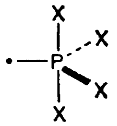
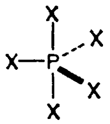
Electron Spin Resonance Studies of the Structure and Reactivity of Some Spirophosphoranyl Radicals in Solution [1]

By **David Griller** and **Brian P. Roberts,*** Christopher Ingold Laboratories, University College London, London WC1H 0AJ

Spirophosphoranyl radicals have been generated by abstraction of hydrogen from 1,4,6,9-tetraoxa-5-phosphaspiro-[4,4]nonane (IV; R = H) and related compounds. The e.s.r. spectra of these radicals have been observed and correlated with their structures. The radical (VII) from 2,2,7,7-tetramethyl-1,6-diaza-4,9-dioxa-5-phosphaspiro-[4,4]nonane was also detected. These spirophosphoranyl radicals possess trigonal bipyramidal structures in which the unpaired electron is stereochemically active and occupies an equatorial ligand site. There is no evidence that any rapid exchange of apical and equatorial ligands (*e.g.* by pseudo-rotation) occurs on the e.s.r. time scale. A tertiary alkoxy-group occupies an equatorial position in preference to a primary alkoxy-group in these radicals The spirophosphoranyl radicals are remarkably stable towards unimolecular α- or β-scission, but they will add to terminal olefins and to 2-methyl-2-nitrosopropane.

THE relationships between the structure and reactivity of phosphoranyl radicals (I) in solution are subjects of intensive study at present.[1-5] The chemistry of the phosphoranes (II) is much better understood than that of the related phosphoranyl radicals.[6] Many data are available on the relationships between the phosphorane structure and the nature of the ligands around phosphorus, and empirical rules, supported by theoretical calculations, have been developed to enable assignment of the most stable configuration at phosphorus to be made when a number of isomeric possibilities exist.[6]


(I)


(II)

The structure and configuration of phosphoranyl radicals appear to exert a profound effect on the reactivity of these species, particularly upon the rates at which they undergo unimolecular α- or β-scission [process (1)].[1-5]

$$\mathrm{AB\dot{P}X_3} - \begin{cases} \xrightarrow{\alpha\text{-scission}} \mathrm{ABPX_2 + X\cdot} \\ \xrightarrow[\beta\text{-scission}]{} \mathrm{A\cdot + B{=}PX_3} \end{cases} \qquad (1)$$

When the central phosphorus atom in a phosphorane is incorporated into one or two small (four- or five-membered) rings, two important effects are apparent. The ring(s) prefer to span apical and equatorial ligand sites in the trigonal bipyramidal molecule, and the molecule as a whole is stabilised with respect to its acyclic analogues.[6] One dramatic effect is that phosphites of the type (III) exist mainly as the spirophosphorane tautomers (IV), derivatives of 1,4,6,9-tetraoxa-5-phosphaspiro[4,4]nonane.[7]

We report here an e.s.r. study of the spirophosphoranyl

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[1] For a preliminary account of part of this work see D. Griller and B. P. Roberts, *J. Organometallic Chem.*, 1972, **42**, C47.

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

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

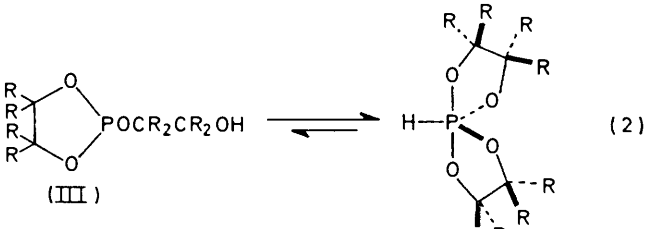
[4] P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 6033.

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

[6] I. Ugi and F. Ramirez, *Chem. in Britain*, 1972, 198; *Adv. Phys. Org. Chem.*, 1971, **9**, 25, and references therein.

