Homolytic Organometallic Reactions. Part XII.[1] An Electron Spin Resonance Study of the α-Scission of Alkoxyalkylphosphoranyl Radicals in Solution

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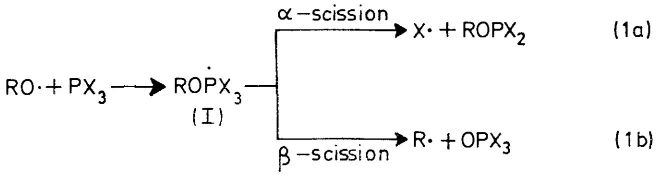
The structures and the kinetics of α-scission of a series of alkoxyalkylphosphoranyl radicals have been studied by e.s.r. spectroscopy in solution. These radicals were generated by the addition of photolytically produced alkoxyl radicals to alkoxyalkylphosphines. The stability towards α-scission of the radicals $Et_n\dot{P}(OR)_{4-n}$ exhibits a maximum for $n = 2$. Phosphoranyl radicals $R_2\dot{P}(OBu^t)_2$ fragment by loss of an alkyl radical, R·, with increasing rate along the series R = Me < Bu^t < Et ~ Pr^n < Pr^i ~ Bu^s < allyl. These results are interpreted in terms of a preference for departure of an alkyl radical from an apical rather than an equatorial site, in α-scission of the trigonal bipyramidal phosphoranyl radical. Factors which influence the relative rates of α- and β-scission of alkoxyalkylphosphoranyl radicals are discussed.

COMPOUNDS of tervalent phosphorus react with alkoxyl radicals in solution to form phosphoranyl radicals (I),



which may decompose unimolecularly by α- or β-scission.[2] The great strength of the P=O bond formed in reaction (1b) means that β-scission is generally the favoured process thermodynamically.[2] However, when alkoxyalkylphosphines react with alkoxyl radicals below room temperature, the intermediate phosphoranyl radicals undergo α-scission more rapidly, resulting in overall homolytic displacement of an alkyl group by the S_H2 (stepwise) mechanism.[2] At higher temperatures, fragmentation of (I) can become less selective and competing α- and β-scission of the radical $Bu^n_3\dot{P}OBu^t$ has been

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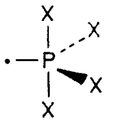
[1] Part XI, A. G. Davies and J. C. Scaiano, *J.C.S. Perkin II*, 1973, 1777.

[2] For recent reviews see (*a*) K. U. Ingold and B. P. Roberts, 'Free Radical Substitution Reactions,' Wiley-Interscience, New York, 1971, ch. 6; (*b*) A. G. Davies and B. P. Roberts, in 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, 1973, vol. 1, ch. 10; (*c*) W. G. Bentrude, in 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, 1973, vol. 2, ch, 22.

inferred from product analysis of the reaction of tributylphosphine with t-butoxyl radicals at 130°.[3]

Phosphoranyl radicals possess distorted trigonal bipyramidal structures (II) in which the unpaired electron is stereochemically active with its orbital directed towards an equatorial ligand site in the most stable isomer.[4-6] Apical and equatorial ligands are chemically non-equivalent and we[5] and others[7] have previously advanced evidence for configurational selectivity in the β-scission of tetra-alkoxyphosphoranyl radicals.


(II)

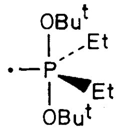
This paper describes a study of the e.s.r. spectra and the kinetics of α-scission of a series of alkoxyalkylphosphoranyl radicals. The emphasis is on the dialkoxydialkylphosphoranyl radicals, $R^1{}_2\dot{P}(OR^2)_2$, which possess sufficient stability towards unimolecular fragmentation and self-reaction to enable their decay kinetics to be investigated without the aid of computer-averaging techniques.

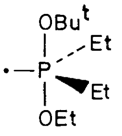
RESULTS

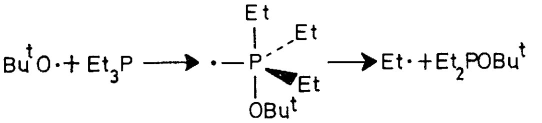
Sufficiently high concentrations of radicals in solution for direct detection by e.s.r. spectroscopy were obtained by high intensity u.v. irradiation of appropriate precursors in the presence of the alkylalkoxyphosphines.[5] Di-t-butyl peroxide and diethyl peroxide were the sources of t-butoxyl and ethoxyl radicals respectively, and azomethane was the source of methyl radicals.

When di-t-butyl peroxide was photolysed in the presence of triethylphosphine in cyclopropane at −100° a strong spectrum of the ethyl radical was detected. Although no phosphoranyl radical is detectable * initially, a spectrum attributable to such a radical [a(P)705 G, a(H) 2·3 G (4H); −100°] became apparent after a few minutes' irradiation. A similar spectrum [a(P) 707 G, a(H) 2·3 G (4H)] is immediately apparent † when t-butoxyl radicals react with diethylethoxyphosphine, and both spectra thus result from diethyldialkoxyphosphoranyl radicals with structures (IIIa) and (IIIb) respectively,[6,8] the more electronegative alkoxy-groups occupying apical positions (alkoxy-groups have a greater apicophilicity[9] than alkyl groups).

