)_2 \xleftarrow{Bu^tO\cdot} (EtO)_2PN(SiMe_3)_2 \qquad (16)$$

(9)

At low temperature (162 K) the spectrum of (9) appeared

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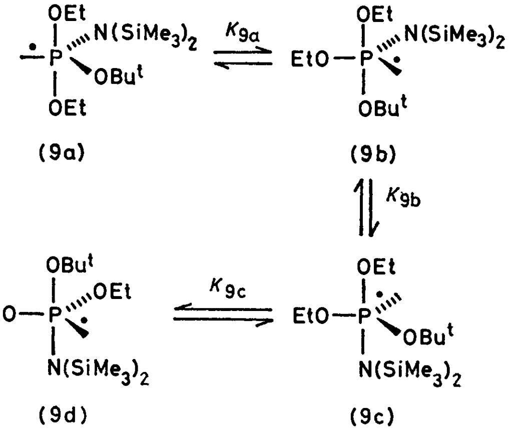
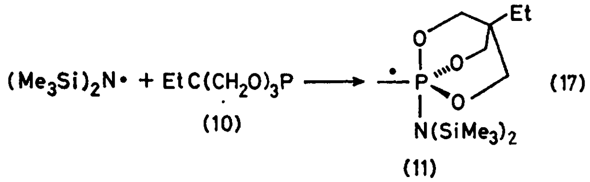
[*] The splittings from apical and equatorial nitrogens are designated $a(N_{ap})$ and $a(N_{eq})$ respectively; $\bar{a}(N)$ is the average splitting.

[†] The form of the differential broadening at lower temperatures indicates [5] that $a(P)$ for (7b) is larger than that for (7a), as it is when R = Me_3Si.

(apart from ^{31}P splitting) as a single line of width 5 G, but at higher temperatures nitrogen splitting (*ca.* 2 G) was partially resolved (see Figure 3). Optimum resolution was obtained at *ca.* 182 K and above this temperature it deteriorated. The smaller radical $(MeO)_3\dot{P}N(SiMe_3)_2$ [formed by addition of $(Me_3Si)_2N\cdot$ to $(MeO)_3P$] showed narrower lines at low temperatures and nitrogen splitting of 2.1 G was clearly resolved at 165 K (see Figure 3). This spectrum is assigned to the TBP isomer with an equatorial silylamino group. At higher temperatures the spectrum showed differential line broadening (Figure 3) consistent with exchange of this isomer with another (undetected) containing an apical nitrogen ligand. We thus interpret the spectrum of (9) in terms of the presence of mainly (9a and b), although exchange with small concentrations of (9c and d) causes line broadening at higher temperatures.



SCHEME 1



If the phosphoranyl radical formed by addition of $(Me_3Si)_2N\cdot$ to the caged phosphite (10) has a TBP structure, the silylamino ligand must be apical as shown in (11) [equation (17)]. The e.s.r. spectrum showed a large nitrogen splitting (32.0 G, see Figure 3) consistent with such a structure.* At high temperatures (11) undergoes ring-opening β-scission to give $(Me_3Si)_2NP(O)(OCH_2)_2C(Et)\dot{C}H_2$ [$a(2H_\alpha)$ 22.3, $a(4H_\gamma)$ 1.05 G, g 2.002 4 at 260 K].†

(b) β-*Scission of Phosphoranyl Radicals.*—As the temperature was increased the e.s.r. signals from the phosphoranyl radicals became weaker and were progressively replaced by spectra of the carbon-centred radicals produced by their β-scission.

The phosphoranyl radicals (7; R = Et or Me_3Si) underwent only ring cleavage to give (12) [equation (18a)] the e.s.r. spectra of which show non-equivalence of the β-protons, probably because of the presence of the proximate asymmetric phosphorus centre (see Table 3).‡ When R = Bu^t, (7) gave both (12; R = Bu^t) and t-butyl radicals, and in the range 230—263 K the value of k_{18b}/k_{18a} {assumed equal to $[Bu^t\cdot]/[(12)]$} was 1.42 ± 0.05.

