An Electron Spin Resonance Study of the Structure and Reactivity of Aminophosphoranyl Radicals in Solution

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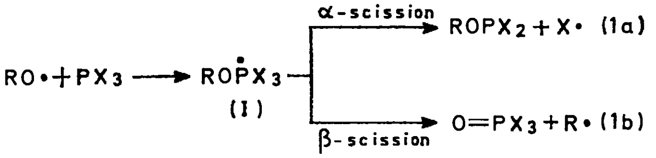
The structure and reactivity of a series of aminophosphoranyl radicals, generated by addition of photochemically produced alkoxyl radicals to aminophosphines, have been investigated by e.s.r. spectroscopy in solution. These phosphoranyl radicals possess a trigonal bipyramidal structure and some are stereochemically non-rigid, showing temperature-dependent line-shape effects in their spectra. In many cases, two isomers may be detected differing in the apical or equatorial placement of a dialkylamino-group.

The apicophilicities of alkoxy- and dialkylamino-groups in phosphoranyl radicals are very similar, although the latter generally have a greater preference for equatorial placement. In monocyclic aminophosphoranyl radicals in which two ligands form part of a five-membered ring, the two acyclic ligands appear to exchange position more rapidly than the endocyclic ligands, precluding pseudorotation, with the unpaired electron as pivot, as the mechanism of ligand permutation in such species. Both five- and six-membered ring systems incorporating two P–N bonds preferentially bridge apical and equatorial positions in aminophosphoranyl radicals.

Alkoxy(dialkylamino)phosphoranyl radicals fragment by α- or β-scission, depending upon the structure of the radical, but preliminary kinetic studies indicate that interconversion of isomers differing in the apical or equatorial placement of a dimethylamino-group is rapid in comparison with α-scission with P–N bond cleavage.

PHOSPHORANYL radicals (I) are now well established as intermediates in the reactions of compounds of tervalent phosphorus with alkoxyl radicals.[1] The phosphoranyl radicals may undergo subsequent α- or β-scission [equation (1)] and, since these radicals possess a trigonal bipyramidal structure in which apical and equatorial ligands are non-equivalent, such fragmentations may be configurationally selective processes.[1-3]



In attempting to rationalise the chemistry of phosphoranyl radicals four important related questions arise. (*a*) In phosphoranyl radical formation, does the attacking radical enter stereoselectively (*e.g.* into an apical position as in nucleophilic attack on PX_4, $X_3P{=}O$, and probably $:PX_3$)? (*b*) Can the interconversion of configurational isomers occur during their lifetimes (which will of course vary with experimental conditions)? (*c*) Does fragmentation of a phosphoranyl radical take place stereoselectively; in particular, when a phosphoranyl radical contains a pair of identical ligands, one of which is apical and the other equatorial, which is involved in α- or β-scission most readily? (*d*) Which of the isomers of a phosphoranyl radical detected (or undetected) by e.s.r. spectroscopy undergoes fragmentation most rapidly, and which isomer is the major source of fragmentation products?

The present study of aminophosphoranyl radicals was initiated to explore the use of e.s.r. spectroscopy as a structural probe for species with a spin-active nucleus (^{14}N has $I = 1$) bonded directly to phosphorus, and also to attempt to correlate configuration with reactivity. Preliminary communications concerned with part of this work have appeared.[4,5]

RESULTS AND DISCUSSION

Ethoxyl and t-butoxyl radicals were produced by photolysis of diethyl and di-t-butyl peroxide, respectively, with a high intensity u.v. source [equation (2; R = Et or Bu^t)]. Irradiation of solutions containing the aminophosphine and the dialkyl peroxide

$$ROOR \xrightarrow{h\nu} 2RO\cdot \qquad (2)$$

in situ in the cavity of the e.s.r. spectrometer at low temperatures, gave rise to the aminophosphoranyl radical whose spectrum was detected. At higher temperatures the spectra of the radicals produced by fragmentation of these phosphoranyl radicals could often be detected. Quantitative measurements of the rates of scission of aminophosphoranyl radicals were obtainable by monitoring the decay of their e.s.r. signals when the irradiation was interrupted; computer-averaging was used to improve the signal-to-noise ratio if necessary.[6]

(i) *Alkoxy*(*dialkyl*)*dialkylaminophosphoranyl Radicals.*—Photolysis of di-t-butyl peroxide in the presence of dimethylaminodiethylphosphine in cyclopropane at −120° gave rise to a spectrum assigned to the radical (II) (see Table 1). This assignment is based upon the greater apicophilicity of the dimethylamino-group

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[1] A. G. Davies, R. W. Dennis, and B. P. Roberts, *J.C.S. Perkin II*, 1974, 1101.

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

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

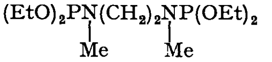
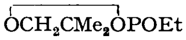
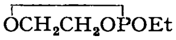
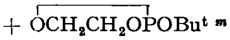
[4] R. W. Dennis and B. P. Roberts, *J. Organometallic Chem.*, 1972, **43**, C2.

[5] R. W. Dennis and B. P. Roberts, *J. Organometallic Chem.*, 1973, **47**, C8.

[6] K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1971, **93**, 902.

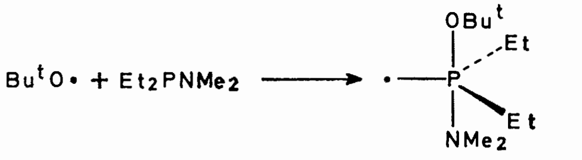
TABLE 1

E.s.r. parameters of aminophosphoranyl radicals and related species

Radical	Source	Solvent [a]	Temp. (°C)	a(P) [b,c]/G	Other splittings (G)
(II)	$\mathrm{Bu^tO\cdot + Et_2PNMe_2}$	C	−120	581	a(N) 12·6 (1N) a(H) *ca.* 2 (4H)
(IV)	$\mathrm{Bu^tO\cdot + Bu^tOP(Et)NMe_2}$ [d]	C	−100	741	a(N) not resolved $\Delta H_{p'-p}$ † 6 G
(V)	$\mathrm{EtO\cdot + (EtO)_2PNMe_2}$	P	−120	843	a(N) 3·5 (1N)
(VI)	$\mathrm{Bu^tO\cdot + (EtO)_2PNMe_2}$	C	−120	841	a(N) 2·8 (1N)
(VII)	$\mathrm{Bu^tO\cdot + (EtO)_2PNMe_2}$	P	−150	697	a(N) 12·7 (1N)
(IX)	$\mathrm{Bu^tO\cdot}$ + (VIII)	P	−120	849 [e]	a(N) 8·4 [f] (1N)
(X)	$\mathrm{Bu^tO\cdot}$ + (VIII)	P	−120	784	a(N) 24 (1N)
(XI)	$\mathrm{EtO\cdot}$ + (VIII)	P	−100	866	a(N) 7·6 (1N)
(XII)	$\mathrm{Bu^tO\cdot + [(CH_2)_2O]_2PNMe_2}$	C	−100	833	a(N) 7·5 (1N) [g]
(XIV)	$\mathrm{Bu^tO\cdot}$ + (XII)	C	−95	818	a(N) 12 (1N)
(XVIIIa)	$\mathrm{EtO\cdot}$ + (XVIIa)	C	−94	900	a(N) *ca.* 4·2 (1N) a(H) *ca.* 4·2 (1H)
(XIXa)	$\mathrm{EtO\cdot}$ + (XVIIa)	C	−94	710	a(N) 20·0 (1N) a(H) 3·8 (2H)
(XVIIIb)	$\mathrm{Bu^tO\cdot}$ + (XVIIb)	P	−95	908	a(N) 3·4 (1N) a(H) 4·7 (1H)
(XIXb)	$\mathrm{Bu^tO\cdot}$ + (XVIIb)	P	−120	780	a(N) 27·0 (1N) a(H) not resolved
(XX)	$\mathrm{EtO\cdot}$ + (XVIIb)	C + P	−100	902	a(N) 4·2 (1N) a(H) 4·2 (1H)
(XXI)	$\mathrm{EtO\cdot}$ + (XVIIb)	C + P	−100	720	a(N) 23·0 (1N) a(H) *ca.* 5 (1H)
(XX)	$\mathrm{Bu^tO\cdot}$ + (XVIIa)	C + P	−100	902	a(N) 4·2 (1N) a(H) 4·2 (1H)
(XXI)	$\mathrm{Bu^tO\cdot}$ + (XVIIa)	C + P	−100	723	a(N) 23·2 (1N) a(H) *ca.* 5 (1H)
(XXIIa)	$\mathrm{EtO\cdot + (EtO)_2PNHEt}$	C	−62	859	a(N) 3·4 (1N)
(XXIIb)	$\mathrm{Bu^tO\cdot + (EtO)_2PNHEt}$	C	−70	866	a(N) 3·5 (1N)
(XXIV)	$\mathrm{EtO\cdot + EtOP(NMe_2)_2}$	P	−118	808	a(N) 3·5 (2N)
(XXV)	$\mathrm{EtO\cdot + EtOP(NMe_2)_2}$	P	−120	654 [h]	a(N) 11·5 (1N) [i] a(N) *ca.* 3 (1N) [i]
(XXVI)	$\mathrm{Bu^tO\cdot + Bu^tOP(NMe_2)_2}$	C	−110	770	a(N) not resolved $\Delta H_{p'-p}$ † 5 G
(XXVII)	$\mathrm{Bu^tO\cdot + P[N(CH_2)_4]_3}$	C	−90	792	a(N) *ca.* 3 (2N)
(XXVIII)	$\mathrm{EtO\cdot + Bu^tOP(NMe_2)_2}$	P	−110	788	a(N) not resolved
(XXIX)	$\mathrm{EtO\cdot + Bu^tOP(NMe_2)_2}$	P	−110	665	a(N) 12·3 (1N)
(XXVIII)	$\mathrm{Bu^tO\cdot + EtOP(NMe_2)_2}$	P	−110	786	a(N) not resolved
(XXIX)	$\mathrm{Bu^tO\cdot + EtOP(NMe_2)_2}$	P	−110	666	a(N) 12 (1N)
(XXXIIa)	$\mathrm{EtO\cdot}$ + (XXXIa)	P	−90	725	a(N) 14 (1N) a(H) 4·5 (2H) [j]
(XXXIIb)	$\mathrm{EtO\cdot}$ + (XXXIb)	C	−100	729	a(N) 15·4 (1N) a(H) 8·5 (1H)
(XXXIIb)	$\mathrm{Bu^tO\cdot}$ + (XXXIa)	P	−100	731	a(N) 15·5 (1N) a(H) 8·5 (1H)
(XXXIIc)	$\mathrm{Bu^tO\cdot}$ + (XXXIb)	C + P	−80	752	a(N) 19·0 (1N) a(H) 5·0 (2H) [j]
(XXXIV)	$\mathrm{Bu^tO\cdot}$ +  $\mathrm{(EtO)_2P\underset{Me}{N}(CH_2)_2\underset{Me}{N}P(OEt)_2}$	C	−100	841	a(N) not resolved
(XXXVIa)	$\mathrm{EtO\cdot}$ + (XXXVa)	P	−100	640	a(N) 12·5 (1N) a(H) not resolved
(XXXVIb)	$\mathrm{EtO\cdot}$ + (XXXVb)	P	−130	644	a(N) 12·5 (1N) a(H) not resolved
(XXXVIc)	$\mathrm{Bu^tO\cdot}$ + (XXXVb)	P	−150	674	a(N) *ca.* 12 (1N) a(H) not resolved
(XXXIX)	$\mathrm{Bu^tO\cdot}$ + (XXXVIII)	P	−100	839	a(N) 4·5 (2N) a(H) 4·5 (1H)
(XLI)	$\mathrm{Bu^tO\cdot + [(CH_2NMe)_2]PNMe_2}$	C	−100	677	a(N) 12·6 (1N) [k] a(H) 8·5 (1H) [k] a(H′) 1·8 (1H) [k]
(XLII)	$\mathrm{Bu^tO\cdot}$ + spirophosphorane [l]	T	−70	910	a(H) 3·3 (2H) a(H′) 1·0 (2H)
(XLIII)	$\mathrm{Bu^tO\cdot}$ + spirophosphorane [l]	C	−70	902	a(H) 4·1 (2H)
(XLIV)	$\mathrm{Bu^tO\cdot}$ + spirophosphorane [l]	T	+35	807	a(N) 6·1 (2N) a(H) 3·6 (2H)
(XLV)	$\mathrm{EtO\cdot}$ +  $\mathrm{OCH_2CMe_2OPOEt}$	P	−48	903	a(H) 2·0 (2H)
(XLVIa)	$\mathrm{EtO\cdot}$ +  $\mathrm{OCH_2CH_2OPOEt}$	H	−70	906	a(H) 1·8 (2H)
(XLVIb)	$\mathrm{Bu^tO\cdot}$ +  $\mathrm{OCH_2CH_2OPOBu^t}$ [m]	P	−70	903	a(H) 1·7 (2H)
(XLVII)	$\mathrm{Bu^tO\cdot}$ +  $\mathrm{OCH_2CH_2OPCl}$ [n]	C	−30	1033	a(H) 1·3 (2H)

