

## Preliminary communication

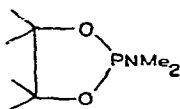
### Pseudorotation of trialkoxydimethylaminophosphoranyl radicals in solution

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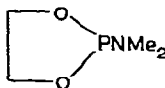
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(Received November 7th, 1972)

Although the existence of phosphoranyl radicals has been recognised for some years, they have only recently been observed by ESR spectroscopy. There is much current interest in the relation between their distorted trigonal bipyramidal configuration and their reactivities by the  $\alpha$ - and  $\beta$ -scission processes<sup>1</sup>. Alkoxyaminophosphines of the type  $(RO)_nP(NR'_2)_{3-n}$ , where  $n = 0-2$ , react rapidly with *t*-butoxyl radicals to give dialkylaminyl radicals from  $\alpha$ -scission of an intermediate phosphoranyl radical<sup>2</sup>. We now report evidence for a fast isomerisation, probably by pseudorotation, of the phosphoranyl intermediates in the corresponding reaction of *t*-butoxyl radicals with the 2-dimethylamino-1,3,2-dioxaphospholans (I) and (II). It appears that incorporation of the phosphorus atom in a five-



(I)



(II)

membered ring increases the rate of pseudorotation of a trialkoxydialkylaminophosphoranyl radical, relative to the acyclic analogues, such that isomerisation becomes rapid on the ESR time scale at low temperatures<sup>3</sup>.

When a mixture of (I) and di-*t*-butyl peroxide in propane or cyclopropane was photolysed in the cavity of an ESR spectrometer the spectra shown in Fig.1 were obtained. The spectrum BB' is assigned<sup>2</sup> to the phosphoranyl radical (III) [ $a(P)$  849 G,  $a(N)$  9.5 G in propane at  $-120^\circ$ ] in which the dimethylamino group is equatorial. Spectrum CC' is only detectable below about  $-110^\circ$  and is assigned on the basis of the hyperfine splittings to the radical (IV) [ $a(P)$  784 G,  $a(N)$  24 G in propane at  $-120^\circ$ ] in which the dimethylamino group is apical.

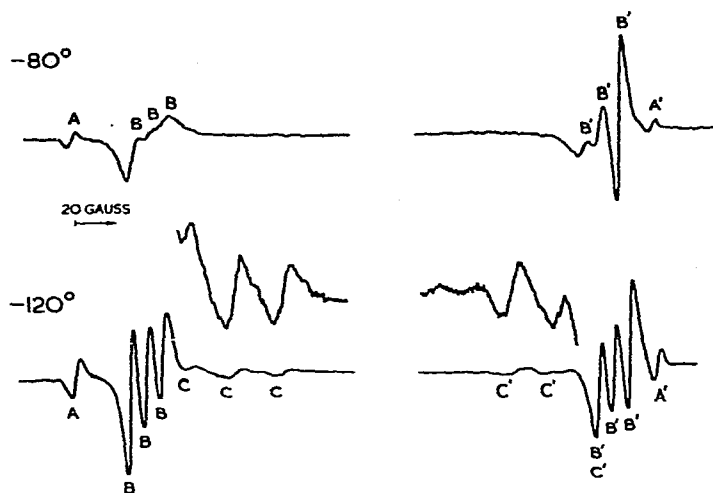
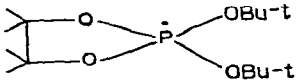
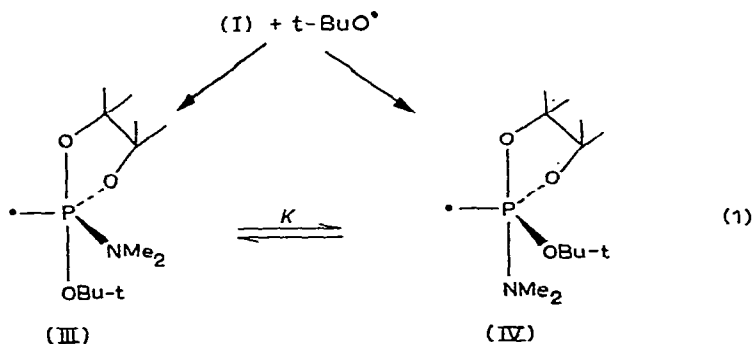


Fig.1. ESR spectra obtained during photolysis of di-*t*-butyl peroxide in the presence of (I) in propane solution. The spectrum AA' is assigned to  which is formed in a secondary reaction<sup>2</sup>.