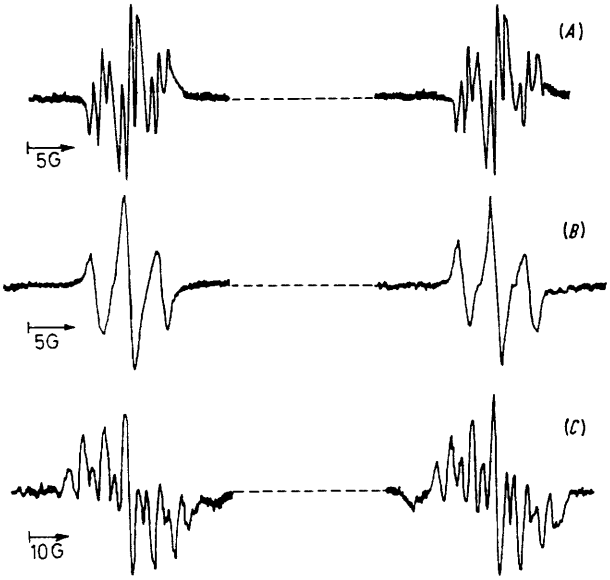
[7] D. Houalla, M. Sanchez, L. Beslier, and R. Wolf, *Org. Magnetic Resonance*, 1971, **3**, 45.

radicals produced by abstraction of hydrogen from the P–H bond of phosphoranes such as (IV).

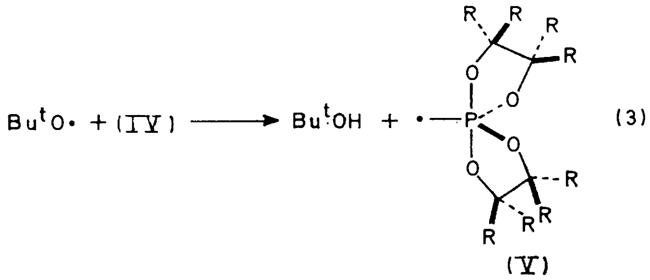


RESULTS AND DISCUSSION

When hydrocarbon solutions containing di-t-butyl peroxide and the spirophosphorane were irradiated with u.v. light whilst the sample was in the cavity of the e.s.r. spectrometer,[2,4] strong spectra of the corresponding spirophosphoranyl radicals (V) were observed (see Figure).[1] The spectroscopic parameters are summarised in Table 1.



E.s.r. spectra of spirophosphoranyl radicals in cyclopropane: (*A*) (V; R = H) at +10°; (*B*) (VI) at +20°; (*C*) (VII; R = H) at +13°



The phosphorane parents of the radicals in Table 1 possess trigonal bipyramidal structures in which the P–H bond is equatorial and the five-membered rings span apical and equatorial positions.[7] Wolf and his collaborators have made extensive studies of the synthesis and structures (determined mainly by n.m.r. spectroscopy) of spirophosphoranes of these types.[7]

TABLE 1

E.s.r. spectroscopic parameters of spirophosphoranyl radicals in solution

Spirophosphoranyl radical	Solvent	Temp. (°C)	$a(^{31}P)$ (G) [a]	Further splittings (G)
(V; R = H)	Toluene	−70	910	
		−20	920	
		0		a(H) 3·4,[b] a(H′) 1·0[b]
	Cyclopropane	−50		a(H) 3·3, a(H′) 1·0
		+10		a(H) 3·2, a(H′) 0·9
(V; R = Me)	Toluene	−70	911	Not resolved
		−20	914	
		+45	916	
(VI)	Cyclopropane	−70	902	a(H) 4·1[b]
		−20	907	a(H) 3·9
		+20	910	a(H) 3·8
	Propane	−63		a(H) 4·0
		−3		a(H) 3·7
	Toluene	+52		a(H) 3·6
		+120		a(H) 3·5
(VII; R = H)	Toluene	+35	807	a(H) 3·6,[b] a(N) 6·1[c]
(VII; R = D)	Toluene	+30	805	a(H) 3·5,[b] a(N) 6·1[c]
	Cyclopropane	+13	809	a(H) 3·5, a(N) 6·1