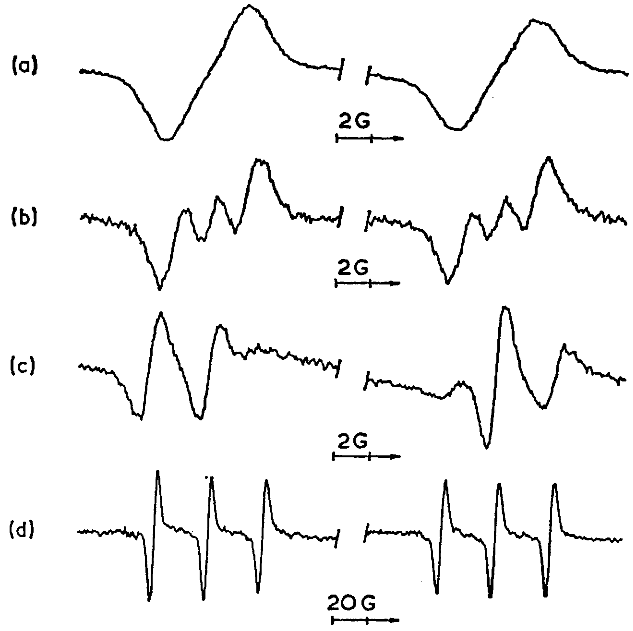
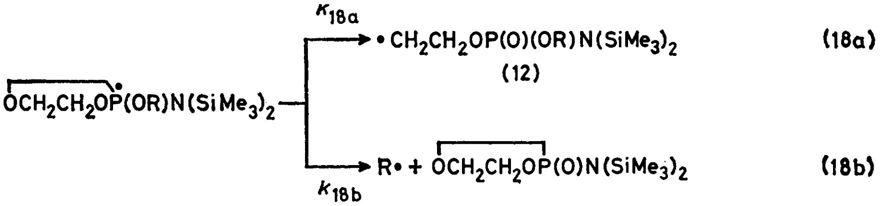


FIGURE 3 E.s.r. spectra of the phosphoranyl radicals; (a) (9) in ethylene at 182 K, (b) $(MeO)_3\dot{P}N(SiMe_3)_2$ in ethylene at 165 K, and (c) at 220 K, (d) (11) in cyclopropane–diethyl ether (4 : 1 v/v) at 184 K

The phosphoranyl radical (9) also underwent β-scission with competitive cleavage of primary and tertiary alkyl–O bonds, and between 213 and 290 K the value of k_{19b}/k_{19a} (assumed equal to $[Bu^t\cdot]/[Et\cdot]$) was 6.5 ± 0.1.



(12)

(18a)

(18b)

As reported previously,[4] (2) and (3) underwent β-scission to give only t-butyl radicals as judged by e.s.r. spectroscopy. The rates of first-order decay of the spectra of (2), (3), (7; R = Bu^t), and (9) were measured by the rotating sector technique [4,10] and the rate constants (k_{decay}) are given in Table 4. The rate constants for β-scission (k_β) are taken

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* It is possible that this phosphoranyl radical adopts a σ*-P–N structure with local C_{3v} symmetry at P and in which the unpaired electron is contained in an antibonding P–N σ orbital.[1] It would be difficult to distinguish between (11) and the σ*P–N structure on the basis of isotropic e.s.r. parameters.

† The assignment of the γ-proton splittings is not known.

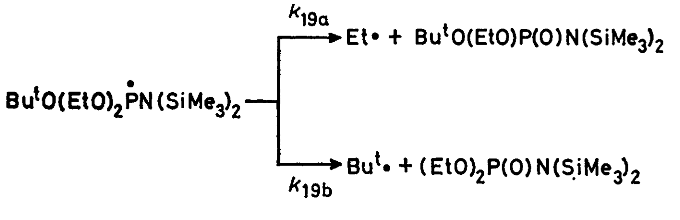
‡ Such non-equivalence was not resolved for $\cdot CH_2CH_2OP(O)(OBu^t)OSiMe_3$ which is produced by β-scission of (5).[4]

as equal to k_{decay}.* Arrhenius parameters were obtained from plots of $\log(k_{\text{decay}})$ against $1/T$ and good straight lines were obtained for all radicals. Changing the solvent from cyclopropane to toluene had no significant effect on the rates of β-scission.