With triethylphosphine the primary phosphoranyl radical (IV) is clearly very unstable towards α-scission, and (IIIa) is formed by addition of a t-butoxyl radical to the fragmentation product Et_2POBu^t. The primary phosphoranyl radical (V) from t-butoxyl radicals and trimethylphosphine is more stable towards α-scission, its e.s.r. spectrum being readily detectable at −81°.[6]

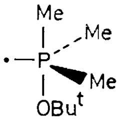

(IIIa)

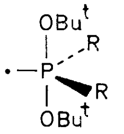

(IIIb)


(IV)

(2)

$$Bu^tO\cdot + Et_2POBu^t \longrightarrow (IIIa) \longrightarrow Et\cdot + EtP(OBu^t)_2 \qquad (3)$$


(V)


(VI)

Phosphoranyl radicals of the structure (VI) have been similarly detected as secondary products during photolysis of di-t-butyl peroxide in the presence of a series of trialkylphosphines R_3P and the spectroscopic parameters are given in Table 1.

Phosphoranyl adducts were also formed between R_2POEt or $RP(OEt)_2$ and t-butoxyl radicals, and, in the temperature ranges studied (<0°), these phosphoranyl radicals underwent only α-scission to give the alkyl radical R· with no detectable concentration of t-butyl radicals resulting from β-scission, even when R was a methyl group. Similar conclusions regarding the relative rates of α- and β-scission of alkylalkoxyphosphoranyl radicals have been reached by analysis of reaction products.[10] Secondary phosphoranyl radicals were detectable in many cases, resulting from the addition of t-butoxyl radicals to the phosphorus(III) compounds produced in the fragmentation of the primary adduct radicals. These results are summarised in Table 2.

Similar phosphoranyl radicals were produced by the addition of photolytically generated ethoxyl radicals to dialkylalkoxyphosphines and these results are also given in Table 2.

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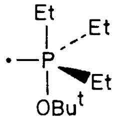
* In propane solvent at −145° a weak spectrum from a phosphoranyl radical was immediately apparent. We very tentatively assign to this radical the structure *A* [a(P) 587 G, a(H) *ca.* 13 G (1H)] in which the equatorial CH_2 groups do not give rise to detectable hyperfine splitting, and the conformation about the apical P–C bond is such that only one apical methylene hydrogen gives a resolvable splitting.


A

† By ' immediately apparent ' we mean that the signal reached a steady-state intensity within a time comparable to its decay time when the light was shuttered.

[3] S. A. Buckler, *J. Amer. Chem. Soc.*, 1962, **84**, 3093.

[4] J. Higuchi, *J. Chem. Phys.*, 1969, **50**, 1001.

[5] A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 2224.

[6] P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 6033.

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

[8] A. G. Davies, R. W. Dennis, D. Griller, and B. P. Roberts, *J. Organometallic Chem.*, 1972, **40**, C33.

[9] (*a*) P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem. Internat. Edn.*, 1971, **10**, 687; (*b*) R. K. Oram and S. Trippett, *J.C.S. Perkin II*, 1973, 1300.

[10] W. G. Bentrude, E. R. Hansen, W. A. Khan, T. B. Min, and P. E. Rogers, *J. Amer. Chem. Soc.*, 1973, **95**, 2286.

When t-butoxyl radicals react with ethyldiethoxyphosphine, the spectra of two phosphoranyl radicals are immediately apparent. The primary phosphoranyl radical (VII) [a(P) 793 G; $-100°$ in isopentane] undergoes α-scission very readily giving ethyl radicals which are also detected. The second phosphoranyl radical is assigned the structure (VIII) [a(P) 698 G, a(H) 2·5 G (4H); $-100°$ in isopentane] and must result from the addition of ethyl radicals to the original phosphine. The feasibility of such a reaction was demonstrated by the generation of methyl radicals, by photolysis of azomethane, in the presence of $EtP(OEt)_2$ when the e.s.r. spectrum of (IX) was detected, with comparable spectroscopic parameters (see Table 2).

TABLE 1

E.s.r. parameters of dialkyldi-t-butoxyphosphoranyl radicals $R_2\dot{P}(OBu^t)_2$, derived from the trialkylphosphines R_3P at $-100°$

R	Solvent	$a(^{31}P)$/G [a]	a(H)/G	g [a]
Me [b]	Cylopropane–propane (1 : 1 v/v)	702	2·5 (6H)	2·004
Et	Cyclopropane	705	2·3 (4H)	2·004
Pr^n	Cyclopropane	702	2·1 (4H)	2·004
Pr^i	Cyclopropane	705	1·6 (2H)	2·005
Bu^s [c]	Cyclopropane–propane (1 : 1 v/v)	705	*ca.* 1·6 (2H)	2·004
Bu^t [d]	Cyclopropane	707		2·004
Allyl	Propane	708	*ca.* 1·8 (4H)	2·004

[a] Calculated using the Breit–Rabi equation; a(P) ± 1 G, $g \pm 0·001$. [b] Also generated by reaction of t-butoxyl radicals with Me_2PPMe_2 (see text). [c] This radical exists in two diastereoisomeric forms which appeared to have slightly different phosphorus hyperfine splittings. [d] Also generated by reaction of t-butoxyl radicals with $Bu^t{}_2PPBu^t{}_2$ and with $Bu^t{}_2POBu^t$ (see text).

TABLE 2

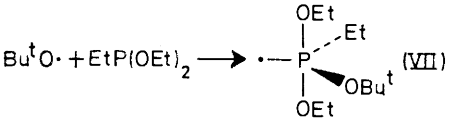
Phosphoranyl radicals generated by addition of ethoxyl and t-butoxyl radicals to alkylethoxyphosphines $R_nP(OEt)_{3-n}$ (n = 1 or 2).