[a] Calculated using the Breit–Rabi equation. The *g* values of all radicals for which phosphorus hyperfine splittings are reported are 2·003 ± 0·001. Splittings are quoted throughout in gauss; 1 mT = 10 gauss. [b] 1 : 2 : 1 Triplet splitting. [c] 1 : 2 : 3 : 2 : 1 Quintet splitting.

The structures of the phosphoranyl radicals listed in Table 1 are probably very close to those of the protic parents from which they were derived,[8] the unpaired electron being stereochemically active and situated in an orbital directed towards the equatorial ligand site previously occupied by hydrogen.

The dioxaphospholan rings will undoubtedly be non-planar. However, the rate of interconversion between the energetically non-equivalent non-planar conformations of each ring is probably rapid compared with the differences in coupling constants (expressed in frequency units) of the four ring protons in the different environments.[9] Although the ' mean conformation ' may be non-planar, for our present purposes we may represent the rings as being planar. We may define *cis*- and *trans*-hydrogen atoms in the spirophosphoranyl radicals as shown in the Scheme.

There are thus four types of hydrogen atom in (V;

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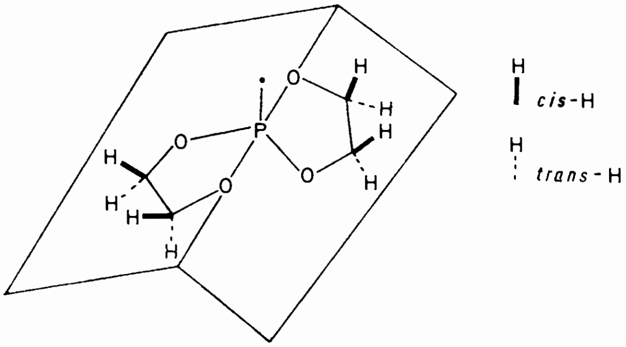
[8] A. G. Davies, R. W. Dennis, D. Griller, K. U. Ingold, and B. P. Roberts, *Mol. Phys.*, 1973, **25**, 989.

[9] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc.* (*A*), 1971, 124; R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.

R = H) *viz.*, *cis*-apical (2H), *trans*-apical (2H), *cis*-equatorial (2H), and *trans*-equatorial (2H). Pseudo-rotation[10] about the unpaired electron as pivot will exchange *cis*-apical with *cis*-equatorial and *trans*-apical with *trans*-equatorial hydrogen atoms. The proton splittings in (V; R = H) are thus probably due to coupling with two of the four types of hydrogen present in a radical which is undergoing pseudo-rotation slowly on the e.s.r. time scale, even at +120° when the spectrum was unchanged apart from an increase in *a*(P).* Inspection of molecular models shows that the *cis*-apical and *cis*-equatorial hydrogen atoms are more favourably positioned than the *trans*-hydrogen atoms so as to form part of a ' W-plan ' arrangement[13] with the orbital of the unpaired electron, and it is these *cis*-hydrogen atoms which probably give rise to the resolved splittings.



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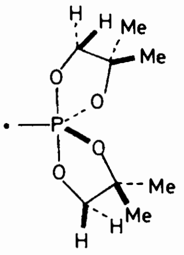
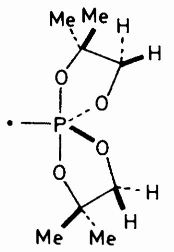
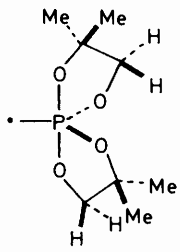


(VIa)



(VIb)

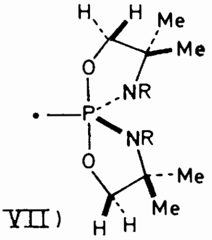


(VIc)

The radical (V; R = Me) gives no resolvable hydrogen splittings, but the spectrum of the spirosphoranyl radical (VI) exhibits a triplet splitting similar in magnitude to the larger splitting in (V; R = H).