[a] C = cyclopropane, P = propane, T = toluene, H = hexane. [b] Calculated by using the full Breit–Rabi equation. [c] All g factors were 2·003 ± 0·001. [d] Secondary product. [e] Apparent value of a(P) = 838 G at −70° in cyclopropane. [f] Misquoted as 9·5 G in ref. 5. [g] Some poorly defined splitting from the ring protons was also present. [h] a(P) = 648 G at −146°. [i] Nitrogen atoms became equivalent on e.s.r. time scale at higher temperatures (see text). [j] Quoted value is $\frac{1}{2}[a(\mathrm{H}_{cis\text{-apical}}) + a(\mathrm{H}_{trans\text{-apical}})]$ (see text). [k] Splittings determined by computer simulation of the spectrum at −80°. Hyperfine coupling attributed to the two equatorial nitrogens was also detected: $a(\mathrm{N_{eq}})$ 3·9 G and $a(\mathrm{N'_{eq}})$ 1·8 G. [l] From ref. 15. [m] M. J. Parrott, unpublished results. [n] From ref. 26. † Peak-to-peak line-width.

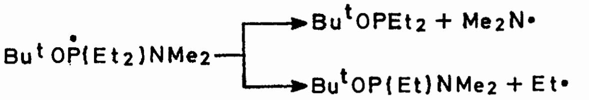
than of the ethyl group in phosphoranes,[7] and upon the fact that hyperfine splitting of *ca.* 2 G from four



(3)

(II)

apparently equivalent protons can just be resolved at $-110°$. As expected[1,2,8] on the basis of the lower group electronegativity of NMe_2 than of OBu^t, (II) has a lower phosphorus hyperfine splitting than $(Bu^tO)_2\dot{P}Et_2$ (707 G at $-100°$[1]). As the temperature was increased from $-120°$ the concentration of the phosphoranyl radical decreased and the spectra of ethyl and dimethylaminyl radicals appeared. Above $-90°$ the phosphoranyl radical (II) was no longer detectable, and at $-80°$ the ratio of product radical concentrations ($[Et\cdot]:[Me_2N\cdot]$) was 1·8 : 1, showing that α-scission occurs with cleavage of both P–N and P–C bonds.

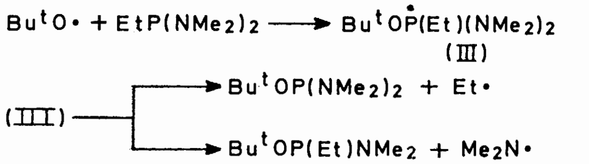


(4a)

(4b)

Close competition between reactions (4a) and (4b) might be expected in view of the probable similarity in the strengths of the bonds being broken [values of $\bar{D}$(P–X) in PX_3 are 62 (X = Et) and 64 kcal mol^{-1} ($X = NR_2$)[9] *]. The diethyl-t-butoxyphosphine formed in reaction (4a) at $-80°$ reacted further with t-butoxyl radicals to give rise to a strong spectrum of $(Bu^tO)_2\dot{P}Et_2$, which is relatively stable to α-scission under these conditions.[1]

(ii) *Dialkoxy(alkyl)dialkylaminophosphoranyl Radicals.*—Reaction of t-butoxyl radicals with bis(dimethylamino)(ethyl)phosphine did not give rise to a detectable e.s.r. spectrum of the radical (III), although the spectra of ethyl and dimethylaminyl radicals, produced by its α-scission, were immediately apparent; the concentration ratio ($[Et\cdot]:[\cdot NMe_2]$) was 0·7 : 1 at $-120°$ (1·0 at $-40°$). As the photolysis progressed the spectra of two secondary phosphoranyl radicals became apparent, produced by the addition of t-butoxyl radicals to the phosphines formed in reactions (6a) and (6b). The radical $(Bu^tO)_2\dot{P}(NMe_2)_2$ is discussed below [section (v)]. Reaction of t-butoxyl radicals with $Bu^tOP(Et)NMe_2$ gave the species (IV), assigned on the basis of the ^{31}P hyperfine splitting[1,2,8] and the low (not resolved although $\Delta H_{p'-p}$ was 6 G) nitrogen splitting.

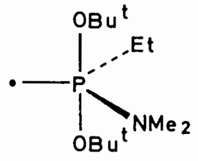


(5)

(6a)

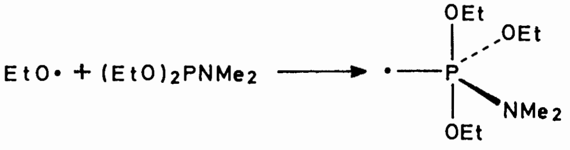
(6b)

The spectroscopic parameters of (II) and (IV) illustrate an important general point, that the isotropic hyperfine splitting from an apical nitrogen is larger than that from an equatorial nitrogen atom in radicals of similar constitution. A similar order has been previously observed for isotropic coupling with apical and equatorial hydrogen,[10,11] fluorine,[12,13] and chlorine atoms.[14]



(IV)

(iii) *Trialkoxy(dialkylamino)phosphoranyl Radicals.*—Ethoxyl radicals add to dimethylaminodiethoxyphosphine at $-130°$ in cyclopropane to produce the phosphoranyl radical (V). The phosphorus hyperfine splitting in (V) (843 G) is less than that in $(EtO)_4\dot{P}$ (884 G),



(7)

(V)

as expected on the basis of the lower group electronegativity of NMe_2 than of OEt.[1,2,8] The assignment of an equatorial position to the dimethylamino-group in (V) is based upon the lower apicophilicity of NR_2 than of OR observed in phosphorane chemistry,[7] and the low (3·5 G) value of the nitrogen hyperfine splitting.

Even at $-120°$ α-scission of $(EtO)_3\dot{P}NMe_2$ gives rise to the e.s.r. spectrum of the dimethylaminyl radical and no β-scission was detectable at higher temperatures. A strong spectrum of the secondary radical $(EtO)_4\dot{P}$, derived by addition of ethoxyl radicals to the triethyl

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* The quoted value of $\bar{D}$(P–N) is the mean of the values given in ref. 9 for $P(NMe_2)_3$ and $P(NEt_2)_3$.