Phosphoranyl radical	Solvent	Temp. (°C)	$a(^{31}P)$/G	[a]a(H)/G	g [a]
$Et_2\dot{P}(OEt)OBu^t$	Cyclopropane	−100	707	2·3 (4H)	2·004
$Et_2\dot{P}(OEt)OBu^t$	Isopentane	−80	708	2·3 (4H)	2·004
$Me_2\dot{P}(OEt)OBu^t$	Isopentane	−100	702	2·5 (6H)	2·005
$Et\dot{P}(OEt)_2OBu^t$	Isopentane	−100	793	Not resolved	2·004
$Me\dot{P}(OEt)_2OBu^t$	Isopentane	−100	794	Not resolved	2·004
$Et_2\dot{P}(OEt)_2$	Hexane–isopentane (1 : 2 v/v)	−100	698	2·5 (4H)	2·004
$Me_2\dot{P}(OEt)_2$	Isopentane	−100	693	2·8 (6H)	2·005
$Me(Et)\dot{P}(OEt)_2$ [b]	Hexane	−90	696	2·5 (5H)	2·004

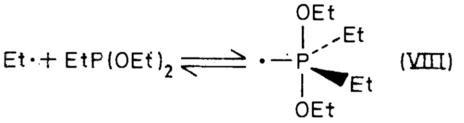
[a] Calculated using the Breit–Rabi equation; a(P) ± 1 G, $g \pm 0·001$. [b] Generated by photolysis of azomethane in the presence of $EtP(OEt)_2$.

Kinetics of α-Scission.—The dialkyldi-t-butoxyphosphoranyl radicals (VI) were sufficiently long-lived at *ca.* $-100°$ to enable the decay of their e.s.r. spectra, when the light was shuttered, to be monitored directly without the aid of computer-averaging techniques. The decays followed first-order kinetics and correspond to the α-scission process of equation (7).

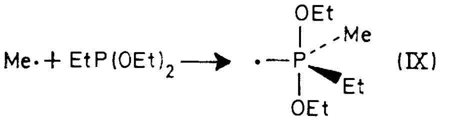
$$R_2\dot{P}(OBu^t)_2 \longrightarrow R\cdot + RP(OBu^t)_2 \qquad (7)$$



(VII) (4)



(VIII) (5)



(IX) (6)

In particular, reaction of t-butoxyl radicals with diethyl-t-butoxyphosphine in the temperature range -20 to $+10°$ gave rise to the spectrum of only the ethyl radical, whilst that of the t-butyl radical was undetectable. At $-30°$ spectra of both the ethyl radical and of the radical $Et_2\dot{P}(OBu^t)_2$ were observed, whilst below $-40°$ only the latter phosphoranyl radical was detectable.

When the major reaction removing R· during the dark period is reaction (8), the observed rate constant for the

$$R\cdot + (VI) \longrightarrow \text{non-radical products} \qquad (8)$$

decay of (VI) will be $2k_7$. The decay of $Et_2\dot{P}(OEt)_2$ or $Me_2\dot{P}(OEt)_2$ was too rapid to follow directly even at $-160°$. With radical concentrations at full light intensity of *ca.* 10^{-6}M, the radical $Et_2\dot{P}(OEt)_2$ decayed by a first-order process at $-50°$, but by a second-order process at $-130°$, as shown by the variation of radical concentration with light intensity.[5] This result indicates that the activation energy for self-reaction is less than that for α-scission. The decay of $Me_2\dot{P}(OEt)_2$ was predominantly second-order even at $+28°$. The use of computer-averaging techniques[11] is clearly required for these radicals and such studies are in progress.

The decay of the radical $Et_2\dot{P}(OEt)OBu^t$ (IIIb) in isopentane between -96 and $-150°$ was observed directly to be first-order at the higher temperatures (-96 to $-128°$). The α-scission of (IIIb) was also studied under conditions of steady irradiation of a solution containing di-t-butyl peroxide and diethylethoxyphosphine. By monitoring the steady-state concentrations of (IIIb) and of the ethyl radical, formed by α-scission of (IIIb), at different light intensities, it was possible to determine k_9 relative to $2k_{10}$.[5,12] The steady state technique allows measurement of k_9 at higher temperatures than could be used for the 'direct-decay' method described previously, and also provides a measure of the rate constant for cross-combination, k_{11}, relative to $2k_{10}$.

$$Et_2\dot{P}(OEt)OBu^t \longrightarrow Et\cdot + EtP(OEt)OBu^t \qquad (9)$$

$$Et\cdot + Et\cdot \longrightarrow \text{non-radical products} \qquad (10)$$

$$Et\cdot + Et_2\dot{P}(OEt)OBu^t \longrightarrow \text{non-radical products} \qquad (11)$$

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[11] G. B. Watts, D. Griller, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 8784.

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

Taking [13] $2k_{10}$ as $2{\cdot}6 \times 10^{10} \exp(-0{\cdot}83/RT)$ l mol^{-1} s^{-1} (RT in kcal mol^{-1}) we may obtain the value of k_9, and in the temperature range −70 to −90° ($2k_{10}/k_{11}$) is *ca.* 50.* The rate constant for self-reaction of R·, generated by α-scission of (VI), will be similar to $2k_{10}$ independently of the nature of R·.[14] Assuming that $k_{11} \approx k_8$, with the concentration ratios [(VI)]/[R·] (>1000) obtained immediately after interrupting the light in the direct decay experiments, it follows that the observed first-order rate constants in these experiments correspond to $2k_7$ (see above).