Exchange of apical and equatorial ring positions (for example by pseudo-rotation) is probably slow on the e.s.r. time scale [*cf.* (V; R = H)]. Hence the radical must exist in the configurations (VIa) or (VIb), since (VIc) has four non-equivalent methyleneoxy-hydrogen atoms.

2,2,7,7-Tetramethyl-1,6-diaza-4,9-dioxa-5-phospha-spiro[4,4]nonane is known[7] to exist in the configuration with both nitrogen atoms in equatorial positions, as would be expected from the relative electronegativities of oxygen and nitrogen. The spirophosphoranyl radical derived from this phosphorane must have a similar structure (VII).[8,11,14] Apart from a 6·1 G splitting from the two equivalent nitrogen atoms, the spectrum of (VII) shows a 3·5 G splitting from two equivalent hydrogen atoms. Assignment of the latter splitting to interaction with ring methyleneoxy-protons was made by deuteriation of the NH groups in (VII).† The similar magnitude of the proton splittings in (VI) and (VII) suggests that the configuration of the former radical is (VIa), the tertiary alkoxy-groups preferentially taking up the equatorial positions. It follows that the larger and smaller proton splittings in (V; R = H) are assigned to the *cis*-apical and *cis*-equatorial hydrogen atoms respectively.



(VII)

It is difficult to assess the relative importance of steric effects and the various electronic effects in determining the most stable configuration of (VI). It has been suggested that bulky groups will prefer to occupy equatorial sites in phosphoranes, although whether this preference extends to phosphoranyl radicals is not clear.[2] Electronic effects probably play a major part in determining the relative tendencies of primary and tertiary alkoxy-groups to occupy equatorial ligand sites. The oxygen atom in a tertiary alkoxy-group will be more electropositive than that in a primary alkoxy-group and simply

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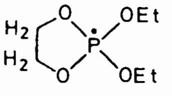
* The spectra of the phosphoranyl radicals A,[2] B,[11] and C[12] also



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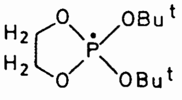

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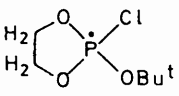


C

exhibit small triplet splittings from two equivalent (or nearly equivalent) ring hydrogen atoms. If the ring bridges apical and equatorial positions in these radicals then either interchange of ring methyleneoxy-groups is rapid on the e.s.r. time scale, or the two hydrogen atoms giving rise to the apparent triplet splitting have different coupling constants but the difference is masked by the line width. The fact that the triplet splittings in the three phosphoranyl radicals with one ring are approximately the mean of the two hydrogen splittings detected in (V; R = H) lends support to the first explanation, but see ref. 12.

† The phosphorus atoms in (V)—(VII) are chiral centres and non-planar nitrogen atoms in (VII) would be expected to lead to diastereoisomeric forms of this phosphoranyl radical; however no effects attributable to this cause were detected in the e.s.r. spectra. It is difficult to predict whether or not the nitrogen atoms in (VII) will invert rapidly on the e.s.r. time scale.

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

[11] R. W. Dennis and B. P. Roberts, *J. Organometallic Chem.*, 1972, **47**, C8.

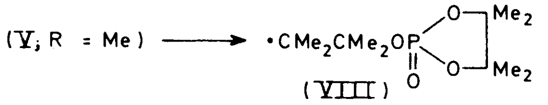
[12] D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1973, 1339.

[13] For a review see G. A. Russell in ' Radical Ions,' eds. E. I. Kaiser and L. Kevan, Interscience, New York, 1968, ch. 3.