[7] R. K. Oram and S. Trippett, *J.C.S. Chem. Comm.*, 1972, 554; *J.C.S. Perkin I*, 1973, 1300; S. Trippett and P. J. Whittle, *J.C.S. Perkin I*, 1973, 2302.

[8] I. S. Ginnes, S. P. Mishra, and M. C. R. Symons, *J.C.S. Dalton*, 1973, 2509.

[9] W. G. Bentrude in ' Free Radicals,' ed. J. K. Kochi, Wiley–Interscience, New York, 1973, vol. 2, ch. 22.

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

[11] M. C. R. Symons, *Mol. Phys.*, 1974, **27**, 785.

[12] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1966, **45**, 1845; see also S. P. Mishra and M. C. R. Symons, *J.C.S. Chem. Comm.*, 1974, 279.

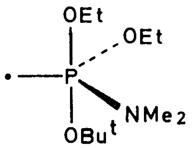
[13] J. Higuchi, *J. Chem. Phys.*, 1969, **50**, 1001.

[14] G. F. Kokoska and F. E. Brinckmann, *Chem. Comm.*, 1968, 349; *J. Amer. Chem. Soc.*, 1970, **92**, 1199.

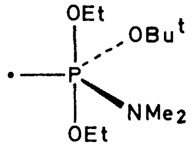
phosphite produced in reaction (8), was observed after a few minutes' photolysis.

$$(\mathrm{EtO})_3\dot{\mathrm{P}}\mathrm{NMe}_2 \longrightarrow (\mathrm{EtO})_3\mathrm{P} + \cdot\mathrm{NMe}_2 \qquad (8)$$

Reaction of t-butoxyl radicals with (EtO)$_2$PNMe$_2$ at −120° gave rise to a strong spectrum of (EtO)$_2$Bu^{t}O$\dot{\mathrm{P}}$NMe$_2$ (VI) in which the amino-group is equatorial. We now have the additional problem of the position of the Bu^{t}O group in (VI). If the incoming group takes up an apical site (and this is not yet proven) and interconversion between (VIa) and (VIb) does not occur within the lifetime of (VI), then the species detected will be (VIa). However, it might be expected that (VIb) will be the more stable isomer,[15] and thus if (VIa) and (VIb) are interconvertible within their lifetimes the latter should predominate.* It seems reasonable that (VIa) and (VIb) should differ in their spectroscopic parameters to some extent.



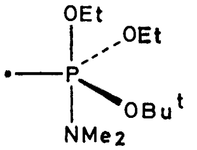
(VIa)



(VIb)

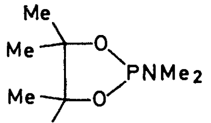
The phosphoranyl radical (EtO)$_2$Bu^{t}O$\dot{\mathrm{P}}$NMe$_2$ underwent exclusively α-scission in the temperature range −120 to −50°. At low temperature (−150°), when the spectrum of the dimethylaminyl radical was very weak, in addition to (VI) a second phosphoranyl radical with a relatively large nitrogen hyperfine splitting (12·7 G) was detected [*cf.* *a*(N) 12·6 G in (II)]. We assign this spectrum to (VII), an isomer of (VI) which has an apical amino-group.

The concentration ratio [(VII)] : [(VI)] was *ca.* 0·1 : 1 at −150°, and if (VI) and (VII) are present in their equilibrium concentrations, this corresponds to a free-energy difference of about 0·6 kcal mol^{-1}. If (VI) and (VII) are not interconvertible within their lifetimes, then the ratio of their concentrations need have no bearing upon their relative thermodynamic stabilities, but will instead reflect the balance between the different rates of their formation and destruction. However, it appears that the cyclic analogues (IX) and (X) (see below) are in equilibrium, and hence it seems reasonable that (VI) and (VII) will be also. The isomer with an apical amino-group was not detectable in the reaction of ethoxyl radicals with (EtO)$_2$-PNMe$_2$, although the signal strength obtained when diethyl peroxide was the source of alkoxyl radicals was in general lower than that when di-t-butyl peroxide was used.



(VII)

The relative magnitudes of the phosphorus hyperfine splittings in (VI) and (VII) appear to be general for aminoalkoxyphosphoranyl radicals (see Table 1). When isomers can be detected (with the unpaired electron orbital maintained in the equatorial position), that isomer with the larger number of equatorial amino-groups (generally the thermodynamically most stable isomer, unless ring strain effects are important) has the higher phosphorus hyperfine splitting, indicating that *a*(P) is more sensitive to the electronegativity of the apical ligands than that of the equatorial groups. Symons has recently found evidence for similar effects with hydridophosphoranyl radicals.[11]



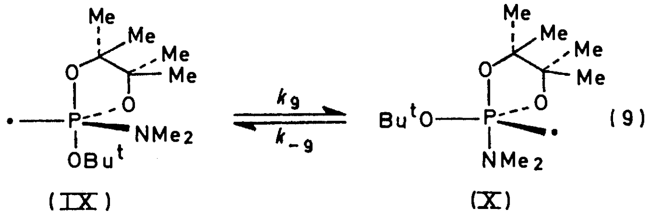


FIGURE 1 E.s.r. spectra obtained from the products of the reaction of photochemically generated t-butoxyl radicals with (VIII) in propane (a) at −120°, (b) at −80°. The computer-simulated spectra are shown on the right. The outer lines in the experimental spectra are due to the tetra-alkoxyphosphoranyl radical generated as a secondary product (see text). (c) E.s.r. spectrum obtained from the reaction of ethoxy radicals with (XVIIa) in cyclopropane at −90°

Similar results were obtained for the reaction of t-butoxyl radicals with the dioxaphospholan (VIII). At −120° two aminophosphoranyl radicals were detected as primary products (see Figure 1) differing

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* In future where isomers differ only in the positions of EtO and Bu^{t}O groups the isomer with the equatorial Bu^{t}O group will be *assumed* to be the species detected, unless more detailed discussion is warranted in the particular context.

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

in the positions of the t-butoxy- and amino-groups, the five-membered ring having a strong preference for the apical-equatorial bridging position[15] (see below).

Line-width effects indicate that the two species assigned as (IX) and (X) are present in approximately their equilibrium concentrations. If we consider the low- and high-field regions separately, as the rate of exchange of (IX) and (X) increases initially all the lines of (IX) [or (X)] will broaden to the same extent, but as the exchange becomes still more rapid a differential contribution to the widths of the ^{14}N hyperfine lines will appear. This differential broadening will depend upon the field shift between the line corresponding to a particular value of M_I (^{14}N) in (IX) and the line corresponding to the same value in (X). Because of the large magnitude of *a*(P), the low- and high-field lines of (IX) and (X) are not equally separated (Breit–Rabi effect) and thus the broadening patterns will be different at high and at low field. As shown in Figure 1, increasing the temperature from −120 to −80° gave rise to a pronounced differential effect upon the widths of the lines due to (IX), although (X) could not be detected at the higher temperature. Computer simulations of the exchange-broadened spectra are also shown in Figure 1, the sign of *a*(N) being the same for (IX) and (X). The ratio [(X)] : [(IX)] was 0·25 : 1 at −120°. The previously reported[5] value of 0·09 is too low because of difficulty in double integration of partially overlapping lines of differing width and with low signal strength. The present result was obtained by using electronic integration,[16] which gives much more reliable and consistent results, in agreement with the computer-simulated spectra.

A similar degree of differential broadening at −80° was obtained with the more viscous toluene as solvent, showing that the line-shape effect was not a result of anisotropy of the hyperfine coupling- or *g*-tensors combined with slow tumbling of the radicals. The computed spectra in Figure 1 were obtained with $k_9 = 2{\cdot}0 \times 10^7$ s^{-1} and $k_{-9} = 8{\cdot}0 \times 10^7$ s^{-1}, [(X)] : [(IX)] 0·25 : 1 at −120°; and with $k_9 = 1{\cdot}0 \times 10^8$ s^{-1}, $k_{-9} = 3{\cdot}3 \times 10^8$ s^{-1}, [(X)] : [(IX)] 0·30 : 1 at −80°. Complete agreement with the experimental spectrum could not be obtained at −120°, probably because of viscosity-dependent contributions to the line widths, and the rate constants at −120° should probably be regarded as upper limits. Between −120 and −80°, the temperature dependence of k_9 may be described by equation (10), where $\theta = 2{\cdot}303RT$ kcal mol^{-1}. In terms of the Eyring equation, $\Delta G_9^{\ddagger} = 4{\cdot}1$ kcal mol^{-1} at −80°.

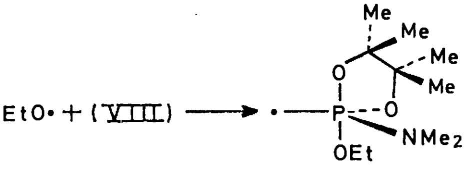
$$\log (k_9/\mathrm{s}^{-1}) = 10{\cdot}7 - 2{\cdot}4/\theta \qquad (10)$$

Decay of the radicals (IX) and (X) when the light was shuttered followed second-order kinetics and took *ca.* 1 s at −120°; the ratio [(X)] : [(IX)] remained constant during the decay. It follows that interconversion of (IX) and (X) is rapid with respect to their decay in the temperature range studied. The temperature dependence of the equilibrium constant K (=[(X)]/[(IX)]) in the range −160 to −120° indicated that $\Delta H_9^0 \simeq \Delta G_9^0 \simeq +0{\cdot}4$ kcal mol^{-1} and $\Delta S_9^0 \simeq 0$ cal deg^{-1} mol^{-1}. At −120°, $\Delta G_9^0 = +0{\cdot}42$ kcal mol^{-1}.