A summary of the kinetic data for the α-scission of alkylalkoxyphosphoranyl radicals is given in Table 3.

The radicals (VI) [$R_2\dot{P}(OBu^t)_2$ where R = Me or Bu^t] were also prepared by irradiation of di-t-butyl peroxide in the presence of the corresponding tetra-alkyldiphosphine, R_2PPR_2. The dialkylphosphinyl radical $R_2P\cdot$ was not detected in these experiments and we suggest that although this radical is formed initially it may rapidly attack the peroxide to give R_2POBu^t. Reaction (14) is very rapid [8]

$$Bu^tO\cdot + R_2PPR_2 \longrightarrow R_2POBu^t + \cdot PR_2 \quad (12)$$

$$R_2P\cdot + Bu^tOOBu^t \longrightarrow R_2POBu^t + Bu^tO\cdot \quad (13)$$

$$Bu^tO\cdot + R_2POBu^t \longrightarrow \underset{\text{(VI)}}{R_2\dot{P}(OBu^t)_2} \quad (14)$$

and a competition probably exists between the cage reaction of the products of reaction (13) to give (VI), and their diffusion into the bulk solution. It is also conceivable that attack of the dialkylphosphinyl radical on the peroxide could give (VI) in a one-step reaction. The radical (VI; R = Bu^t) was also generated by the addition of t-butoxyl radicals to $Bu^t{}_2POBu^t$, and the phosphoranyl radical from this source exhibited kinetic behaviour identical with that of the radical formed from $Bu^t{}_3P$ or $Bu^t{}_2PPBu^t{}_2$.

TABLE 3

Kinetics of α-scission of alkylalkoxyphosphoranyl radicals in solution

Phosphoranyl radical [a]	Solvent	Temp. range (°C)	A/s^{-1}	E_a/ kcal mol^{-1}	Rate constant for α-scission at −100° (s^{-1})
$Me_2\dot{P}(OBu^t)_2$	Isopentane [b]	−55 to −82	$4{\cdot}0 \times 10^{13}$	14·0	$9{\cdot}5 \times 10^{-5}$
$Et_2\dot{P}(OBu^t)_2$	Isopentane [b]	−76 to −102	$1{\cdot}5 \times 10^{11}$	10·5	$8{\cdot}3 \times 10^{-3}$
$Pr^n{}_2\dot{P}(OBu^t)_2$	Propane	−73 to −109	$7{\cdot}5 \times 10^{10}$	10·4	$6{\cdot}5 \times 10^{-3}$
$Pr^i{}_2\dot{P}(OBu^t)_2$	Propane	−95 to −120	$2{\cdot}9 \times 10^{12}$	10·9	$6{\cdot}0 \times 10^{-2}$
$Bu^s{}_2\dot{P}(OBu^t)_2$ [c]	Propane	−95 to −120	$4{\cdot}6 \times 10^{11}$	10·1	$7{\cdot}0 \times 10^{-2}$
$Bu^t{}_2\dot{P}(OBu^t)_2$	Propane	−70 to −101	$2{\cdot}0 \times 10^{12}$	12·0	$1{\cdot}4 \times 10^{-3}$
$(Allyl)_2\dot{P}(OBu^t)_2$	Propane				0·35 [d]
$Me_2\dot{P}(OEt)OBu^t$	Isopentane	−48 to −93	$9{\cdot}0 \times 10^{12}$	13·6	$6{\cdot}0 \times 10^{-5}$
$Et_2\dot{P}(OEt)OBu^t$	Isopentane	−96 to −128	$4{\cdot}0 \times 10^{10}$	8·2	2·0
$Et_2\dot{P}(OEt)OBu^t$ [e]	Isopentane	−37 to −88	$1{\cdot}1 \times 10^{10}$ [f]	7·8 [f]	1·6 [f]
$Et\dot{P}(OEt)_2OBu^t$	Propane	−150 to −170	$2{\cdot}2 \times 10^{8}$ [g]	4·4 [g]	630 [h]

[a] Rate of α-scission determined by direct decay of e.s.r. signal of phosphoranyl radical unless otherwise stated. [b] Rate in propane at −100° was the same within experimental error. [c] The two diastereoisomeric forms appear to decay at similar rates. [d] Rate constant at −140°, decay at −100° was too rapid to follow. [e] Rate constant measured by the 'steady-state' method (see text). [f] Taking $2k_{10} = 2{\cdot}6 \times 10^{10} \exp(-0{\cdot}83/RT)$ l mol^{-1} s^{-1}, where RT is in kcal mol^{-1}. [g] Probably very inaccurate due to small temperature range available within which decay was first-order, and low signal strength. [h] Rate constant at −160° is 0·55 s^{-1}.

DISCUSSION

(a) *Structures of Phosphoranyl Radicals.*—Only one isomer of each of the alkylalkoxyphosphoranyl radicals has been detected by e.s.r. spectroscopy. This isomer has always been that which is predicted to be most stable thermodynamically on the basis of the greater apicophilicity [9] of an alkoxyl group relative to an alkyl group in a trigonal bipyramidal phosphoranyl radical, and when the attack is by an alkoxyl radical, we assume that the phosphoranyl radical which is observed is that which is formed initially.

