

Preliminary communication

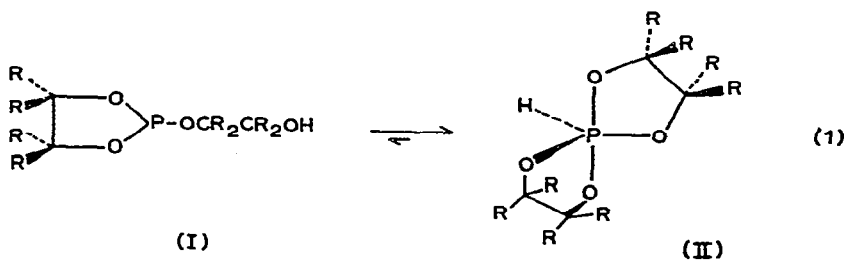
Spirophosphoranyl radicals: Tetra-alkoxyphosphoranyl radicals of remarkable stability towards β -scission

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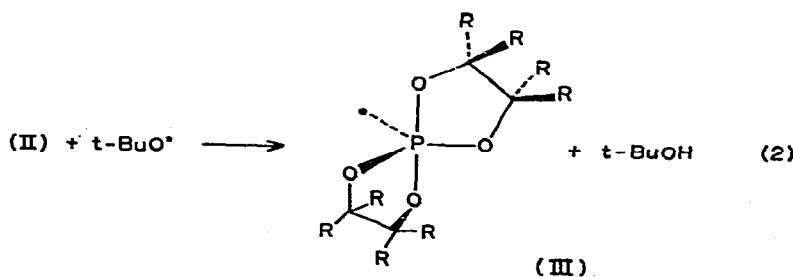
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Attempts to prepare phosphite esters of the type (I) result in the formation of the spirophosphorane tautomer (II)¹. The presence of the five-membered rings stabilises



the phosphorus(V) form². We now report that when a solution containing di-*t*-butyl peroxide and a spirophosphorane(II) is irradiated with high intensity UV light whilst the sample is in the cavity of an ESR spectrometer³, the spectrum of the spirophosphoranyl radical (III) is immediately apparent*. The spectrum of (III, R = H) is shown in Fig.1, the



* A very weak signal from (III) was present in the absence of peroxide. Presumably this arises from direct photolytic cleavage of the P-H bond.

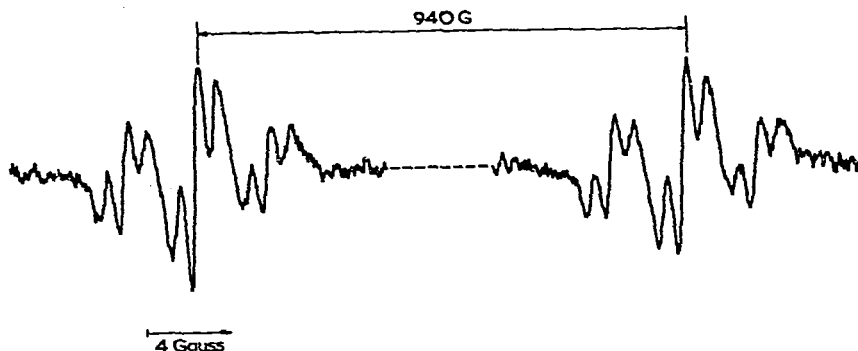


Fig. 1. ESR spectrum at 9.130 GHz of the spiroposphoranyl radical (III, R = H) in toluene at 0°C.

smaller splittings (triplet of triplets) apparent on each line resulting from interaction with the ^{31}P nucleus are tentatively assigned to coupling with H_1 and H_2 (or H_3 and H_4) in a radical with C_2 symmetry. The forms (IV) and (V) must be interconverting slowly on the ESR time-scale even up to +120° when the spectrum was unchanged. The ESR parameters of the spiroposphoranyl radicals are set out in Table 1.

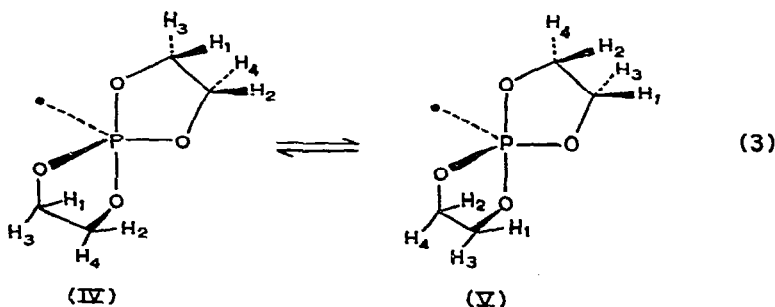
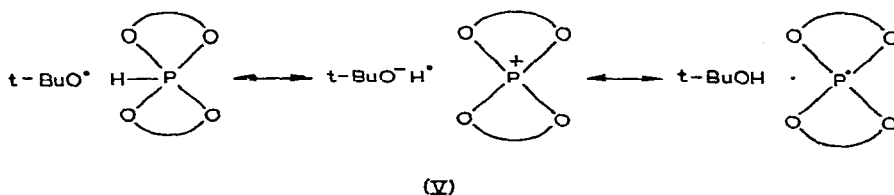


TABLE 1

R	Solvent	Temp. (°C)	$a(\text{P})^a$ (G)	$a(\text{H})^b$ (G)	g^a
H	Toluene	-70	910	3.4(triplet); 1.0(triplet)	2.003
		-20	920		2.003
CH_3	Toluene	-70	911	Not resolved	2.003
		-20	914		2.003
		+45	916		2.003

^a Corrected using the Breit-Rabi equation. ^b At 0°C.