Krusic and Meakin[17] have recently measured the barrier to exchange between the two types of hydrogen in $\mathrm{Bu^tO\dot{P}H_3}$ and find $\Delta G_{11}^{\ddagger} = 5{\cdot}3$ kcal mol^{-1} at −75° and $k_{11} = 3 \times 10^6$ s^{-1} at −80° [equation (11) is not meant to imply the mechanism of the exchange].

(11)

Reaction of (VIII) with ethoxyl radicals gave rise to the spectrum of (XI) and no form with an apical nitrogen could be detected, although the signal strength was poorer than that obtained with t-butoxyl radicals.



(12)

(XI)

At −130° the nitrogen hyperfine lines of (XI) were of approximately equal width, and as the temperature increased all the lines broadened at a similar rate until at −80° it was difficult to resolve the nitrogen splitting (the effects were reversible upon lowering the temperature). These line-shape changes are still consistent with exchange between species with apical and equatorial amino-groups, but the spectroscopic parameters of the 'apical N' isomer may be such that the field shifts encountered on exchange are more similar than those for (IX) and (X).

The phosphoranyl radicals with equatorial amino-groups produced by addition of t-butoxyl radicals to 2-dimethylamino-1,3,2-dioxaphospholan and the dimethyl derivative (XIII) showed differential line broadening with increasing temperature, although in neither case could the 'apical amino' isomer be detected, owing possibly to the poor signal strength.

Secondary cyclic tetra-alkoxyphosphoranyl radicals were detected in the reactions of the 2-dimethylamino-1,3,2-dioxaphospholans with alkoxyl radicals (see Figure 1), produced by addition to the phosphites formed by α-scission of the primary aminophosphoranyl radicals. At −25° in the reaction of 2-dimethylamino-1,3,2-dioxaphospholan with t-butoxyl radicals in cyclopropane,

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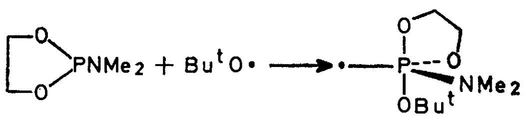
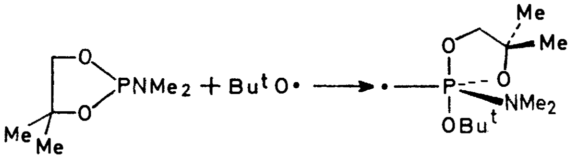
[16] R. Barr, R. J. Holman, and M. J. Perkins, *Chem. and Ind.*, 1972, 43.

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

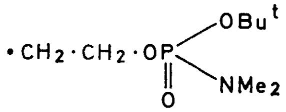
dimethylaminyl and t-butyl radicals and what was possibly the radical (XV) [$a(\mathrm{H}_\alpha)$ 21·5, $a(\mathrm{H}_\beta)$ 27·5 G] were detected, showing that a competition between α- and β-scission exists at this temperature, whereas the acyclic analogues $\mathrm{Bu^tO(EtO)_2\dot{P}NR_2}$ undergo exclusive α-scission.


(13)

(XII)

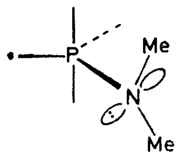

(14)

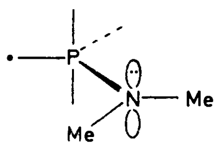
(XIII) (XIV)


(XV)

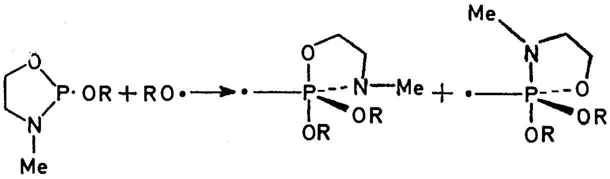
Alkoxy-groups appear to be much more apicophilic than dialkylamino-groups in phosphoranes,[7] but this difference does not seem to extend to phosphoranyl radicals and so we considered alternative assignments of the spectra obtained from (VIII), and alternative origins of the differential line-width effects. Inversion at nitrogen might be responsible for the species with different nitrogen hyperfine splittings, but this seems unlikely in view of the internal consistency of the assignment of small and large values of a(N) to equatorial and apical nitrogen, respectively, as well as experimental results which indicate that the nitrogen in certain alkoxyaminophosphoranes is sp^2-hybridised.[18]

An appreciable four-fold barrier to rotation about an equatorial P–N bond [7] might give rise to rotamers of the type (XVI), which could have different values of a(P) and a(N), and exchange between (XVIa) and (XVIb) might be the process responsible for the differential line-width effects. In order to investigate this possibility, we examined the reaction of alkoxyl radicals with the oxazaphospholidine (XVII; R = Bu^t or Et). As with the other trialkoxydialkylaminophoranyl radicals, two isomeric forms were detected (see Figure 1) although rotation about the P–N bond is now not possible.


(XVIa)


(XVIb)

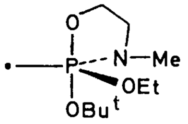
As a general rule, inclusion of an apical and an equatorial ligand in a five-membered ring increases the phosphorus hyperfine splitting in a phosphoranyl radical in comparison with the acyclic analogue, and this effect is clearly seen with the radical (XVIII). Differential line-width effects, of the type observed for (IX) and (X), were not apparent in these systems, but it is likely that the concentration ratio [(XIX)] : [(XVIII)] is close to the equilibrium value. At −95° the ratio [(XIXa)] : [(XVIIIa)] is 0.33 : 1 and [(XIXb)] : [(XVIIIb)] is 0·026 : 1.

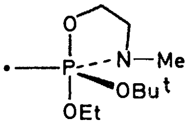

(15)

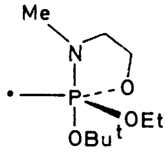
(XVII) (XVIII) (XIX)

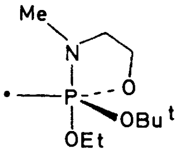
a; R = Et
b; R = Bu^t

The reactions of (XVIIa) with t-butoxyl radicals and of (XVIIb) with ethoxyl radicals give a phosphoranyl radical with identical ligands, but which is capable of existing as four enantiomeric pairs, one member of each pair being shown [see (XX) and (XXI)]. Signals from only one ' equatorial N ' and one ' apical N ' species were detected, and thus either ' a ' or ' b ' isomers predominate, or they are indistinguishable by e.s.r. Only if the isomers (XX) and (XXI) are not exchanging rapidly within their lifetimes, and the alkoxyl radical attacks stereoselectively, should different isomeric ratios result from the two sources. The ratio [(XXI)] : [(XX)] (*ca.* 0·1 : 1 at −95°) did not depend upon the source, and the e.s.r. parameters for the species from the different routes were the same within experimental error.


(XXa)


(XXb)


(XXIa)


(XXIb)

The observation of an apparent *doublet* splitting from an apical ring methylene proton in (XXI), whereas (XIX) shows a *triplet* splitting at similar temperatures, indicates [see section (vii)] that one type of radical, probably the ' b ' isomer, predominates for (XXI).

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[18] R. Mathis and R. Burgada, *Compt. rend.*, 1972, **274C**, 1156.

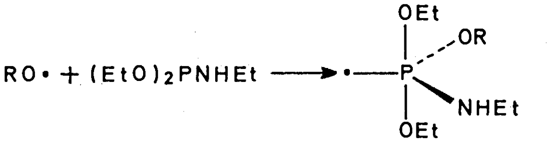
The spectrum of (XX) showed little change in lineshape from −120 to −20°, whereas the spectra of (XVIIIa) and (XVIIIb) showed the temperature-dependent effects expected from exchange of the *cis*- and *trans*-apical ring methyleneoxy-protons. It was difficult to obtain good spectra in the temperature range −60 to −20° where these effects were apparent, and (XVIIIb) was undetectable above −40° on account of its rapid β-scission to give t-butyl radicals. At −20° (XVIIIa) gave the seven-line spectrum with a 2 G spacing expected for almost complete averaging of the environments of the *cis*- and *trans*-apical ring protons [see section (vii)]. Equivalence of these protons is achieved at a higher temperature than equivalence of the apical methyleneamino-protons in (XXXIIa) (see below).

A general result of the present study is that where isomers differing in the position of the dimethylamino-group can both be detected, the isomer with the largest number of equatorial amino-groups is more favoured the greater the number of t-butoxy-groups also attached to phosphorus. This trend is illustrated by the ratios [(XIXa)] : [(XVIIIa)], [(XXI)] : [(XX)], and [(XIXb)] : [(XVIIIb)]. The apicophilicities of alkoxy- and dialkylamino-groups in phosphoranyl radicals are clearly quite similar and will not necessarily be transferable from radical to radical. Their different preferences for apical or equatorial placement will be the result of a balance between electronic and steric effects and as such will depend upon the detailed constitution of the particular phosphoranyl radical.

As with radicals from the 2-dimethylamino-1,3,2-dioxaphospholans, where the amino-group is exocyclic, fragmentation of (XVIII)—(XXI) is retarded by the presence of the five-membered ring. Below −80° these phosphoranyl radicals decay by second-order processes (presumably self-reaction). Nitrogen-centred radicals are not detected, but at −50° the reaction of (XVIIa) with t-butoxyl radicals gives rise to the e.s.r. spectrum of the t-butyl radical, and this species is detectable at −95° in the reaction of (XVIIb) with t-butoxyl radicals. β-Scission thus occurs, although α-scission with P–N cleavage may be readily reversible for such radicals (see below).

The balance between α- and β-scission of the radicals $(RO)_3\dot{P}NR'_2$ is, in fact, very fine. t-Butoxyl radicals react with $(EtO)_2PNR_2$ (R = Me, Et, or Pr^i) to give phosphoranyl radicals which undergo exclusive α-scission with no detectable β-scission to give t-butyl radicals below 0°. However, alkoxyl radicals react with $(EtO)_2PNHEt$ to give (XXII; R = Et or Bu^t), and the radical $(EtO)_2Bu^tO\dot{P}NHEt$ undergoes β-scission to give t-butyl radicals above about −40°.