The isotropic phosphorus hyperfine splitting in the phosphoranyl radicals $(R^1O)_n\dot{P}R^2{}_{4-n}$ decreases as n decreases.[15] This trend is clearly demonstrated by the values of a(P) at −100° for the following radicals: $Bu^tO\dot{P}(OEt)_3$, 887 G;[15] $Bu^tO(EtO)_2\dot{P}Et$, 793 G; $Bu^tO(EtO)\dot{P}Et_2$, 707 G; $Bu^tO\dot{P}Et_3$, 587 G (at −145°); $Bu^tO\dot{P}Me_3$, 611 G.† These changes in isotropic hyperfine splitting result from an increase in the proportion of 3*s* character in the orbital of the unpaired electron on phosphorus as the electronegativity of the ligands increases.[15,16]

(b) *Configurational Effects on Rates of α-Scission.*—Perhaps the most important result to come out of the present work is the evidence for configurational selectivity in the α-scission reactions of alkylalkoxyphosphoranyl radicals. In trigonal bipyramidal phosphoranes, PX_5, the bonds from phosphorus to the apical ligands are longer and weaker than the equatorial bonds.[17] By analogy we would expect that α-scission of the related phosphoranyl radical $\dot{P}X_4$ would be most rapid when an

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* The ratio ($2k_t/k_x$) at −60° is *ca.* 5 for the reactions Bu^t· + Bu^t· ($2k_t$) and Bu^t· + $Bu^tO\dot{P}(OR)_3$ (k_x) (R = Me, Et, or Pr^i).[11]

† This value was obtained during the present work and differs slightly from that given in ref. 6 at −81°. The phosphorus hyperfine splittings reported in ref. 6 appear to be line spacings, without correction using the Breit–Rabi equation.

[13] R. W. Fessenden, *J. Phys. Chem.*, 1964, **68**, 1508.

[14] K. U. Ingold, in 'Free Radicals,' ed. J. Kochi, Wiley-Interscience, New York, 1971, ch. 2.

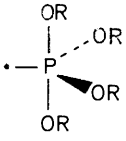
[15] A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 993.

[16] H. Bent, *Chem. Rev.*, 1961, **61**, 275.

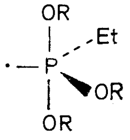
[17] B. J. Walker, 'Organophosphorus Chemistry,' Penguin, London, 1972.

apical P–X bond undergoes cleavage. Similar configurational selectivity is observed in the reactions of phosphoranes.[18]

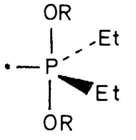
The competition between α- and β-scission of an alkylalkoxyphosphoranyl radical was first examined by Buckler[3] who showed that the reaction of t-butoxyl radicals with tri-n-butylphosphine at 130° gave $Bu^n_2POBu^t$ and Bu^n_3PO in the ratio 4 : 1. More recently Bentrude and his co-workers[10] have investigated the fragmentation of $R^1O\dot{P}(OEt)_2R^2$ by product analysis. When $R^1 = Bu^t$ no β-scission was detected at 65° in benzene where $R^2 = Et$, Bu^t, or $PhCH_2$. However, when $R^1 = PhCH_2$ there existed a competition between α- and β-scission at 60°, with the proportion of the latter increasing along the series $R^2 = PhCH_2 < Bu^t <$ Et. Our e.s.r. results also show that alkylalkoxyphosphoranyl radicals generally decompose by the thermodynamically less favourable α-scission mode, at least below room temperature, and in the series (X)—(XIII) (one alkoxy-group is Bu^tO, the remainder, if any, are EtO), the phosphoranyl radical (XII) is especially stable with respect to fragmentation. Radical (X) undergoes β-scission or self-reaction,[11,15] whilst (XI)—(XIII) undergo α-scission with a facility decreasing in the order (XIII) > (XI) ≫ (XII). There is no smooth change in reactivity on passing from (XI) to (XIII), the radical (XII) being more stable than either of its neighbours. On thermodynamic grounds we might expect (XI) to undergo α-scission least readily, since it contains the most electronegative ligands. However, if we assume that an alkyl radical departs most readily from an apical, rather than an equatorial, site this stability order may be understood, on the following basis.



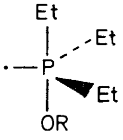
(X)



(XI)



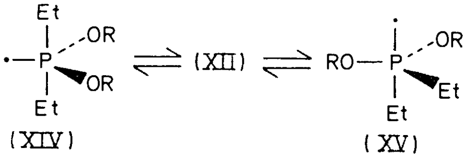
(XII)



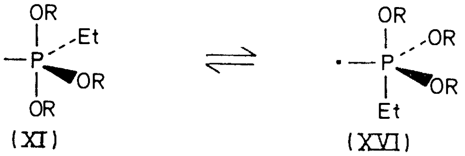
(XIII)

The radical (XIII) has an apical alkyl group appropriately positioned for departure without any prior configurational change. The radicals (XI) and (XII) do not have an apical alkyl group, but both could undergo ligand reorganization (pseudorotation)[19] to give thermodynamically less stable isomers with apical ethyl groups. The unpaired electron appears to be an apicophobic 'ligand' and hence both (XIV) and (XV) will be high energy isomers whose rate of formation from (XII) should be relatively slow. Pseudorotation of (XV) could give rise to other isomers (see Scheme).

Pseudorotation of (XI) to (XVI) involves placing only one apicophobic ligand apical [equation (16)], and this isomerisation would be expected to be more rapid than the pseudorotations shown in equation (15).