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

on this basis the former group should have a greater preference for equatorial placement. However, simple electronegativity effects alone do not govern which will be the most stable configuration of a phosphorane,[12] the ability of a ligand to enter into p_π–d_π bonding with the central phosphorus atom also playing a part. The greater polarisability of the non-bonding electrons on the oxygen atom of a tertiary alkoxy-group, compared with a primary alkoxy-group, leads to the possibility of increased π bonding to phosphorus, which will be most efficient when the donor atom is in an equatorial position.[15]

It should be pointed out that conclusions concerning these spirophosphoranyl radicals are not necessarily transferable to acyclic phosphoranyl radicals, although it seems likely that they will be.



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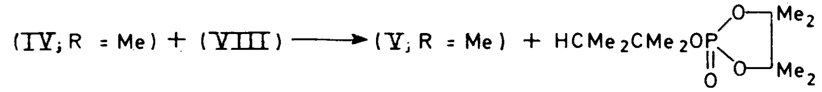


(5)

Reactions of Spirophosphoranyl Radicals.—The e.s.r. spectra of all the spirophosphoranyl radicals listed in Table 1 disappeared immediately (in <1 s) when the u.v. irradiation was interrupted. Under steady illumination the signal strengths were proportional to the square root of the light intensity incident on the sample, indicating that the radicals were being removed by reaction with other radicals, probably by self-reaction to give a P–P coupled bi(spirophosphorane).

No alkyl radicals from the β-scission of (V; R = Me or H) were detectable at +45° in toluene, and no aminyl radicals from α-scission of (VII) were detected.[14] Decomposition of di-t-butyl hyponitrite[16] (0·42M) in the presence of (IV; R = Me) (1·0M) in iso-octane at +45 or +65° showed that the rate of consumption of the phosphorane was equal to the rate of production[16] of t-butoxyl radicals, and there was thus no chain process [reactions (4) and (5)] even at +65°.

The absence of alkyl radicals of the type (VIII) and the presence of phosphoranyl radicals (V; R = Me or H) at high temperatures shows that β-scission of (V) is a very slow process. The radical (V; R = Me) is the spirocyclic analogue of the tetra-t-butoxyphosphoranyl radical $(Bu^tO)_4\dot{P}$ which undergoes extremely rapid β-scission at low temperatures.[2,5] The large difference in stability towards β-scission of these two tetra-t-alkoxyphosphoranyl radicals is probably attributable to stabilisation of the spirophosphoranyl ground state relative to the transition state for β-scission by the ring systems.[17] Methyl substitution of the rings in spirophosphoranes of the type (IV) has been shown to stabilise these compounds relative to their monocyclic tautomers (III).[18] In addition, the transition state for β-scission may be destabilised, by the development of strain in the remaining five-membered ring.[2,19] Entropy effects may also be important in determining the stability of these spirophosphoranyl radicals.[20]

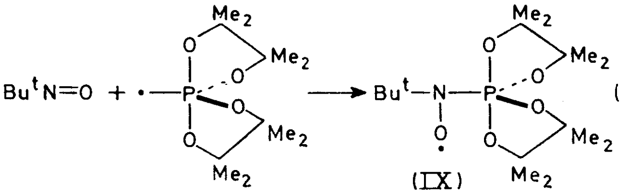
α-Scission of (VII) is much slower than loss of dimethylaminyl radicals from acyclic phosphoranyl radicals of the type $(RO)_2\dot{P}(NMe_2)_2$.[14] Ground and transition state effects of the types discussed above are the probable cause of the increased stability of the spirophosphoranyl radical (VII).