(iv) *Ligand Reorganisation Mechanisms*.—At this point it is appropriate to consider the mechanisms of isomerisation of phosphoranyl radicals. The unpaired electron may be considered an apicophobic 'ligand',

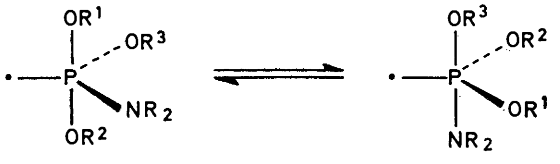


(16)

(XXII)

a; R = Et b; R = Bu^t

and Berry pseudorotation [19] (BPR) about this as pivot will interconvert (XXIIIa) and (XXIIIb). However,



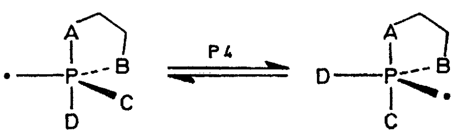
(17)

(XXIIIa) (XXIIIb)

if pseudorotation is the mechanism of isomerisation of, for exanple, (VIb) and (VII), then more than one step is required and a high energy intermediate with an apical unpaired electron must be traversed. Operation of the turnstile rotation (TR) mechanism [20] might obviate the need to pass through such an unstable isomer, but it must always be borne in mind that a phosphoranyl radical has one less ligand than a phosphorane, and also the degree of distortion from regular trigonal bipyramidal geometry in the former is not known with certainty.[21]

The observation of a hyperfine splitting from the two quasi-apical ring protons in the e.s.r. spectrum of (XLVIa) at +20° [see section (vii)] indicates that exchange of the apical and equatorial endocyclic methyleneoxy-groups cannot be taking place with a rate constant $>10^6$—10^7 s^{-1} at this temperature. Extrapolation to +20° gives the value of k_9 for the conversion of (IX) into (X) as *ca.* 10^9 s^{-1}. Thus it seems that whilst the *acyclic* groups in radicals such as (IX), (X), and (XLVIa) can exchange rapidly, the endocyclic apical and equatorial groups do not exchange at the same time, and thus the isomerisation is not a Berry pseudorotation with the unpaired electron as pivot.

We suggest that the isomerisation undergone by these monocyclic phosphoranyl radicals may be that described by Muetterties [22] for phosphoranes as 'process 4'



(18)

(P4). Although such a mechanism was shown not to operate in the exchange of apical and equatorial fluor-

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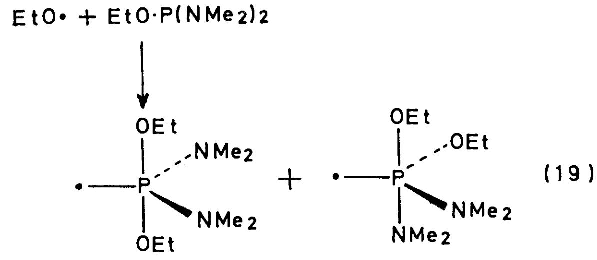
[19] R. S. Berry, *J. Chem. Phys.*, 1960, **32**, 933.

[20] 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; P. Gillespie, F. Ramirez, I. Ugi, and D. Marquarding, *ibid.*, 1973, **12**, 91.

[21] A. G. Davies, R. W. Dennis, D. Griller, K. U. Ingold, and B. P. Roberts, *Mol. Phys.*, 1973, **25**, 989.

[22] E. L. Muetterties, *J. Amer. Chem. Soc.*, 1969, **91**, 1636, 4115.

ines in Me_2NPF_4 (the Whitesides-Mitchell experiment [23]), this does not preclude its occurrence with monocyclic phosphoranyl radicals.* The angle between the exchanging ligands in the transition state for P4 may be unfavourable if the ligands form part of a small ring. As required by these ideas the barrier to exchange of apical and equatorial ligands in spirophosphoranyl radicals of the type (XLII) is much higher than for acyclic radicals; k_{exchange} appears to be less than about 10^6—10^7 s^{-1} at +120° for (XLII).[15] Also, whereas (IX) and (X) exchange rapidly, exchange of the endocyclic ligands in the radicals (XVIII) and (XIX) is much slower since it does not give rise to detectable line-shape effects.



(XXIV) (XXV) (19)

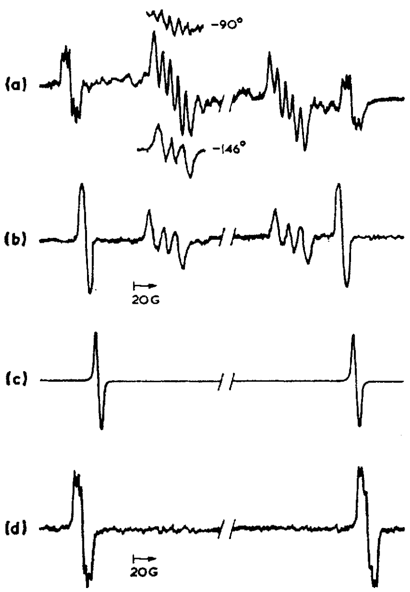
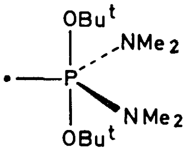
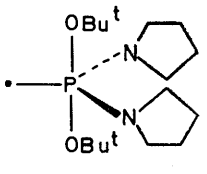


FIGURE 2 E.s.r. spectra obtained from the reactions of (a) ethoxyl radicals with bis(dimethylamino)(ethoxy)phosphine, (b) t-butoxyl radicals with bis(dimethylamino)(ethoxy)phosphine, (c) t-butoxyl radicals with bis(dimethylamino)-t-butoxyphosphine, (d) t-butoxyl radicals with dipyrrolidino-t-butoxyphosphine, all in propane at −110°

(v) *Dialkoxybis(dialkylamino)phosphoranyl Radicals.*—Reaction of ethoxy radicals with bis(dimethylamino)(ethoxy)phosphine gives rise to a mixture of the phosphoranyl radicals (XXIV) and (XXV) (see Figure 2), the assignments being based upon the hyperfine coupling constants and the internal consistency of the results. At −126° the concentration ratio [(XXV)] : [(XXIV)] was *ca.* 6 : 1. At −140° the low- and high-field lines of (XXV) appeared as 1 : 1 : 1 triplets [$a(N) = 11{\cdot}5$ G], although the lines were relatively broad ($\Delta H_{p'-p} = 7$ G). However, on raising the temperature to −110° (see Figure 2) five lines became apparent, spaced by about 7·5 G, and on further increasing the temperature to −90° the central three lines of each group gained in intensity relative to lines 1 and 5, such that the spectrum approached a 1 : 2 : 3 : 2 : 1 quintet. These changes are consistent with increasingly rapid exchange between the apical and equatorial amino-groups in (XXV) as the temperature is increased. At −110°, computer simulation shows that the exchange rate constant is about 10^8 s^{-1}, taking the nitrogen hyperfine splittings to be $a(N_{ap}) = 11{\cdot}5$ G, $a(N_{eq}) = 3$ G. In contrast the radical $(Bu^tO)_2\dot{P}(NMe_2)_2$ generated in an analogous manner was only detected as the isomer (XXVI) with two equatorial amino-groups, The relative concentration of the isomer with an apical amino-group must have been very small, since the absolute steady-state concentration of (XXVI) was relatively large on account of its high stability (see Figure 2). Although the nitrogen splitting in (XXVI) could not be resolved ($\Delta H_{p'-p}$ 5 G), this was readily detectable (Figure 2) in (XXVII), which was generated as a secondary product in the reaction of tripyrrolidinophosphine with t-butoxyl radicals [see section (vi)].

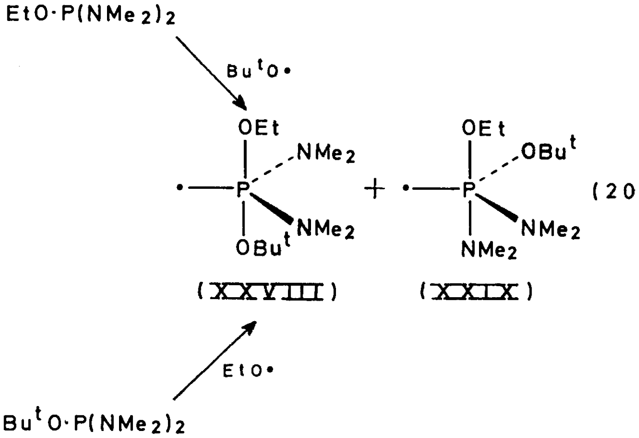


(XXVI)



(XXVII)

The radical $EtO(Bu^tO)\dot{P}(NMe_2)_2$ was produced in two ways [equation (20)], and both types of isomer were detectable (see Figure 2). The concentration ratio [(XXIX)] : [(XXVIII)] was *ca.* 2 : 1 at −110°, and was



(XXVIII) (XXIX) (20)

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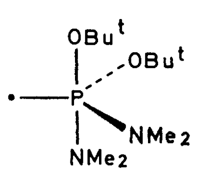
* The result of ' process 4 ' is the same as a $(TR)^2$ turnstile rotation [20] with the endocyclic ligands acting as the ' pair '.

[23] G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, 1969, **91**, 5384.

independent of the source. The spectroscopic parameters of the two isomers from different sources were identical within experimental accuracy.