(15)



(16)

The relative rates of decay of (XI) and (XII) may be rationalised by assuming that they reflect the rates at which the phosphoranyl radicals are converted, by pseudorotation, into less stable isomers containing apical ethyl groups [for (XII) this corresponds to a situation close to case (ii) kinetic behaviour (see below)].

Stronger evidence for apical departure in α-scission comes from an examination of the rates of fragmentation of the series of dialkyldi-t-butoxyphosphoranyl radicals $R_2\dot{P}(OBu^t)_2$ (VI). The rate constants reported in Table 3 refer to the decay of the isomer (VI) which is detected by e.s.r. spectroscopy. If this isomer were undergoing α-scission directly by loss of an alkyl radical from an equatorial site we would expect the rates of α-scission to increase as the strength of the P–C bond in (VI) decreases, *viz.*, $R = Me < Et \sim Pr^n < Pr^i \sim Bu^s < Bu^t <$ allyl. This is *not* the observed order, $Bu^t_2\dot{P}(OBu^t)_2$ being intermediate in reactivity between $Me_2\dot{P}(OBu^t)_2$ and $Et_2\dot{P}(OBu^t)_2$.

The Scheme shows all possible trigonal bipyramidal * isomers of $R_2\dot{P}(OBu^t)_2$, connected by pseudorotation processes.[20]

Of the forms with an apical alkyl group, the isomer (XVII) will be the most stable. It is possible that (VI) can be converted into (XVII) by a different mechanism of ligand reorganization[20] without the necessity of passing through isomers of higher energy. Without identifying the particular isomer(s) (A) with an apical alkyl group, if the equilibrium constant K for the interconversion (VI) $\rightleftharpoons$ (A) is small then equation (17) may be derived for the rate of decay of (VI) when the light is shuttered, where k_{VI} and k_A are the rate constants for α-scission of (VI) and (A) respectively. We may identify two

$$-\,d(VI)/dt = k_{VI}[(VI)] + k_A[(A)] \qquad (17)$$

extremes of kinetic behaviour: (i) (VI) and (A) are in equilibrium, when $k_7 = (k_{VI} + Kk_A)$, and (ii) the conversion of (VI) into (A) (with a rate constant k_i) is followed by rapid α-scission of (A) such that $k_A > k_{-i}$, when

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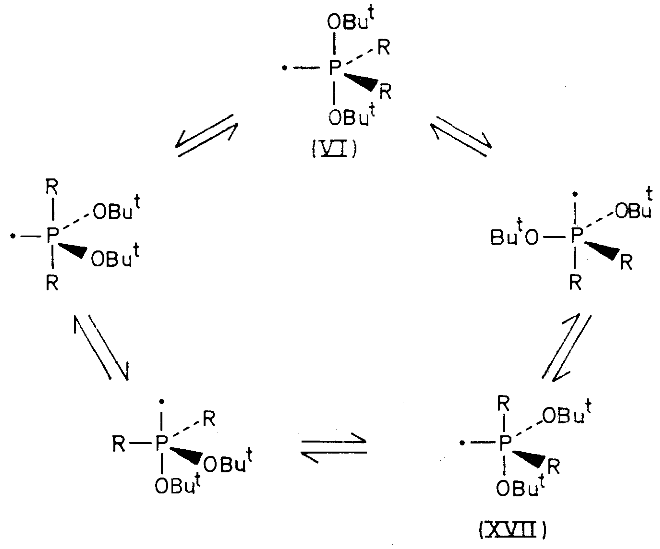
* The degree of distortion from a regular trigonal bipyramid is not important for our argument. We require only that there be two general types of ligand site that we may label (approximately) apical and equatorial.

[18] For reviews see for example F. H. Westheimer, *Accounts Chem. Res.*, 1968, **1**, 70; P. Gillespie, F. Ramirez, I. Ugi, and D. Marquarding, *Angew. Chem. Internat. Edn.*, 1973, **12**, 91.

[19] R. S. Berry, *J. Chem. Phys.*, 1960, **32**, 933.

[20] For a discussion of an alternative mechanism of ligand reorganisation, 'turnstile rotation,' see I. Ugi and F. Ramirez, *Chem. in Britain*, 1972, 918.

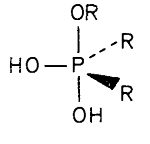
$k_7 = (k_{VI} + k_i)$. The term k_{VI} disappears from these relations if (A) is the major source of alkyl radicals. We suggest that for the radicals $R_2\dot{P}(OBu^t)_2$ (R = Me, Et, or Pr^i), over the temperature range specified, a situation close to case (i) above obtains.

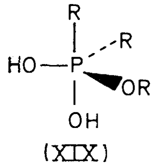


SCHEME

On passing along the series R = Me, Et, Pr^i, and Bu^t the rate constant k_A should steadily increase. Any decrease in K on passing from R = Me to Pr^i could be more than offset by the increase in k_A, giving the observed increase in k_7. For R = Bu^t steric effects become important and both K and k_i decrease appreciably. The slow rate of decay of (VI; R = Bu^t) then would result from a relatively low value of the product Kk_A or possibly a switch to kinetic behaviour close to case (ii).