Acyclic tetra-alkoxyphosphoranyl radicals react readily with molecular oxygen to give peroxyphosphoranyl radicals [reaction (6)].[2,5] When the spirophosphoranyl

$$(RO)_4P\cdot + O_2 \longrightarrow (RO)_4POO\cdot \qquad (6)$$

radicals (V; R = Me or H) were generated in the presence of air, only transient, unidentified e.s.r. signals were detected even at −100°, and the spectra of the radicals (V) rapidly appeared presumably when oxygen had been removed from the photolysis region. This result implies that the peroxyspirophosphoranyl radicals are unstable in this system, perhaps rapidly abstracting hydrogen from the parent phosphorane giving rise to a chain autoxidation. The spirophosphoranyl radical (V; R = Me) will add to 2-methyl-2-nitrosopropane to give the t-butyl phosphoranyl nitroxide (IX).

The spectrum of the nitroxide (IX) consists of six lines of equal intensity and is analysed in terms of *a*(N) 14·7 and *a*(P) 1·73 G in benzene at 40°. The low value of *a*(P) in (IX) compared with that found for adducts of spirophosphoranyl radicals with olefins (see below) is probably a result of the virtual planarity of the nitrogen in (IX), the phosphorus atom lying in the nodal plane of the unpaired electron's π orbital.



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

[16] H. Kiefer and T. G. Traylor, *Tetrahedron Letters*, 1966, 6163.

[17] For a summary of this effect in phosphorane chemistry see S. Trippett, *Chem. Soc. Specialist Reports Organophosphorus Chem.*, 1971, **1**, 42.

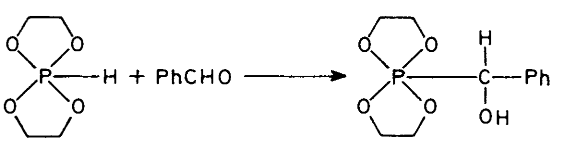
[18] H. Germa, M. Willson, and R. Burgada, *Compt. rend.*, 1970, **270C**, 1426, 1474.

[19] For a review of this effect in phosphorane chemistry see F. H. Westheimer, *Accounts Chem. Res.*, 1968, **1**, 70.

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

Relatively little is known of the reactions of spirophosphoranes of the type (IV). The P–H bond in (IV) will add to the carbonyl group of benzaldehyde or chloral[21] [equation (8)] but the mechanisms of these reactions have not been investigated. The spirophosphorane (IV; R = H) will add to certain substituted alkenes under the influence of sodium ethoxide or azobisisobutyronitrile (AIBN) catalysis.[22] When ethyl vinyl ether and the spirophosphorane (IV; R = H) were heated in toluene at 105—110° for 6 h in the presence of AIBN, 5-(2-ethoxyethyl)-1,4,6,9-tetraoxa-5-phosphaspiro[4,4]nonane (X) was obtained,[22] and it seems likely that this addition follows a homolytic mechanism, although the chain length is probably small.

We have now obtained e.s.r. evidence that spirophosphoranyl radicals will add to terminal olefins. When the alkene (15% v/v) was added to a system in which (V; R = H or Me), (VI), or (VII) were being generated, the steady state concentration of the phosphoranyl radical decreased to varying extents and the spectra of the adduct radicals (XI) became apparent. The results are listed in Table 2.



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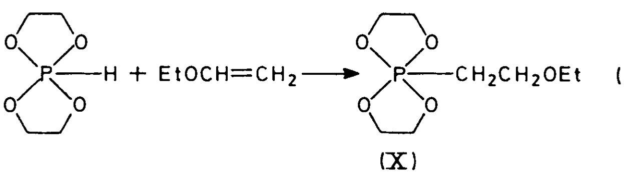


(9)

(X)

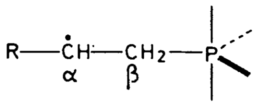
TABLE 2

E.s.r. parameters of the radicals (XI) tormed by addition of spirophosphoranyl radicals to hex-1-ene or 3,3-dimethylbut-1-ene in toluene solution