At −110° the dimethylaminyl radical was detected as the product of α-scission of the radicals $Bu^tO(RO)\dot{P}(NMe_2)_2$, but t-butyl radicals were not detected as primary products. At a given temperature, (XXVI) is exceptionally long-lived in comparison with (XXIV), (XXV), (XXVIII), and (XXIX), and this relatively high stability may in part be due to configurational selectivity in the α-scission of these aminophosphoranyl radicals. Departure of an apical amino-group from (XXV) or (XXIX) may be more rapid than loss of an equatorial amino-group from (XXIV) and (XXVIII), and, in fact, direct α-scission of (XXIV) and (XXVIII) may be slower than their conversion into (XXV) and (XXIX), respectively, followed by α-scission of these isomers. The relative inaccessibility of (XXX) may then result in the observed low rate of production of dimethylaminyl radicals from (XXVI).



(XXX)

In order to test these ideas we examined the rates of decay of the radicals $(RO)_2\dot{P}(NMe_2)_2$ when the u.v. irradiation was interrupted; the results are gathered in Table 2.

TABLE 2

First-order rate constants for the decay of dialkoxybis(dimethylamino)phosphoranyl radicals in cyclopropane at −125°

Radical	Rate constant [a] (s^{-1})
(XXIV)	20·2
(XXV)	19·5
(XXVIII)	7·2 [b]
(XXIX)	5·7 [b]
(XXVI)	0·12 [c]

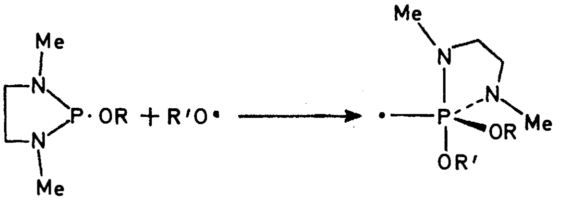
[a] If the major process removing the dimethylaminyl radicals produced by α-scission is reaction with the phosphoranyl radicals then the observed rate constants could be up to twice k_α.[1] [b] Rate constant similar in propane solvent. [c] Decay over the temperature range −90 to −135° fits an Arrhenius equation with E_a = 9·1 kcal mol^{-1} and $\log_{10}(A/s^{-1})$ = 12·5.

The rate of primary radical production at full light intensity in our system is usually 10^{-3}—10^{-4} mol l^{-1} s^{-1}, and hence if a primary phosphoranyl radical reaches a steady-state concentration of 10^{-5}—10^{-6} mol l^{-1} and it decays by α-scission with first-order kinetics, it follows that k_α is 10^1—10^3 s^{-1}. It will not be possible to distinguish kinetically which isomer of a phosphoranyl radical is the major source of fragmentation products if the two isomers are interconverting with rate constants much in excess of k_α, and it appears from the present work that these isomerisation rate constants are *ca.* 10^6—10^7 s^{-1} at −125°. It follows from this discussion and the results in Table 2 that (XXIV) and (XXV), and (XXVIII) and (XXIX) remain in equilibrium during the decays. We are seeking more suitable systems to clarify whether the ' apical N ' or ' equatorial N ' isomer undergoes the more rapid α-scission.*

In order to determine whether the α-scission of (XXIV) and (XXV) was reversible under our conditions, tetramethyltetrazene ($Me_2N{\cdot}N{=}N{\cdot}NMe_2$) was irradiated in the presence of $(EtO)_2PNMe_2$ in cyclopropane solution at −110°. However, although an e.s.r. spectrum of the dimethylaminyl radical was readily observed, no signal from (XXIV) or (XXV) was detected.

The e.s.r. spectra of phosphoranyl radicals derived from diazaphospholidines and perhydrodiazaphosphorines provide evidence for the preference of five- and six-membered rings for bridge apical and equatorial sites in these radicals.

Reaction of alkoxyl radicals with the diazaphospholidines (XXXI) gave rise to spectra assigned to the phosphoranyl radicals (XXXII) (R and R′ = Et or Bu^t) in which the nitrogen atoms are non-equivalent.



(21)

(XXXI)

a; R = Et
b; R = Bu^t

(XXXII)

a; R = R′ = Et
b; R = Bu^t, R′ = Et
c; R = R′ = Bu^t

No signals ascribable to a radical with equivalent equatorial nitrogen atoms were detected, even where R = R′ = Bu^t, whereas for the analogous acyclic species, $(Bu^tO)_2\dot{P}(NMe_2)_2$, *only* the diequatorial isomer (XXVI) was detected. These results provide clear evidence for the preference for apical-equatorial placement of five-membered rings in phosphoranyl radicals.

The radicals with identical alkoxy-groups (XXXIIa and c) showed temperature-dependent e.s.r. spectra which appear to result from modulation of the apical methyleneamino-proton hyperfine splittings while *a*(P) and *a*(N) remain unchanged. The temperature-dependent spectrum of (XXXIIc) is shown in Figure 3; (XXXIIa) showed similar line-width effects but the spectra were weaker. We attribute these changes to the P4 isomerisation shown in equation (22). The smaller apical ring proton splitting could not be resolved at low temperatures, but the isomerisation rate constant must be *ca.* 10^7—10^8 s^{-1} at −100°.†

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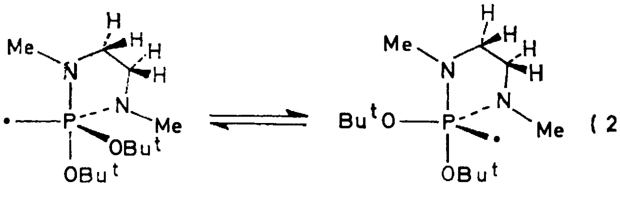
* In view of the results of the present work the explanation [1] of the relative rates of α-scission of the radicals $Et_n\dot{P}(OR)_{4-n}$ in terms of rate-controlling Berry pseudorotation [case (ii) kinetics [1]] may be incorrect. The interpretation of the relative stabilities of the radicals $R_2\dot{P}(OBu^t)_2$ is unaffected since the mechanism of isomerisation is not important [case (i) kinetics [1]].

† Computer simulation, taking the quasi-apical ring proton coupling constants as 9·5 and 0·5 G, yields rate constants for the exchange between −60 and −105° which fit the equation $\log_{10}(k_{exch}/s^{-1}) = 12{\cdot}5 - 3{\cdot}7/\theta$.

Although the size of the coupling to the apical methylene amino-protons appears to be determined predominantly by whether a proton is *cis* or *trans* to the unpaired electron, ring conformation might also play a part. The P4 isomerisation shown in equation (22) may be coupled with a ring flip such that the ring protons are in identical environments before and after the isomerisation. Alternatively, ring flipping may be fast with respect to the P4 exchange, or the ring system may be sufficiently close to planar that its detailed conformation is unimportant in determining the hyperfine splittings. If we assume the ring is non-planar, it is conceivable that some change in ring conformation occurs which alters the environments of the two apical protons such that their hyperfine splittings are modulated out-of-phase between similar limits, and this could be responsible for the observed temperature dependence of the spectra. We consider such a cause is unlikely since the spectrum of (XXXIIb) is temperature independent (see below), the sum of the apical proton splittings would have to remain constant upon exchange, and acyclic phosphoranyl radicals show temperature-dependent spectra indicative of ligand permutation with a similar energy barrier.



(22)

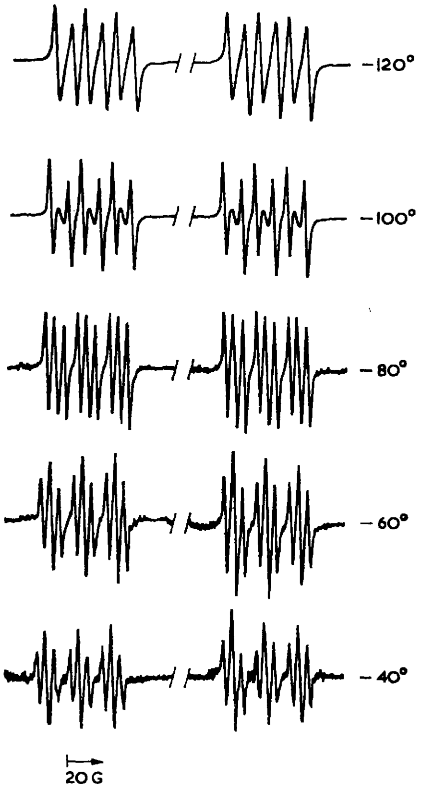


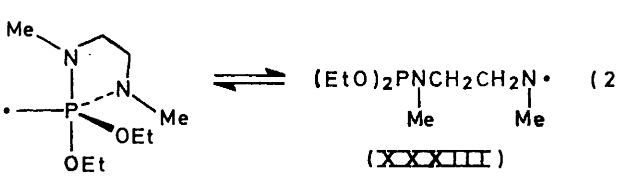
FIGURE 3 E.s.r. spectra obtained from the reaction of t-butoxyl radicals with (XXXIb) in cyclopropane–propane (1 : 1 v/v) at various temperatures

The extent of apical P–N bond stretching that exists in the transition state for the isomerisation reaction shown in equation (22) is difficult to assess. Complete bond cleavage to give an intermediate aminyl radical followed by a rotation about the remaining P–N bond and re-formation of the apical P–N bond cannot be ruled out at present. In this limiting case, where α-scission is a prerequisite of exchange, the isomerisation is an irregular process.[7,20] Indeed, if some degree of weakening of the apical endocyclic bond accompanies the exchange of quasi-apical ring protons in (XVIIIa) and (XIXa), this might explain why these protons become equivalent, on the e.s.r. time scale, in (XIXa) at a lower temperature than those in (XVIIIa).

The spectrum of (XXXIIb) was temperature-independent from −120 to −20°, consistent with this radical existing predominantly as one isomer, probably that with an equatorial t-butoxy-group. Whether exchange btween these two isomers is fast or slow on the e.s.r. time scale the observed spectroscopic parameters will be close to those of the more stable species. The radical (XXXIIb) was obtained from two routes, *viz.* equation (21) (XXXIa) with t-butoxyl radicals or (XXXIb) with ethoxyl radicals, and showed behaviour and spectroscopic parameters which were independent of the source.