For kinetic behaviour similar to case (i) above, the observed activation energy for the decay of (VI) will be the sum of the activation energy (E_A) for α-scission of (A) and the enthalpy change (ΔH_A^0) for the isomerisation of (VI) to (A). The experimental values * (Table 3) appear to be consistent with this interpretation, since the difference in energy of the phosphoranes (XVIII) and (XIX) is thought [21] to be *ca.* 7 kcal mol^{-1}, and the difference in apicophilicities of alkyl and alkoxyl groups in a phosphoranyl radical could be somewhat less than in a phosphorane.


(XVIII)


(XIX)

Our explanation of the low reactivity of (VI; R = Bu^t) requires that the bulky t-butyl group has a greater preference for equatorial placement than the less branched alkyl groups. On purely electronic grounds the apicophilicity of R would be expected to decrease in the order Me > Et > Pr^i > Bu^t. Bulky groups probably prefer equatorial sites in phosphoranes [22] and it appears that this preference extends to phosphoranyl radicals.[23] A large increase in the tendency of the alkyl group to take up an equatorial site on going from isopropyl to t-butyl is consistent with operation of a steric effect.

It is more difficult to explain the changes in behaviour brought about by substitution of the t-butoxy-groups in $R_2\dot{P}(OBu^t)_2$ by ethoxy-groups, but because of the complex kinetics involved, a detailed discussion is not warranted at this time.

(c) *Comparison of Rates of* α- *and* β-*Scission*.—We have previously advanced evidence for a configurational effect in the β-scission of tetra-alkoxyphosphoranyl radicals,[5,15] and suggested that if the bulky neopentoxy-groups prefer apical placement in (neo-$C_5H_{11}O)_3\dot{P}OEt$ then β-scission is more rapid when an equatorial C–O bond breaks. Conversely, if the neopentoxy-groups prefer equatorial placement, β-scission is faster when an apical C–O bond cleaves. In our previous paper [5] we expressed the feeling that the former pair of circumstances were perhaps more likely. In view of the results obtained in the present work and in a study of the structures of some spirophosphoranyl radicals,[23] it appears that a bulky ligand may, in fact, have a greater preference than a less bulky group for an equatorial site. It would follow that β-scission of a tetra-alkoxyphosphoranyl radical is most rapid when an *apical* C–O *bond is cleaved*. Clearly a decision between these two mechanistic alternatives must await firm experimental evidence, but as a rationalisation of more rapid apical C–O cleavage it may be worthwhile to consider the following.

β-Scission of $(RO)_4P\cdot$ is highly exothermic [5,15] and the transition state will be close to the phosphoranyl radical in structure. As the C–O bond breaks the electronegativity of the oxygen atom will increase and its ability to participate in p_π–d_π interaction with the phosphorus atom [9,24] will decrease. Both these changes will lead to a smaller increase in energy if the C–O bond which breaks is in the apical position, since more electronegative ligands favour this site and better π-donors prefer equatorial positions.[9,24]

Stereoelectronic effects would also be expected to favour β-scission with cleavage of an apical C–O bond. Inspection of models shows that, in a trigonal bipyramidal tetra-alkoxyphosphoranyl radical, overlap between the (approximately) sp^2 orbital of the unpaired electron and the anti-bonding σ orbital on oxygen will be greater for

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* The use of computer-averaging techniques is clearly desirable to enable the range of temperatures over which the fragmentation reactions can be studied to be extended. A detailed discussion of the activation parameters for these fragmentation reactions will be postponed until more accurate values are available.

[21] R. F. Hudson and C. A. Brown, *Accounts Chem. Res.*, 1972, **5**, 204.

[22] K. E. De Bruin and K. Mislow, *J. Amer. Chem. Soc.*, 1969, **91**, 7393; D. Gorenstein, *ibid.*, 1970, **92**, 644.

[23] D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1973, 1416.

[24] R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 3047.

an apical oxygen than for an equatorial oxygen. The ease of scission of carbocyclic radicals has been found to increase with the degree of overlap between the orbital of the unpaired electron and an antibonding σ orbital of the adjacent bond undergoing cleavage.[25]

Phosphoranyl radicals containing P–H bonds possess a remarkably stability towards fragmentation.[6,26,27] For example,[26,27] $\mathrm{Bu^tO\dot{P}H_3}$ may still be detected by e.s.r. spectroscopy at +40°, whereas $\mathrm{Bu^tO\dot{P}R_3}$ undergoes rapid α-scission [6,8] and $\mathrm{Bu^tO\dot{P}(OR)_3}$ [5,15] undergoes rapid β-scission at much lower temperatures. The phosphoranyl radical $\mathrm{Bu^tO\dot{P}H_2Me}$ does not lose methyl radicals readily,[6] and whereas [27] $\mathrm{Bu^tO\dot{P}(CF_3)_3}$ is too unstable towards α-scission to be detected at −140°, the radical $\mathrm{Bu^tO\dot{P}H_2CF_3}$ (which also possesses an apical $\mathrm{CF_3}$ group) is readily detectable at −20° and loses $\mathrm{CF_3^{\bullet}}$ only slowly.[27]

The P–H bond in a phosphoranyl radical is probably stronger than the P–C bond in such a species, accounting in part for the less ready cleavage of the P–H bond in α-scission of hydridophosphoranyl radicals.

It is clear from our results that alkylalkoxyphosphoranyl radicals undergo self-reaction more slowly than tetra-alkoxyphosphoranyl radicals of similar bulk.[11,28] These differences are accountable in terms of the reduced strength of the P–P bond in the dimer with increasing substitution at the phosphorus atoms by electropositive ligands.