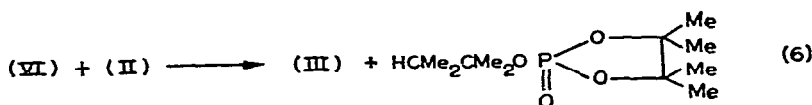
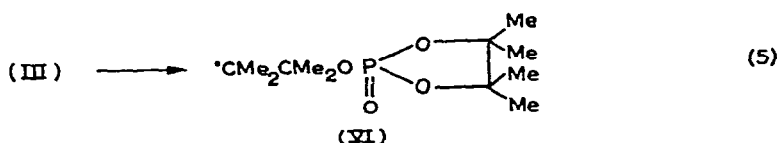
Reaction (2) appears to be extremely rapid even at low temperatures and this can be partly understood in terms of polar effects, the transition state for hydrogen abstraction being stabilised by a contribution from the canonical structure (V).



Below $+45^\circ$ the steady-state concentration of the phosphoranyl radical (III, R = Me or H) was proportional to the square-root of the incident light intensity indicating that the radical is being removed by reaction with other radicals, probably by P-P coupling to give a bis(spirophosphorane). The tetra-*t*-butoxyphosphoranyl radical undergoes rapid unimolecular β -scission (reaction 4) and k_4 is $5.1 \times 10^2 \text{ s}^{-1}$ at -60° .

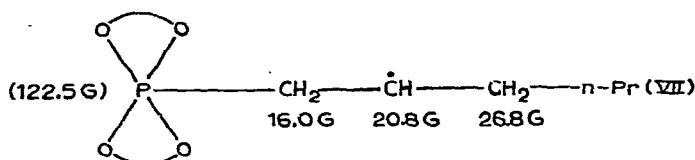


No alkyl radicals from the β -scission of (III, R = Me or H) were detectable at $+45^\circ$. Decomposition of di-*t*-butyl hyponitrite⁵ (0.42 M) in the presence of (II, R = Me) (1.0 M) in isooctane at $+45^\circ$ or $+65^\circ$ showed that the rate of consumption of the phosphorane was equal to the rate of production⁵ of *t*-butoxyl radicals, and there was thus no chain process (reactions 5 and 6) even at $+65^\circ$.



The absence of alkyl radicals (VI) and the presence of phosphoranyl radicals (III, R = Me or H) at high temperatures shows that β -scission of (III) is a very slow process. In fact, whilst the spectrum of $(t\text{-BuO})_4\text{P}^\bullet$ is undetectable above about -40° that of (III, R = Me) is still strong at $+120^\circ$. The large difference in stability towards β -scission of these two tetra-*t*-alkoxyphosphoranyl radicals is probably attributable to stabilisation of the ground state of (III) relative to the transition state for scission by the ring systems². In addition the transition state for β -scission of (III) will be destabilised by the development of strain in the remaining five-membered ring^{4a,6}.

The spirophosphoranyl radicals (III, R = Me or H) will add to terminal olefins. For example, addition of 1-hexene (15% v/v) to a system in which (III, R = H) was being generated brought about a decrease in the steady-state concentration of the phosphoranyl radical and the spectrum of the adduct-radical (VII) became apparent (coupling constants are given for toluene solution at -50°). Similar ESR studies of the addition of dialkoxyphosphonyl radicals to olefins have been reported⁷



The study of the ESR spectra and reactions of these spirophosphoranyl radicals should prove important in the understanding of the chemistry of phosphoranyl radicals, particularly of configurational effects. The radical reactions of spirophosphoranes containing a P-H bond are also being explored.

REFERENCES

- 1 M. Sanchez, R. Wolf, R. Burgada and F. Mathis, *Bull. Soc. Chim. Fr.*, (1968) 773.
- 2 See for example S. Trippett, *Chem. Soc. Specialist Reports in Organophosphorus Chemistry*, 1 (1969) 42.
- 3 A.G. Davies, D. Griller and B.P. Roberts, *J. Chem. Soc. B*, (1971) 1823.
- 4 (a) A.G. Davies, D. Griller and B.P. Roberts, *J. Chem. Soc., Perkin II*, in press.
(b) G.B. Watts, D. Griller and K.U. Ingold, *J. Amer. Chem. Soc.*, in press.
- 5 H. Kiefer and T.G. Traylor, *Tetrahedron Lett.*, (1966) 5163.
- 6 F.H. Westheimer, *Accounts Chem. Res.*, 1 (1968) 70.
- 7 A.G. Davies, D. Griller and B.P. Roberts, *J. Amer. Chem. Soc.*, 94 (1972) 1782.