(23)

No nitrogen-centred radicals resulting from the α-scission of (XXXII) could be detected, providing another demonstration of the reticence with which five-membered rings undergo cleavage in phosphoranyl radicals. However, it is possible that P–N cleavage is reversible for these radicals [equation (24)], and to test this possibility we attempted to generate the radical (XXXIII) independently. Photolysis of di-t-butyl peroxide in the presence of NN'-diethoxyphosphino-NN'-dimethylethylenediamine [equation (25)] at −110° gave rise to the e.s.r. spectra of (XXXIV) and (XXXIIa), but no nitrogen-centred radical (XXXIII) could be detected. The radical $(EtO)_2\dot{P}(OBu^t)_2$ was detected

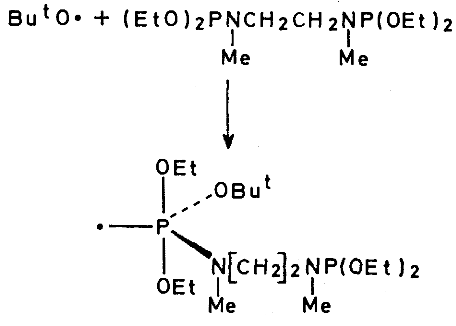


(XXXIIa)

(XXXIII)

(24)

as a secondary species in this system. The α-scission of (XXXII) would thus be readily reversible under our conditions. The phosphoranyl radical (XXXIIc) also undergoes rapid β-scission above about −40° to give the t-butyl radical.

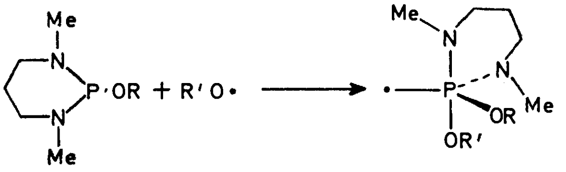

(25)

(XXXIV)

$$(\text{XXXIV}) \longrightarrow (\text{XXXIII}) + (EtO)_2POBu^t \qquad (26)$$

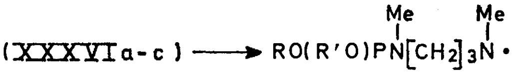
$$(\text{XXXIII}) \longrightarrow (\text{XXXIIa}) \qquad (27)$$

Although apical-equatorial placement of five-membered rings in phosphoranes is well-established,[24] there is more doubt about the preferred positioning of a six-membered ring, although diequatorial placement has been suggested.[20] Addition of alkoxyl radicals to the perhydrodiazaphosphorines (XXXV) gave the corresponding phosphoranyl radicals (XXXVI), which undergo very rapid α-scission at −100°.


(28)

(XXXV)
a; R = Et
b; R = Bu^t

(XXXVI)
a; R = R′ = Et
b; R = Bu^t,R′ = Et
c; R = R′ = Bu^t



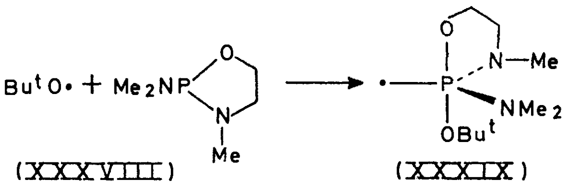
$$(\text{XXXVIa–c}) \longrightarrow RO(R'O)P\overset{Me}{N}[CH_2]_3\overset{Me}{N}\cdot \qquad (29)$$

(XXXVII)

a; a(N) 14·5, $a(CH_3)$ 26·4, $a(CH_2)$ 37·4 G at −100°
b; a(N) 14·4, $a(CH_3)$ 26·3, $a(CH_2)$ 37·0 G at −100°
c; a(N) 14·4, $a(CH_3)$ 26·4, $a(CH_2)$ 37·2 G at −128°

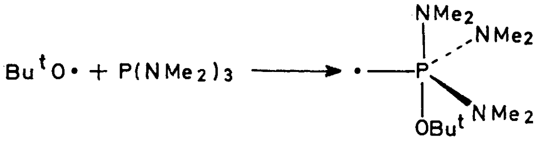
The detection of only (XXXVIc) and not the diequatorial isomer provides fairly good evidence for the preferred apical-equatorial placement of the six-membered ring in these phosphoranyl radicals. The radicals (XXXVIa—c) undergo α-scission much more readily than their five-membered ring analogues (XXXIIa—c), and P–N cleavage in (XXXVI) is not readily reversible. The e.s.r. spectra of the aminyl radicals (XXXVII) at −100 to −120° showed selective broadening of the lines corresponding to $M_I(CH_2\beta) = 0$. This is attributable to out-of-phase modulation of the hyperfine splitting from the β-methylene protons, probably as a result of restriction of rotation about the C_β–C_γ bond.

Addition of t-butoxyl radicals to (XXXVIII) gave the phosphoranyl radical (XXXIX), in which ring strain does not prevent both amino-groups from occupying equatorial sites. No species with an apical amino-group was detected, but there are two possible isomers of such a radical and the spectra of both could be more complex than that of (XXXIX), making detection difficult.


(30)

(XXXVIII) (XXXIX)

(vi) *Alkoxytris(dialkylamino)phosphoranyl Radicals.*—When di-t-butyl peroxide was photolysed in the presence of tris(dimethylamino)phosphine in cyclopropane at −120° no phosphoranyl radicals were detected initially, although a strong spectrum of the dimethylaminyl radical was observed. After a few minutes' photolysis the spectrum of the radical (XXVI) appeared and steadily increased in intensity as the irradiation continued. It appears that (XL) undergoes rapid α-scission even at −120°, and (XXVI) results from addition of t-butoxyl radicals to the Bu^{t}OP(NMe$_2$)$_2$ produced in the fragmentation. It should be noted that (XL) has an apical P–N bond which would be expected to undergo very ready cleavage (see above). In fact, β-scission of (XL) is the thermodynamically favoured fragmentation process rather than the observed α-scission. From bond energy data[9] we calculate $\Delta H_{32} - \Delta H_{33}$ to be *ca.* 17 kcal mol^{-1}, but despite this, α-scission occurs exclusively, at least below 0°. Such behaviour of acyclic aminoalkoxyphosphoranyl radicals is general and parallels that observed for alkoxy(alkyl)phosphoranyl radicals.[1]


(31)

(XL)

$$(\text{XL}) \xrightarrow{\alpha\text{-scission}} Me_2N\cdot + Bu^tOP(NMe_2)_2 \qquad (32)$$

$$(\text{XL}) \xrightarrow{\beta\text{-scission}} Bu^t\cdot + (Me_2N)_3P{=}O \qquad (33)$$

When photolytically generated t-butoxyl radicals were caused to react with a mixture of triethyl phosphite

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[24] F. G. Westheimer, *Accounts Chem. Res.*, 1968, **1**, 70.

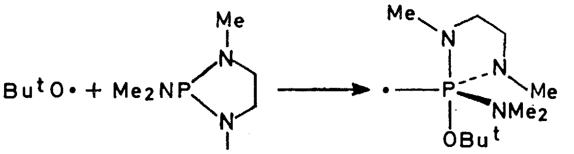
and tris(dimethylamino)phosphine at $-25°$ both t-butyl radicals [reactions (34) and (35)] and dimethylaminyl radicals [reactions (31) and (32)] were detected, but the concentration of phosphoranyl radicals was negligibly small at this temperature. If the formation of

$$\mathrm{Bu^tO\cdot + P(OEt)_3 \longrightarrow Bu^tO\dot{P}(OEt)_3} \qquad (34)$$

$$\mathrm{Bu^tO\dot{P}(OEt)_3 \longrightarrow Bu^t\cdot + OP(OEt)_3} \qquad (35)$$

the phosphoranyl radicals is irreversible [reactions (31) and (34)] it follows from the relative concentrations of t-butyl and dimethylaminyl radicals that (k_{31}/k_{34}) is about 1·1 at $-25°$, since the rate constants for self-reaction of t-butyl and dimethylaminyl radicals are similar.[25]

The stabilising effect of the five-membered ring system is clearly demonstrated by the ready detection of the phosphoranyl radical (XLI) at $-100°$. At temperatures up to $-30°$ the concentration of dialkylaminyl radicals did not reach detectable levels, although above $-120°$ the decay of (XLI) when the light was shuttered followed first-order kinetics with $k = 3{\cdot}2 \times 10^{-2}$ s^{-1} at $-100°$. The spectrum of (XXXIIc) became apparent after an extended period of photolysis.

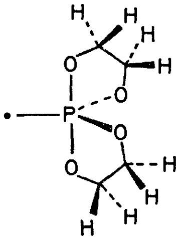


(36)

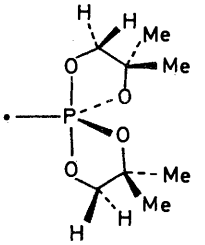
(XLI)

(vii) *Phosphoranyl Radicals Incorporating a Five-membered Ring.*—Acyclic methyleneoxy- and methyleneamino-protons in alkoxy- and amino-groups attached to phosphorus in phosphoranyl radicals do not normally give rise to resolvable hyperfine splitting. However, when these groups form part of a five-membered ring system such protons can couple with the unpaired electron to an appreciable extent, and such hyperfine splitting was often detected in this work.

