Pseudo-rotation of Spin-labelled Phosphoranes formed by Cyclisation of Triazenylphosphoranyl Radicals

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Summary Triazenylphosphoranyl radicals undergo cyclisation to give paramagnetic phosphoranes and the rapid pseudo-rotation of the latter can be monitored by e.s.r. spectroscopy.

ALTHOUGH phosphorus(III) compounds X_3P are readily converted into the corresponding oxides $X_3P{=}O$ by treatment with nitrogen dioxide/dinitrogen tetraoxide, the mechanism of this oxidation and the relative reactivities of the paramagnetic $\dot{\mathrm{N}}\mathrm{O}_2$ and diamagnetic N_2O_4 are unknown.[1] The triazenyl radical $\mathrm{H}\overset{\bullet}{\widehat{\mathrm{NNN}}}\mathrm{H}$ is isoelectronic with nitrogen dioxide and we report here an e.s.r. study of the interaction of 1,3-dialkyltriazenyl radicals (**1**) (which, like $\dot{\mathrm{N}}\mathrm{O}_2$, are σ radicals[2]) with trialkyl phosphites.

The e.s.r. spectrum of the 1,3-di-t-butyltriazenyl radical (**1**; R = Bu^t)[2] was observed during continuous u.v. photolysis in the spectrometer cavity of a cyclopropane solution containing the parent triazene (*ca.* 1 M) [equation (1)].†

$$\mathrm{RN(H)N{=}NR} \xrightarrow{h\nu} \underset{(\mathbf{1})}{\mathrm{R}\overset{\bullet}{\widehat{\mathrm{NNN}}}\mathrm{R}} + [\mathrm{H}\cdot] \qquad (1)$$

When trimethyl phosphite (*ca.* 1 M) was also present at 205 K, the spectrum of (**1**; R = Bu^t) was replaced by one (see the Figure) which can be analysed in terms of a(1N) 13·0, a(1N′) 2·6, a(P) 7·3 G, g 2·0034 and which we assign, on the basis of the results reported below, to the cyclic 'spin-labelled' phosphorane (**2**). The larger nitrogen splitting presumably arises from N^2 and qualitative considerations‡ suggest that in (**2a**) the splitting from N^3 could be significantly greater than that from N^1. At higher temperatures, the spectrum of (**2**) exhibits changes which indicate that exchange of N^1 and N^3 is taking place on the e.s.r. time scale, as a result of interconversion of (**2a**) and (**2b**). At any given temperature, the spectrum was independent of the concentrations of triazene (0·5—1·6 M) and phosphite (0·7—2·0 M) confirming that exchange is intramolecular. Exchange