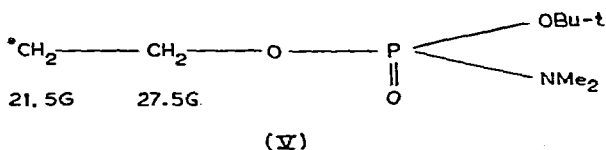


As the temperature was increased from  $-120^\circ$  the six hyperfine lines of spectrum BB' became progressively different in width and amplitude the broadening being most apparent in the low-field triplet (B). Within each triplet the inner lines were broader than the central lines which in turn were broader than the outer lines. The spectrum at  $-80^\circ$  is shown in Fig.1. As the temperature increased the apparent phosphorus hyperfine splitting in (III) decreased [ $a(\text{P})$  838 G at  $-70^\circ$ ]. The relative linewidths in toluene at  $-80^\circ$  were similar to those found in the less viscous propane or cyclopropane at this temperature. We attribute these effects to an increasingly rapid interconversion of (III) and (IV) as the temperature is increased, the differential broadening being associated with the different shifts in line position brought about by isomerization. The signs of the nitrogen hyperfine splittings in (III) and (IV) must be the same.

The rate of interconversion of (III) and (IV) is beginning to approach the fast ex-

change region above  $-120^\circ$ . Since decay of BB' and CC' when the light is shuttered takes ca. one second at  $-120^\circ$  it follows that (III) and (IV) are in equilibrium with  $K = 0.09$  at  $-120^\circ$ , corresponding to  $\Delta G^\circ = 0.7 \text{ kcal}\cdot\text{mol}^{-1}$ . To give rise to the observed differential linewidth effects the rate constant describing the conversion of (III) into (IV) must be in the range  $10^7$ – $10^8 \text{ s}^{-1}$  at  $-100^\circ$  and, assuming  $A$ -factors of  $10^{13} \text{ s}^{-1}$ , the activation energies for the isomerisation in both directions must be 4–5  $\text{kcal}\cdot\text{mol}^{-1}$ .

The phosphoranyl radical with an equatorial dimethylamino group produced by addition of a *t*-butoxyl radical to (II) showed similar differential linewidth effects, but the lower solubility of (II) precluded detailed low temperature studies. When a mixture of (II) and di-*t*-butyl peroxide in cyclopropane was irradiated at  $-25^\circ$  phosphoranyl radicals were no longer detected but three other spectra were observed. These were assigned to the dimethylaminyl radical, the *t*-butyl radical and (V)\*\*. The concentration of *t*-butyl radicals increased with the extent of photolysis indicating that these



radicals derive in part from a secondary reaction<sup>2</sup> (see Fig.1).

#### REFERENCES

- 1 A.G. Davies, D. Griller and B.P. Roberts, *J. Chem. Soc., Perkin II*, (1972) 993 and unpublished work
- 2 R.W. Dennis and B.P. Roberts, *J. Organometal. Chem.*, 43 (1972) C2.
- 3 *Specialist Reports in Organophosphorus Chemistry, Volume 3*. The Chemical Society, London, 1972, Ch. 11. p. 257.

\* At  $-131^\circ$  for a small radical concentration the decay of (III) followed first order kinetics with  $k = 1.3 \text{ s}^{-1}$ . At higher concentrations decay was second order.

\*\* The phosphoranyl radicals derived from (I) and (II) appear to undergo competing  $\alpha$ - and  $\beta$ -scission under conditions where  $(\text{EtO})_2\text{-t-BuOPNMe}_2$  gave only dimethylaminyl radicals<sup>2</sup>.