TABLE 3

E.s.r. parameters for alkyl radicals (12) produced by ring-opening β-scission of (7) in cyclopropane at 260 K

R	*g* Factor	Hyperfine splittings (G)		
		$a(2H\alpha)$	$a(1H\beta^1)$	$a(1H\beta^2)$
Me_3Si	2.0027	22.0	28.5	30.0
Et	2.0028	22.0	27.8	29.0
Bu^t	2.0029	22.0	28.3	30.0



(19a)

(19b)

TABLE 4

Rate constants and activation parameters for the decay of phosphoranyl radicals

Radical	Solvent [a]	T/K	$\log_{10}$ (A/s^{-1}) [b,c]	E_a/kJ mol^{-1} [b,c]	k_{decay}/s^{-1} at 233 K
(2)	C	198—238	10.6 (10.6)	32.1 (32.2)	2.5×10^3
(3) [d]	C	225—252	10.4 (10.4)	34.6 (34.3)	4.4×10^2
(3) [e]	C	225—254	10.5	35.3	3.9×10^2
(7; R = Bu^t) [f]	C	188—232	9.4	33.5	7.8×10^1
(7; R = Bu^t) [f]	T	197—233	9.7	34.8	7.9×10^1
(7; R = Bu^t) [g]	C	193—233	9.8	35.0	9.0×10^1
(9) [h]	C	169—226	11.6	36.7	2.4×10^3
(9) [h]	T	190—221	11.6	36.8	2.2×10^3
(9) [i]	C	169—212	11.4	36.1	2.0×10^3
(14)	T	213—234	12.9 (13.3)	42.8 (43.8)	2.0×10^3

[a] C = Cyclopropane, T = toluene. [b] Probable maximum errors in log A and E_a are ±1 and ±4 kJ mol^{-1}, respectively. [c] Values in parentheses are taken from ref. 4. [d] From $\overline{\mathrm{OCH_2CH_2OP}}\mathrm{OEt}$ and $Bu^tO\cdot$; an unidentified phosphoranyl radical [a(P) 886.2 G, g 2.0021 at 174 K] was always present with this source of (3) and probably arises from an impurity in the dioxaphospholan. [e] From $\overline{\mathrm{OCH_2CH_2OP}}\mathrm{OBu^t}$ and $EtO\cdot$; no unidentified radicals were detected. [f] From $\overline{\mathrm{OCH_2CH_2OP}}\mathrm{N(SiMe_3)_2}$ and $Bu^tO\cdot$. [g] From $\overline{\mathrm{OCH_2CH_2OP}}\mathrm{OBu^t}$ and $(Me_3Si)_2N\cdot$. [h] From $(EtO)_2PN(SiMe_3)_2$ and $Bu^tO\cdot$. [i] From $(EtO)_2POBu^t$ and $(Me_3Si)_2N\cdot$.

DISCUSSION

The proton splittings shown by the phosphoranyl radicals (3), (5), and (7) indicate that the five-membered rings bridge apical and equatorial sites in the trigonal bipyramids.[8] This preference for attachment of the ring is found for all similar cyclic phosphoranyl radicals detected so far.[1] Exchange of the exocyclic RO and $(Me_3Si)_2N$ ligands in (7; R = Et, Bu^t, or Me_3Si) takes place much more rapidly than any of these radicals undergo β-scission. When attempting to interpret the relative rates of β-scission of phosphoranyl radicals we may therefore assume that different permutational isomers of comparable stability are present in their equilibrium concentrations.[1,8] Table 5 lists the relative rates (at 233 K) of t-butyl radical-forming β-scission of the phosphoranyl radicals examined in this work and earlier.[4]

The phosphoranyl radical (3) undergoes β-scission six times slower than (2) and, since it is reasonable that K_2 and K_3 should be similar, we have attributed this difference to the presence of the ring in the former radical.[4,11] The radical (7; R = Bu^t) undergoes t-butyl-forming β-scission 38 times slower than the acyclic analogue (9). We suggest that this difference is too large to be accounted for by the presence of the ring in (7), and, since the Bu^tO group is largely confined to the apical site in (7; R = Bu^t), *equatorial* site selectivity in β-scission is indicated. This intepretation can be put on a semi-quantitative basis if the mole fraction (m_{eq}) of isomers having equatorial Bu^tO groups can be estimated for each phosphoranyl radical.