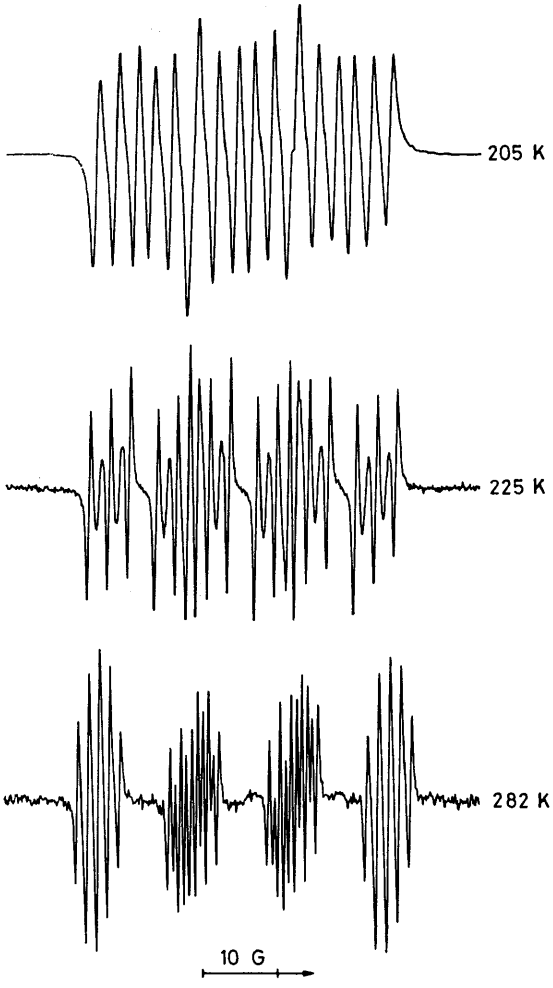

FIGURE. E.s.r. spectra of the radical (**2**) obtained by photolysis of 1,3-di-t-butyltriazene in the presence of trimethyl phosphite in cyclopropane at different temperatures.

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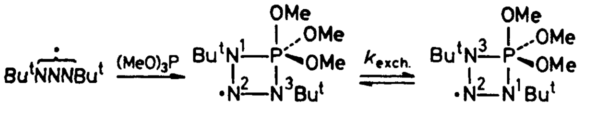
† Photolytic cleavage of the N–H bond or hydrogen transfer to or from a photo-excited state of the triazene may be involved. Hydrogen abstraction from the triazene by photochemically generated $\mathrm{R\dot{N}H}$ is also possible (see footnote ¶).

‡ The canonical structure (A) should make a larger contribution than (B), since in trigonal bipyramidal phosphoranes electronegative ligands preferentially occupy apical sites and π-electron pair donors preferentially occupy equatorial sites.



(2)

(2a) (2b)

of apical and equatorial ligands in diamagnetic trigonal bipyramidal phosphoranes is a well documented phenomenon[3] and is usually considered to take place by the Berry pseudo-rotation mechanism.[4]

Above *ca.* 280 K exchange between (**2a**) and (**2b**) takes place sufficiently rapidly to render N^1 and N^3 magnetically equivalent. Computer simulation of these temperature-dependent lineshape effects, assuming the nitrogen splitting which is unresolved at low temperature to be 0·01 G, leads to equation (3) and k_{exch} is $4\cdot4 \times 10^7$ s^{-1} at 225 K.

$$\log_{10}(k_{\text{exch}}/\text{s}^{-1}) = (12\cdot7 \pm 0\cdot3) - (21\cdot8 \pm 1\cdot5)/2\cdot303RT \text{ kJ mol}^{-1} \quad (3)$$

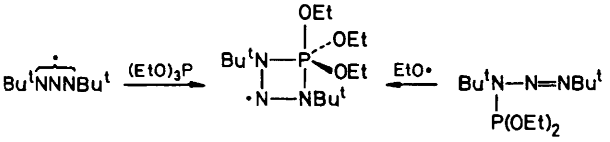
Similarly, (**1**; R = Bu^t) undergoes addition to triethyl phosphite, although lineshape effects due to exchange of apical and equatorial nitrogens in (**3**) were detected only above *ca.* 270 K [compared with *ca.* 215 K for (**2**)] and thus pseudo-rotation appears to be inhibited by the more bulky EtO ligands. The e.s.r. parameters of (**2**) and (**3**) are given in the Table.

Table. E.s.r. parameters for the radicals (**2**), (**3**), and (**6**) in cyclopropane.

				Hyperfine splittings/G		
Radical[a]	*T*/K	*g*-Factor	*a*(P)	*a*(1N²)	*a*(N′)[b]	*a*(6H)
(**2**)	205	2·0034	7·3	13·0	2·6 (1)	—
	282		12·3	13·0	1·4 (2)	—
(**3**)	218	2·0036	7·5	13·0	3·0 (1)	—
	295		12·3	13·0	1·5 (2)	—
(**6**)	219	2·0033	11·3	13·1	1·9 (2)	1·9
	255		12·5	13·2	1·9 (2)	1·9

[a] Radicals (**2**) and (**3**) are much longer-lived than (**6**). For example, at 249 K the first half-life for decay of (**2**) was *ca.* 45 s. [b] Number of nuclei coupling shown in parentheses.