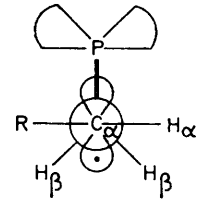
Phosphoranyl radical	R in (XI)	Temp. (°C)	a(P) G	a(α-H) G	a(β-H) G	a(β-H′) G[a]
(V; R = H)	Bu^n	−50	122·5	20·8	16·0	26·8
(V; R = H)	Bu^t	−60	104·5	20·1[b]	20·1	
(VI)	Bu^t	−60	98·0	20·6	18·3	
(V; R = Me)	Bu^t	−60	*c*	*c*	*c*	*c*
(V; R = Me)	Bu^n	−70	112·4	*d*	*d*	*d*
(VII; R = H)	Bu^t	−60	77·5	22·2	19·5	

[a] Methylene protons in the n-butyl group. [b] The splittings from α- and β-protons could not be differentiated because of the large line-width (3·6 G peak–peak). [c] The spectrum of the spirophosphoranyl radical was not quenched, and no adduct radical could be detected. [d] The spectrum of the spirophosphoranyl radical was partially quenched but the adduct radical was present in insufficient concentration to allow complete spectral analysis.

The low values of a(β-H) in these radicals are attributable[23,24] to their preference to exist in a conformation similar to (XII) in which the P–C bond eclipses the $2p_z$ orbital occupied by the unpaired electron.* The large magnitude of a(P) is also consistent with this assignment. Such conformational preferences are commonly encountered in alkyl radicals substituted in the β-position with a heavy atom (*e.g.* Si, Ge, Sn, S, Cl, P, or As), a hyperconjugative mechanism[23] and a conjugative mechanism involving heavy atom *d* orbitals[24] having been proposed to account for the effect. Similar conformational preferences were found in the adducts produced by the addition of dialkoxyphosphonyl radicals to olefins.[25]



(XI)



(XII)

The reactivity of (V; R = Me) towards terminal olefins was less than that of (V; R = H) (as judged by the degree of quenching of the phosphoranyl radical spectrum) and this is probably a result of the increased bulk of the former radical.

EXPERIMENTAL

The apparatus for u.v. irradiation of samples *in situ* in the e.s.r. spectrometer has been described previously.[2] The spirophosphoranes (IV) derived from ethylene glycol and pinacol were prepared from the glycol and tris(dimethylamino)phosphine as described.[26]

2,2,7,7-*Tetramethyl*-1,4,6,9-*tetraoxa*-5-*phosphaspiro*-[4,4]*nonane*.—2-Methylpropane-1,2-diol was prepared by reduction of α-hydroxyisobutyric acid using lithium aluminium hydride.[27] The diol (5·52 g) and tris(dimethylamino)phosphine (5·00 g) were heated to 160° for 2 h. when dimethylamine was evolved. The residue was distilled and the fraction with b.p. 58—60° at 0·1 mmHg collected; this solidified on standing in a refrigerator, m.p. 32—34° (Found, C, 46·1; H, 8·2; P, 14·9. $C_8H_{17}O_4P$ requires C, 46·2; H, 8·1; P, 15·1%), ^1H n.m.r. (benzene, 35°) showed $^1J_{H-P}$ 818 Hz, $^3J_{POCH_2}$ 2·4 Hz; methyleneoxy-protons gave the AB part of an ABX pattern, J_{AB} 8·7

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* The β-protons in the conformation (XII) are non-equivalent. Even if rotation around Cα–Cβ and P–Cβ is rapid on the e.s.r. time scale, this non-equivalence is retained because the phosphorus atom in the spirocyclic system is an asymmetric centre. The β-proton splittings in the adduct radicals we have detected have always been equal within the limits imposed by the line widths.