TABLE 5

Relative rates of β-scission of phosphoranyl radicals to give t-butyl radicals at 233 K

Radical	m_{eq}	Relative $k_\beta^{Bu^t}$		Ref.
		Experimental	Calculated	
(2)	0.33	(1)	(1)	This work, 4
(3)	0.33	0.17	(0.17)	This work, 4
(9)	0.23	0.76	0.70	This work
(7; R = Bu^t)	0.056	0.020	0.028	This work
(4)	0.23	1.0	0.70	4
(5)	0.061	0.036	0.031	4
(14)		0.8		This work

For the radicals discussed herein, we assume that the rate constant (k_{eq}) for cleavage of the C–O bond in an equatorial Bu^tO group is reduced by a factor of 6 if a five-membered ring is present, but is otherwise independent of the nature of the remaining three ligands attached to phosphorus. β-Scission is assumed to be highly site selective (*i.e.* $k_{\text{ap}} \ll k_{\text{eq}}$). Thus, the observed rate constants for β-scission of acyclic and cyclic phosphoranyl radicals to give t-butyl radicals will be given by equations (20) and (21), respectively.

$$k_\beta^{Bu^t}(\text{acyclic}) = m_{\text{eq}}k_{\text{eq}} \qquad (20)$$

$$k_\beta^{Bu^t}(\text{cyclic}) = m_{\text{eq}}k_{\text{eq}}/6 \qquad (21)$$

---

* Especially at low temperatures, k_{decay} may be up to twice $k\beta$ because of possible removal of the phosphoranyl radicals by reaction with the alkyl radicals produced by their β-scission.[1] It seems likely that any differences between k_{decay} and $k\beta$ will be similar for the radicals studied here.

We begin by assuming that $K_2 = K_3$. The values of K_7 (Table 1) may be used to obtain estimates of K_3 and K_5, if we assume that the linear free energy relationships (22) and (23) hold.

$$\log K_3 = \log K_7\,(\mathrm{R = Bu^t}) - \log K_7\,(\mathrm{R = Et}) \quad (22)$$

$$\log K_5 = \log K_7\,(\mathrm{R = Bu^t}) - \log K_7\,(\mathrm{R = Me_3Si}) \quad (23)$$

At 233 K the values of K_7 are 16.8 (R = $\mathrm{Bu^t}$), 8.3 (Et), and 1.1 ($\mathrm{Me_3Si}$), and the calculated values of K_3 and K_5 are 2.0 and 15.3, respectively. These values of K_3 and K_5 are consistent with the ring proton splittings [8] shown by (3) and (5) (see Figure 4 *).

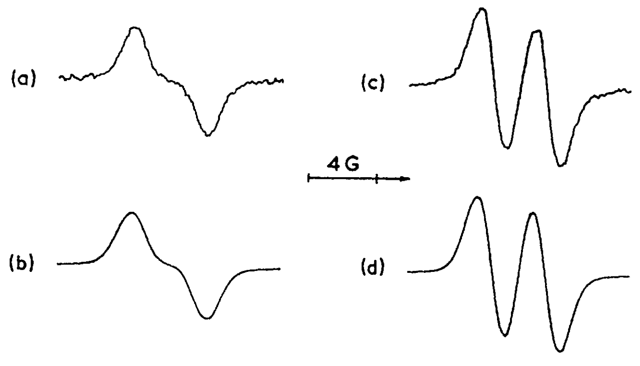
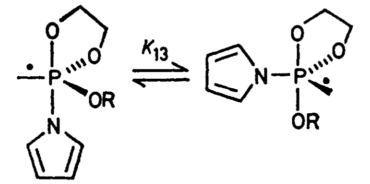


FIGURE 4 Experimental [(a) and (c), in ethylene at 233 K] and simulated [(b) and (d)] e.s.r. spectra of (3) [(a) and (b)] and (5) [(c) and (d)]. Only the low field [$m_I(^{31}P) + \frac{1}{2}$] transitions are shown

The value of K_{13} [equation (24)] has been estimated previously for the radical (13; R = $\mathrm{Bu^t}$, Et, or $\mathrm{Me_3Si}$) and is 6.1 (R = $\mathrm{Bu^t}$), 1.5 (Et), and 0.23 ($\mathrm{Me_3Si}$) at *ca.* 232 *K*.[5] Using equations analogous to (22) and (23), K_{13} may also be used to obtain values of K_3 and K_5 (4.1 and 26.5, respectively) which are in reasonable agreement with those obtained from K_7.