We have established that methyl and ethyl radicals react with $\mathrm{EtP(OEt)_2}$ to give the dialkyldiethoxyphosphoranyl radicals $\mathrm{Et(R)\dot{P}(OEt)_2}$ (R = Me or Et). This result suggests that the reversal of α-scission of $\mathrm{R^1{}_2\dot{P}(OR^2)_2}$ may compete with diffusion of $\mathrm{R^{1\bullet}}$ and $\mathrm{R^1P(OR^2)_2}$ from the solvent cage. The direct decay of $\mathrm{Et_2\dot{P}(OBu^t)_2}$ was monitored in propane and in toluene at −90°, and, even though toluene is relatively much more viscous at this temperature, the rate constant for α-scission was only *ca.* 20% greater in this solvent than in the more fluid propane. A similar pair of experiments with the radical $\mathrm{Bu^t{}_2\dot{P}(OBu^t)_2}$ gave rates of α-scission in the two solvents which were the same within experimental error at −90°. The decay of $\mathrm{Et_2\dot{P}(OBu^t)_2}$ was unaffected by the presence of an excess of $\mathrm{EtP(OEt)_2}$ in isopentane at −100°, indicating that addition of ethyl radicals to $\mathrm{EtP(OBu^t)_2}$, produced by α-scission of the phosphoranyl radical, is not important under our experimental conditions.

(d) *Rate of Self-reaction of Ethyl Radicals in Solution.*—The rate of α-scission of $\mathrm{Et_2\dot{P}(OEt)OBu^t}$ has been measured by both the 'direct-decay' and 'steady-state' methods. The former technique gives k_9 directly, whilst the latter method gives $(2k_{10}/k_9)$, and hence combination of the two sets of results gives an independent measure of the rate constant for self-reaction of ethyl radicals in isopentane. The value of $2k_{10}$ obtained in this way is $9 \times 10^{10} \exp(-1{\cdot}2/RT)$ l mol^{-1} s^{-1} where RT is in kcal mol^{-1}, and at −100° $2k_{10} = 2{\cdot}7 \times 10^9$ l mol^{-1} s^{-1}. This result is in close agreement with that determined directly by Fessenden [13] in liquid ethane [$2{\cdot}6 \times 10^{10} \exp(-0{\cdot}83/RT)$ l mol^{-1} s^{-1}; $2{\cdot}3 \times 10^9$ l mol^{-1} s^{-1} at −100°.] It should be noted that the rate constants for alkyl radical self-reaction in solution may be substantially different from those determined in the gas phase.[11,14,29] The rate constants for dimerisation of ethyl and t-butyl radicals in the gas phase at 400 K are $10^{8{\cdot}7}$ and $10^{5{\cdot}7}$ l mol^{-1} s^{-1} respectively,[29] whilst in solution both these rate constants are close to 2×10^9 l mol^{-1} s^{-1} at ambient temperatures,[14] in common with the values for most simple alkyl radicals. The reason for this difference between the two phases is not clear at present.

EXPERIMENTAL

The apparatus for the generation of transient free radicals for study by e.s.r. spectroscopy, and the kinetic methods employed, have been described elsewhere.[5,12,15]

The temperature of the samples was monitored by a copper–constantan thermocouple positioned by the side of the tube just above the photolysis region. This thermocouple was regularly calibrated against a second thermocouple placed in a sample tube in the sensitive region of the cavity.

In the direct decay experiments only 9% of the available light intensity was used in order to avoid complications due to temperature changes brought about by interrupting irradiation, since at full intensity the sample temperature was increased by *ca.* 11° over its value in the absence of irradiation.

The organosphosphorus compounds used in this work were either commercially available or were prepared by standard procedures. t-Butoxydi-t-butylphosphine was prepared by addition of a solution of di-t-butylchlorophosphine (0·033 mol) in isopentane (15 ml) to a stirred solution of t-butyl alcohol (0·033 mol) and *NN*-diethylaniline (0·033 mol) in isopentane (30 ml) at room temperature. After stirring for 2 h the supernatant liquid was removed, di-t-butyl peroxide (10% v/v) added, and the solution used directly as an e.s.r. sample without isolation of the phosphine. Diethyl-t-butoxyphosphine, prepared in a similar manner, decomposed upon attempted distillation, but was shown by ^{31}P n.m.r. to be essentially pure: in $\mathrm{C_6D_6}$ it showed a single resonance (proton decoupled) 109 p.p.m. downfield from external $\mathrm{H_3PO_4}$.

We thank the Ethyl Corporation for generous gifts of $\mathrm{MePCl_2}$ and $\mathrm{EtPCl_2}$ which were used to prepare the corresponding alkyldiethoxyphosphines. We are grateful to the S.R.C. for the award of a Research Studentship (to R. W. D.) and to the Central Research Fund of the University of London for the gift of apparatus.

[3/2519 *Received, 10th December, 1973*]

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[25] A. L. J. Beckwith, in 'Essays in Free Radical Chemistry,' ed. R. O. C. Norman, *Chem. Soc. Special Publ.*, No. 24, 1970, ch. 9.

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

[27] A. G. Davies, R. C. Dobbie, R. W. Dennis, D. Griller, and B. P. Roberts, unpublished results.

[28] D. Griller, A. G. Davies, B. P. Roberts, and K. U. Ingold, *J. Amer. Chem. Soc.*, in the press.

[29] H. E. O'Neal and S. W. Benson, in 'Free Radicals,' ed. J. Kochi, Wiley-Interscience, New York, 1973, ch. 17.