The radical (**3**) was also detected during photolysis of a solution containing diethyl peroxide (as a source of ethoxyl radicals) and the phosphinotriazene (**4**)§ [equation (4)], but no intermediate phosphoranyl radical could be detected even at very low temperatures.

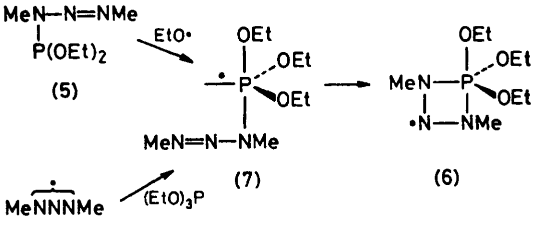


(4)

(3) (4)

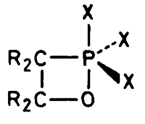
Similarly, photolysis of diethyl peroxide in the presence of the phosphine (**5**) at *ca.* 220 K gave rise to a spectrum which we ascribe to (**6**), but at temperatures below *ca.* 180 K this was replaced by the spectrum expected[5] for the triazenylphosphoranyl radical (**7**) [*a*(P) 931·5, *a*(1N) 26·7 G, *g* 2·0020 at 163 K].

Photolysis of 1,3-dimethyltriazene in cyclopropane solvent afforded a weak spectrum of (**1**: R = Me)[2]¶ and if triethyl phosphite was also present at 251 K this spectrum was replaced by a weak spectrum of (**6**) [equation (5)]. Thus we conclude that the triazenylphosphoranyl radical (**7**) undergoes cyclisation to give the paramagnetic phosphorane (**6**).



(5)

The e.s.r. parameters of (**2**), (**3**), and (**6**) indicate that the unpaired electron is centred mainly on N² and occupies a π-type orbital; the phosphorus and three nitrogen atoms are probably co-planar in the most stable conformation. For comparison, the acyclic radical $(\text{Me}_3\text{Si})_2\text{N}\dot{\text{N}}\text{N}(\text{SiMe}_3)_2$ shows *a*(1N) 14·6 and *a*(2N) 1·5 G at room temperature.[6] The ^{31}P splittings increase rapidly with increasing temperature (see Table), probably as a result of population of excited ring vibrational states in which the phosphorus atom is out of the plane defined by the three nitrogen atoms. In such excited states the P-3s orbital would contribute to the semi-occupied molecular orbital, giving rise to a positive contribution to *a*(P). The implication is that *a*(P) is positive at all temperatures studied.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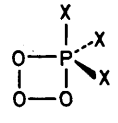
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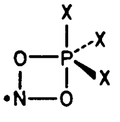
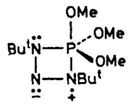
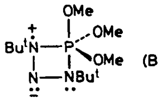

(10)

The spin-labelled phosphoranes (**2**), (**3**), and (**6**) are closely related to the Wittig intermediate (**8**) and to the phosphine–ozone adduct (**9**) and we suggest that the species (**10**) may play a part in the reaction of $\dot{\text{N}}\text{O}_2/\text{N}_2\text{O}_4$ with phosphorus(III) compounds.

(A) 

 (B)

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§ A satisfactory elemental analysis and spectroscopic data were obtained for this and the other new compounds described herein.

¶ Photolysis of RN(X)N=NR [X = H or P(OEt)_2] also affords the spectrum of R• and, presumably, $\text{R}\dot{\text{N}}\text{X}$ is also produced in equal yield.

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[3] R. Luckenbach, 'Dynamic Stereochemistry of Pentaco-ordinated Phosphorus and Related Elements,' Thieme, Stuttgart, 1973.
[4] R. S. Berry, *J. Chem. Phys.*, 1960, **32**, 933; R. R. Holmes and J. A. Deiters, *J. Am. Chem. Soc.*, 1977, **99**, 3318.
[5] For a review of phosphoranyl radical chemistry see B. P. Roberts, *Adv. Free Radical Chem.*, 1980, **6**, 225.
[6] R. West and B. Bichlmeir, *J. Am. Chem. Soc.*, 1973, **95**, 7897.