The value of m_{eq} for (9) was estimated by taking $K_{9a} = 2K_3$, $K_{9b} = 1/K_7$ (R = $\mathrm{Bu^t}$), and $K_{9c} = 0.5\ K_3$ (see Scheme 1).† The value of m_{eq} for (4) was calculated in a similar way [replace $(\mathrm{Me_3Si})_2\mathrm{N}$ by $\mathrm{Me_3SiO}$ in Scheme 1] but taking the equilibrium constant corresponding to K_{9b} as $1/K_5$. With these assumptions, the values of m_{eq} and hence the calculated values of $k_\beta^{\mathrm{Bu^t}}$ in Table 5 were obtained.



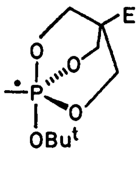
(24)

(13a) (13b)

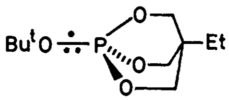
Considering the assumptions involved, agreement between the calculated and experimental values of $k_\beta^{\mathrm{Bu^t}}$ is good and supports the conclusion that β-scission involves an equatorial rather than an apical $\mathrm{Bu^tO}$ group. β-Scission with ring opening is observed for (5) and (7; R = $\mathrm{Bu^t}$) but not for (3). All isomers of these radicals contain equatorial endocyclic $\mathrm{CH_2{-}O}$ groups, but access of the $\mathrm{Bu^tO}$ group to the equatorial site is much more restricted for (5) and (7) than for (3) and ring cleavage becomes competitive with $\mathrm{Bu^t{-}O}$ cleavage in the former two radicals.

We reported previously [4] that the phosphoranyl radical $\mathrm{Bu^tO\dot{P}(OCH_2)_3CEt}$ (14), derived by addition of t-butoxyl radicals to (10), undergoes β-scission about as rapidly as (2). As was pointed out,[4] if (14) has a TBP structure the $\mathrm{Bu^tO}$ group must be apical [see (14a)] and the high rate of β-scission is thus incompatible with a high degree equatorial site selectivity.

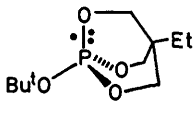
However, (14) may adopt a quasi-tetrahedral σ* structure [1,12-14] (14b or c) rather than (14a). The ligand attached by the two-centre three-electron bond in a σ* radical is analogous to the apical ligand in a TBP radical, but (14c), in which the $\mathrm{Bu^tO}$ group is in a basal site, would probably be of similar stability to (14b). Even if (14) is better described as a TBP species, the presence of the cage could cause it to be distorted towards the σ* structure,[14] and the difference in stabilities of (14a—c) could be very small.



(14a)



(14b)



(14c)

We suggest that both TBP and σ* isomers of an alkoxyphosphoranyl radical can undergo β-scission, the former with equatorial and the latter with basal site selectivity. The ready fragmentation of (14) may be explained in terms of basal site selectivity for β-scission. The difference in energy of TBP and σ* isomers is probably small for most radicals, for example exchange of (7a and b) (R = $\mathrm{Me_3Si}$) probably takes place *via* a σ* intermediate,[9] and thus the activation energy for exchange (18.2 kJ mol^{-1}) represents an upper limit for the TBP — σ* energy difference. The ring proton splittings detected for (3), (5), and (7) imply that these are TBP radicals [1,8] and since the other e.s.r. parameters [a(P), a(N)] of these species are similar to those of their acyclic analogues (2), (4), and (9) we conclude that the latter also adopt quasi-TBP structures.

At present we do not have an entirely convincing explanation for these site selectivities, but some understanding may be obtained by considering the effectiveness of polar contributions to the transition states for β-scission. For TBP radicals, the stabilising contribution