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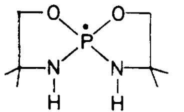
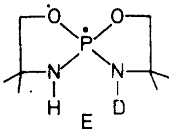
Hz, J_{AX} 16·8 Hz, J_{BX} 11·2 Hz, $\Delta\nu_{AB}$ 9·6 Hz. As the temperature was decreased (in [$^2H_8$]toluene solvent) the spectrum showed no gross changes. The methyleneoxy-protons still appeared as part of an ABX system at −70°, although coupling constants and the chemical shift difference varied with temperature. At low temperatures the methyl proton doublet (−70°) and the doublet of the hydrogen atom bound to phosphorus (−89°) showed no sign of further splitting. These observations are consistent with (but do not prove) that the spirophosphorane exists in the configuration in which both tertiary alkoxy-groups are equatorial. It is also possible that exchange between this configuration and the structure in which both tertiary alkoxyl groups are apical is rapid on the n.m.r. time scale at all temperatures studied.

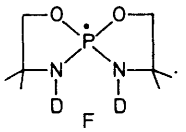
2,2,7,7-*Tetramethyl*-1,6-*diaza*-4,9-*dioxa*-5-*phosphaspiro*-[4,4]*nonane*.—The spirophosphorane from 2-amino-2-methylpropanol was prepared as described by Wolf and his co-workers.[26] The amino- and hydroxy-groups of 2-amino-2-methylpropanol were deuteriated by slow addition of an excess of D_2O to a refluxing mixture of the amino-alcohol and benzene, the H_2O–D_2O being removed in a Dean and Stark trap. After removal of the water and benzene the deuteriated amino-alcohol was heated with 0·5 mol. equiv. of tris(dimethylamino)phosphine to give the spirophosphorane,[26] m.p. 95—97° [from light petroleum (b.p. 80—100°)]. The spirophosphorane so prepared was shown by i.r. and ^1H n.m.r. spectroscopy to be *at least* 80% deuteriated in both P–H and N–H groups. Working with this minimum deuteriation it follows that 5/125 of the total can give rise to the radical D by H or D abstraction. The remainder will give E and F, in the ratio 1 : 2. The e.s.r. spectrum of the spirophosphoranyl radical from the deuteriated phosphorane was identical in all respects with that from the undeuteriated compound.



D



E



F

Reaction of Compound (IV; R = Me) *with thermally produced t-Butoxyl Radicals*.—The spirophosphorane (IV; R = Me) (1·361 g) was dissolved in deoxygenated iso-octane (5 ml) and benzene (50 µl) was added as an internal standard. A sample of this solution (0·8 ml) was sealed into an n.m.r. tube under nitrogen as a control. Di-t-butyl hyponitrite[16] (0·2559 g) was dissolved in the above solution to a total volume of 4 ml and a sample was sealed into an n.m.r. tube. The tubes were heated in a thermostatted oil-bath and the decay of the P–*H* resonance of the phosphorane was monitored by ^1H n.m.r. spectroscopy. Assuming that 90% of the t-butoxyl radicals from the hyponitrite become free, the n.m.r. signal from the phosphorane was shown to decrease at the same rate as t-butoxyl radicals were formed at +45 and +65°. At +65° the rate of production of t-butoxyl radicals by hyponitrite thermolysis is approaching the rate of production by photolysis of di-t-butyl peroxide in our apparatus.

Reaction of Radical (V, R = Me) with 2-*Methyl*-2-*nitrosopropane*.—The spirophosphorane (IV; R = Me) (0·1 g) and 2-methyl-2-nitrosopropane (0·004 g) were dissolved in benzene (0·6 ml) under nitrogen in the dark. No e.s.r. signal was detected on heating the sample at 40°. A solution of di-t-butyl hyponitrite (30 µl; 0·21M) was added and the e.s.r. spectrum assigned to (IX) rapidly developed at 40°. After removal of the sample from the spectrometer the solution was still pale blue (the colour of the monomeric nitroso-compound) indicating the nitroxide had not been formed by rapid addition of (IV; R = Me) to the nitroso-compound followed by abstraction of hydrogen from the resulting hydroxylamine.

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