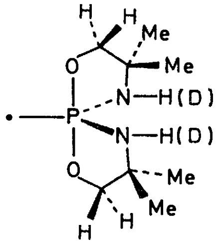
A study [15] of the e.s.r. spectra of the three spirophosphoranyl radicals (XLII)—(XLIV) indicated that (XLIII) exists in the configuration shown, with apical methyleneoxy-groups. The resolved proton hyperfine splittings in (XLII) were tentatively assigned [15] to the quasi-apical *cis*- and quasi-equatorial *cis*-hydrogen atoms. However, comparison of the proton hyperfine splittings in (XVIII) and (XLIV) (Table 1) suggests that only the quasi-apical ring protons give rise to detectable coupling, and this proposal is in accord with the e.s.r. spectra of all the phosphoranyl radicals incorporating five-membered rings that we have examined so far. The e.s.r. spectrum of (XLV), like those of (XLVI) [2] and (XLVII),[26] exhibits a proton splitting of about 2 G from two apparently equivalent nuclei, indicating that (XLV) exists predominantly in the configuration shown, with the t-alkoxy-group equatorial. Thus, whilst it is nevertheless clear that (XLIII) is the detected isomer of this radical, it is the quasi-apical ring protons in (XLII) which are responsible for the observed hyperfine splitting.



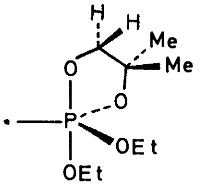
(XLII)



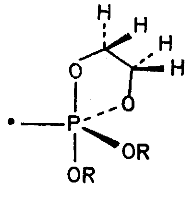
(XLIII)



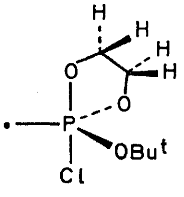
(XLIV)



(XLV)



(XLVI)
a; R = Et
b; R = Bu^t



(XLVII)

As an approximate rule it appears that the sum of the hyperfine splittings from apical *cis*- and *trans*-methyleneoxy ring protons is about 3—5 G in tetra-alkoxy- and aminoalkoxy-phosphoranyl radicals. The splitting from apical methyleneamino ring protons appears to follow a similar pattern, and the sum of the apical *cis*- and *trans*-coupling constants is 8—10 G in trialkoxyamino-, dialkoxydiamino-, and alkoxytriamino-phosphoranyl radicals. When the observed hyperfine splittings from the two apical ring protons are not the same, we assign the larger to the quasi-apical *cis*-proton, which forms part of a W-plan arrangement with the orbital of the unpaired electron on phosphorus.[15] When equal splittings from the apical ring protons are detected this is probably due, in many cases, to a rapid isomerisation of the type shown in equation (22). However, although the radical (XLVII) exhibits splitting of 1·3 G from two apparently equivalent ring protons, these probably give rise to unequal splittings where the difference is within the line-width. It is notable that the sum of the apical ring proton splittings for (XLVII) is only 2·6 G.

EXPERIMENTAL

The apparatus and sample handling technique for the photolytic generation of free radicals for e.s.r. study have been described previously.[1,2] The decay of unstable radicals when the light was shuttered was monitored by by using a Varian 620L-100 computer to improve the

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[25] K. U. Ingold in 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, 1973, vol. 1, ch. 2; J. R. Roberts, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1973, **95**, 3228.

[26] D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1973, 1339.

signal-to-noise ratio by averaging a large number of identical decays. The design of the apparatus used in these experiments followed closely that employed by Ingold and his co-workers in similar studies.[6]

Computer simulation of the exchange-broadened spectra of (IX) and (X) was accomplished by using a program based on the modified Bloch equations,[27] kindly provided by Dr. M. F. Chiu. The problem of the very large phosphorus hyperfine splitting in (IX) and (X) was circumvented in the following manner. The low- and high-field regions were treated separately and the exchange was taken as occurring between two different species without phosphorus splitting but with g values close to 2. The input data used [the actual g values of (IX) and (X) were close to 2·003] are given in Table 3. The errors involved in this approach are very small, and we are indebted to Professor D. Kivelson for a discussion of this point.

TABLE 3

Temp. (°C)	Spectrum region	$a[N_{(IX)}]$/G	$a[N_{(X)}]$/G	$g_{(IX)}$	$g_{(X)}$	K_9 [c]	k_9 [d]/s^{-1}
—80	Low [a] field	7·9	24·0	2·0165	1·9897	0·30	$1·0 \times 10^8$
	High [b] field	7·9	24·0	1·9954	2·0107	0·30	$1·0 \times 10^8$
−120	Low [b] field	8·4	24·0	2·0173	1·9889	0·25	$2·0 \times 10^7$
	High [b] field	8·4	24·0	1·9950	2·0111	0·25	$2·0 \times 10^7$

[a] Line-width in the absence of exchange, 2·5 G. [b] Line-width in the absence of exchange, 3·0 G. [c] Equilibrium constant = [(X)]/[(IX)]. [d] $k_{-9} = k_9/K$.

Most of the phosphorus compounds employed in this work were known previously and were prepared by standard methods. New compounds are described below.

2-*Dimethylamino*-4,4-*dimethyl*-1,3,2-*dioxaphospholan* (XIII) was prepared by heating a mixture of 2-methylpropane-1,2-diol (6·64 g) and tris(dimethylamino)phosphine (12·0 g) at 100—110° for 1·5 h (until all the dimethylamine had been evolved). The residue was distilled; the product (XIII) had b.p. 54—55° at 5 mmHg (Found: C, 44·3; H, 8·6; N, 8·4. $C_6H_{14}NO_2P$ requires C, 44·2; H, 8·7; N, 8·6%). Compound (XIII) was converted into 2-*ethoxy*-4,4-*dimethyl*-1,3,2-*dioxaphospholan* by heating (4·6 g) with ethanol (1·47 g) under reflux in a bath at 115° for 1·5 h. Distillation gave the dioxaphospholan, b.p. 44° at 6 mmHg (Found: C, 44·2; H, 8·0. $C_6H_{13}O_3P$ requires C, 43·9; H, 8·0%).

2-*Ethoxy*-3-*methyl*-1,3,2-*oxazaphospholidine* (XVIIa) was prepared by dropwise addition during 2 h of ethyl dichlorophosphite (25 g) in pentane (25 ml) to a solution of 2-methylaminoethanol (12·8 g) and triethylamine (35 g) in pentane (50 ml) with stirring and cooling in an ice-bath. Triethylamine hydrochloride was removed by filtration and, after removal of the pentane and excess of triethylamine at the pump, the residue was distilled to yield (XVIIa), b.p. 61—62° at 13 mmHg (Found: C, 40·5; H, 8·1; N, 9·4. $C_5H_{12}NO_2P$ requires C, 40·3; H, 8·1; N, 9·4%). The 2-*t-butoxy-analogue* (XVIIb) was prepared by heating a mixture of bis(dimethylamino)-t-butoxyphosphine (13·7 g) and 2-methylaminoethanol (5·35 g) at 105° for 3 h (until evolution of dimethylamine had ceased). Distillation gave (XVIIb), b.p. 56° at 6 mmHg (Found: C, 47·7; H, 9·2; N, 7·6. $C_7H_{16}NO_2P$ requires C, 47·5; H, 9·1; N, 7·9%).

2-*Ethoxy*-1,3-*dimethyl*-1,3,2-*diazaphospholidine* (XXXIa) was synthesised by refluxing 2-dimethylamino-1,3-dimethyl-1,3,2-diazaphospholidine (15·8 g) and ethanol (4·5 g) in benzene (20 ml) for 2 h (until evolution of dimethylamine ceased) and had b.p. 60—62° at 16 mmHg (Found: C, 44·1; H, 9·4; N, 17·3. $C_6H_{15}N_2OP$ requires C, 44·4; H, 9·3; N, 17·3%). The *t-butoxy-analogue* (XXXIb) was prepared by heating a mixture of bis(dimethylamino)-t-butoxyphosphine (9·8 g) and *NN'*-dimethylethylenediamine (4·5 g) for 1 h at 95° and a further 1 h at 115°, and had b.p. 62—64° at 5 mmHg (Found: C, 50·6; H, 10·2; N, 14·5. $C_8H_{19}N_2OP$ requires C, 50·5; H, 10·1; N, 14·7%). 2-*Ethoxy*-1,3-*dimethylperhydro*-1,3,2-*diazaphosphorine* (XXXVb) was prepared in a similar way from *NN'*-dimethylpropane-1,3-diamine, and had b.p. 89—90° at 13 mmHg (Found: C, 52·6; H, 10·7; N, 13·6. $C_9H_{21}N_2OP$ requires C, 52·9; H, 10·4; N, 13·7%). The *ethoxy-analogue* (XXXVa) was prepared from ethyl dichlorophosphite and *NN'*-dimethylpropane-1,3-diamine in the presence of triethylamine in pentane, and had b.p. 80° at 13 mmHg (Found: C, 47·6; H, 9·7; N, 16·1. $C_7H_{17}N_2OP$ requires C, 47·7; H, 9·7; N, 15·9%).

NN'-*Bis*(*diethoxyphosphino*)-NN'-*dimethylethylenediamine* was prepared by dropwise addition during 0·5 h of diethyl chlorophosphite (11·1 g) in pentane (25 ml) to *NN'*-dimethylethylenediamine (3·1 g) and triethylamine (7·2 g) in pentane (25 ml) with stirring and cooling in ice. The triethylamine hydrochloride was filtered off and the residue distilled to give the product, b.p. 107° at 0·1 mmHg (Found: C, 43·0; H, 9·1; N, 8·0. $C_{12}H_{30}N_2O_4P_2$ requires C, 43·9; H, 9·2; N, 8·5%).

We thank Dr. K. U. Ingold for advice concerning the construction of the rotating sector-CAT apparatus used to measure radical decays. One of us (R. W. D.) thanks the S.R.C. for a studentship.

[4/1653 *Received*, 6*th August*, 1974]

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[27] H. S. Gutowsky and C. L. Holm, *J. Chem. Phys.*, 1956, **25**, 1228.