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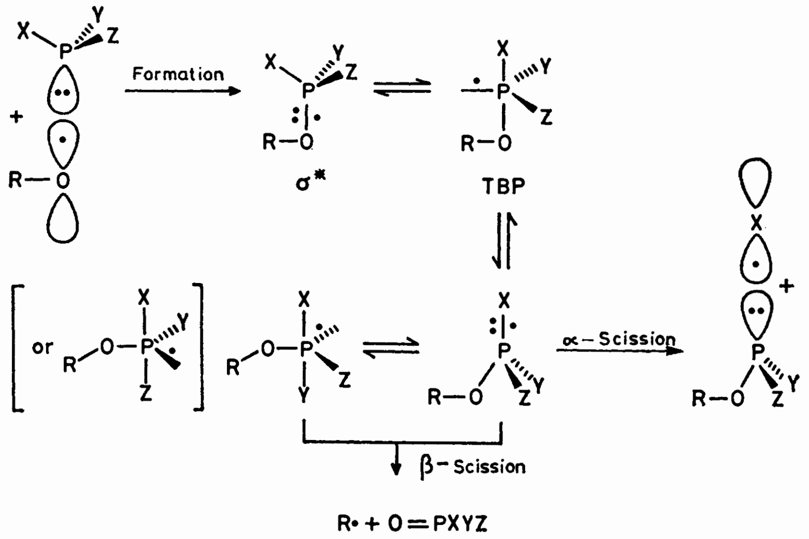
* The computer simulations in Figure 4 were based on the assumption that the apical methyleneoxy ring proton *cis* to the unpaired electron gives rise to a splitting of 3.4 G in (a) and (b) isomers of (3) and (5), and that all other proton splittings are zero. Taking $K_3 = 2.0$ gives $\bar{a}(\mathrm{H^2})$ 2.3, $\bar{a}(\mathrm{H^1})$ 1.1 G for (3); taking $K_5 = 15.3$ gives $\bar{a}(\mathrm{H^2})$ 3.2, $\bar{a}(\mathrm{H^1})$ 0.2 G. The peak–peak linewidth is 1.8 G and the lineshape is 80% gaussian, 20% lorentzian for all radicals.

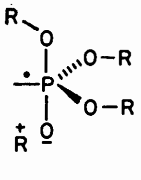
† The multipliers of K_3 are statistical factors.

from (15a) should be less than that from (15b), since the electropositive $\bar{O}$ substituent prefers to occupy an equatorial rather than an apical site in TBP trialkyl phosphate radical anions.[15] For the σ* radicals, the contribution from (16b) should be greater than that of (16a), since it seems likely that electropositive substituents will preferentially occupy basal rather than apical sites in σ* phosphoranyl radicals. Conformation about the P–O bonds in alkoxyphosphoranyl radicals may also be important in determining site selectivity.

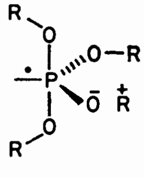


SCHEME 2

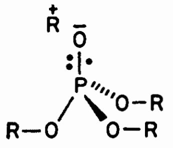
Accepting equatorial–basal site selectivity in β-scission, the scheme for formation, permutational isomerisation, and fragmentation of phosphoranyl radicals given previously [4] should be revised as shown in Scheme 2.*



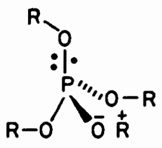
(15a)



(15b)



(16a)



(16b)

One experimental result which cannot readily be reconciled with equatorial–basal site selectivity remains in the literature. Bentrude and Min [16] reported that oxygen is transferred to phosphorus more readily from a benzyloxy group in $(PhCH_2O)_2\dot{P}(OEt)_2$ † when that group was the incoming radical [equation (25)] than when the group was present in the phosphite reactant. The detection of this 'memory effect' implies [16] apical site selectivity in β-scission of a TBP or a σ* phosphoranyl radical, but we note that no other examples of memory effects in phosphite oxidation are known.[1,4] The memory effect reported [17] for oxidations proceeding *via* non-benzylic tetra-alkoxyphosphoranyl radicals could not be confirmed in later work.[18]

$$PhCH_2O\bullet + PhCH_2OP(OEt)_2 \longrightarrow (PhCH_2O)_2\dot{P}(OEt)_2 \qquad (25)$$

EXPERIMENTAL

The techniques employed for the detection of e.s.r. spectra during continuous u.v. irradiation of samples in the cavity of the spectrometer (Varian E-4) have been described previously.[7,19] The microwave frequency was monitored using an EIP Model 331 Autohet counter and the magnetic field was measured using an ^{1}H n.m.r. magnetometer constructed by U.C.L. Electronics Section. The difference in field at the sample and at the magnetometer probe was determined taking the *g* factor of the pyrene radical anion (Na$^+$ counter ion) in THF as 2.002 710.[20] Rate constants for radical decay were measured by the rotating sector technique.[7,10] Relative radical concentrations were determined by electronic integration of suitable lines followed by mechanical integration of the derived absorption signals. E.s.r. spectra showing the effects of isomer exchange were simulated using the program ESREXN available from Q.C.P.E. (program no. 209). The simulations in Figure 4 were obtained using the Varian program no. 995126-OOD in conjunction with a Varian 620L-100 computer interfaced directly to the spectrometer.

Samples consisted of a peroxide (*ca.* 1M) or tetrakis(trimethylsilyl)hydrazine (*ca.* 0.4M) and the phosphorus(III) compound (0.5—1M) in cyclopropane, ethylene, or toluene

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* We have proposed [1,4,9] that when a σ* phosphoranyl radical rearranges to a TBP radical the ligand attached by the two-centre three-electron bond becomes one of the apical ligands in the TBP isomer. Similarly, when a TBP radical rearranges to a σ* species one of the apical substituents becomes the uniquely bound apical ligand in the σ* isomer.

† One phenyl group was 'labelled' with a *p*-methyl substituent.

solvent. Solutions were prepared using a standard vacuum line and were degassed and sealed under vacuum in Suprasil quartz tubes (0.4 mm o.d.).

Materials.—Di-t-butyl peroxide was obtained commercially (Koch–Light) and purified before use. Diethyl [21] and bis(trimethylsilyl) [22] peroxides and tetrakis(trimethylsilyl)hydrazine [23] were prepared by literature methods.

Triethyl phosphite (B.D.H.) and (10) (Aldrich) were obtained commercially. Diethyl t-butyl phosphite (b.p. 61—62 °C at 14 Torr; ^{31}P n.m.r. in benzene showed $\delta + 134.0$ p.p.m. downfield from 85% H_3PO_4),[24] 2-ethoxy-,[25] 2-trimethylsiloxy-,[4] and 2-t-butoxy-1,3,2-dioxaphospholan [26] and diethoxy[bis(trimethylsilyl)amino]phosphine [27] were prepared by published methods. 2-t-Butoxy-1,3,2-dioxaphospholan (b.p. 57 °C at 12 Torr) was also prepared by the action of lithium t-butoxide on 2-chloro-1,3,2-dioxaphospholan in ether at room temperature.

2-*Bis(trimethylsilyl)amino*-1,3,2-*dioxaphospholan* (8). n-Butyl-lithium (83.5 ml of 2.0M solution in hexane) was added dropwise during 45 min with stirring and cooling (ice-bath) to a solution of hexamethyldisilazane (27.5 g, 0.17 mol) in ether (100 ml). After the addition, the solution was refluxed for 45 min and, after cooling to −20 °C, 2-chloro-1,3,2-dioxaphospholan (25 g, 0.17 mol) in ether (50 ml) was added dropwise with stirring. After the addition, the mixture was stirred for 30 min at room temperature, the precipitated lithium chloride was removed by filtration through Kieselguhr, and the ether was removed under reduced pressure. Distillation of the residual oil yielded the *product* (74%), b.p. 95—96 °C at 5 Torr (Found: C, 38.3; H, 8.8; N, 5.7; P, 12.5. $C_8H_{22}NO_2PSi_2$ requires C, 38.2; H, 8.8; N, 5.6; P, 12.3%).

2-*Trimethylacetoxy*-1,3,2-*dioxaphospholan* [6; R = Bu^t-C(O)]. 2-Chloro-1,3,2-dioxaphospholan (20 g, 0.16 mol) in ether (20 ml) was added dropwise to a stirred suspension of dry lithium pivalate (20 g, 0.19 mol) in ether (70 ml) whilst cooling in an ice-bath. After the addition, the mixture was stirred for 30 min at room temperature and then for 3 h under reflux. The mixture was allowed to cool and filtered through Kieselguhr. The solvent was removed under reduced pressure and the residual oil distilled to give the *product*, b.p. 71—72 °C at 0.1 Torr (Found: C, 44.2; H, 7.0; P, 16.1. $C_7H_{13}O_4P$ requires C, 43.8; H, 6.8; P, 16.1%).

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