Cyclisation of Unsaturated Alkoxyphosphoranyl Radicals in Solution

By Alwyn G. Davies,* Maxwell J. Parrott, and Brian P. Roberts
(*Christopher Ingold Laboratories, University College, London,* 20 *Gordon Street, London* WC1H OAJ)

Summary Phosphoranyl radicals containing 2- or 3-alkenoxy-substituents cyclise to give oxaphosphetans or oxaphospholans respectively, with the unpaired electron centred on an exocyclic carbon atom.

THE stability of cyclic phosphoranes (PX_5) which contain 4- or 5-membered rings bridging apical and equatorial positions is well established,[1] but no examples of the cyclisation of unsaturated phosphoranyl radicals ($X_4P\cdot$) appear to have been described. We now report that such a cyclisation can be observed by e.s.r. spectroscopy and the structures of the product radicals can be determined.

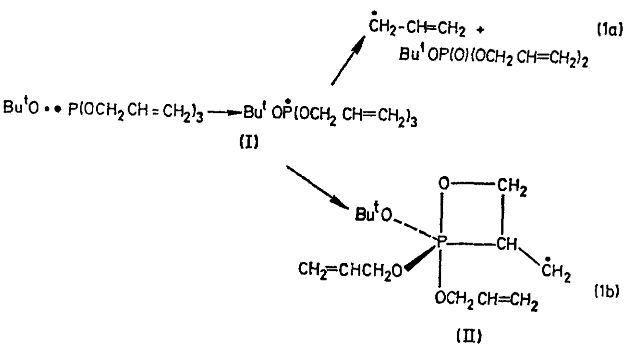
TABLE

Spectroscopic parameters of unsaturated alkoxyphosphoranyl radicals and of the radicals formed by their cyclisation at about −120° in propane

Trialkyl phosphite	Addend radical	Phosphoranyl radical[a] a(P)/G	Cyclised radical a(P)/G	Cyclised radical a(αH)/G	Cyclised radical a(β-H)/G
$(CH_2{=}CHCH_2O)_3P$	$Bu^tO\cdot$	897	179	20·5(2H)	20·5(1H)
	$EtO\cdot$	b	182	20·0(2H)	20·0(1H)
	$Me\cdot$	b	180	20·0(2H)	20·0(1H)
$(CH_3CH{=}CHCH_2O)_3P$	$Bu^tO\cdot$	b	190	19·9(1H)	14·3(1H), 23·0(3H)
	$EtO\cdot$	b	199	19·9(1H)	14·3(1H), 23·0(3H)
	$Me\cdot$	b	195	20·0(1H)	14·3(1H), 23·0(3H)
$(CH_2{=}CHCH_2O)P(OEt)_2$	$Bu^to\cdot$	884	176	20·0(2H)	20·0(1H)
	$EtO\cdot$	865	181	20·0(2H)	20·0(1H)
	$Me\cdot$	b	180	20·0(2H)	20·0(1H)
$(CH_2{=}CHCH_2CH_2O)_3P$	$Bu^tO\cdot$	894	b	b	b
	$EtO\cdot$	893	127	21·0(2H)	25·0(1H)
	$Me\cdot$	b	136	21·0(2H)	25·0(1H)
$(CH_2{=}CHCH_2CH_2CH_2O)_3P$	$Bu^tO\cdot$	893	b	b	b
	$EtO\cdot$	890	b	b	b
	$Me\cdot$	794	b	b	b

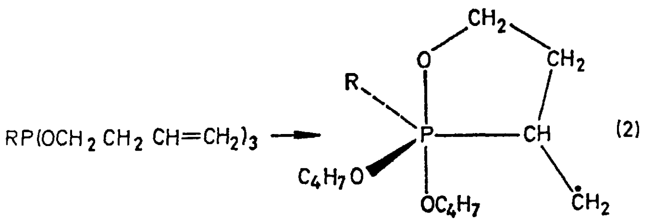
[a] Phosphorus hyperfine splitting corrected using the Breit-Rabi formula.
[b] Radical not detected by e.s.r.

We find that, in contrast with previous reports,[2] photolytically generated t-butoxyl radicals react with triallyl phosphite to give the phosphoranyl radical (I) which can be detected by e.s.r., although the choice of solvent appears to be crucial. The radical (I) undergoes subsequent β-scission[3] [reaction (1a)] to give an allyl radical or cyclises [reaction (1b)] to the oxaphosphetan radical (II);† evidence for the structure of (II) is given by the e.s.r. data in the Table. The large phosphorus hyperfine splitting in (II) is as expected for a β-phosphorus substituted alkyl radical.[5]



Similar results (see Table) were obtained with ethoxyl and methyl radicals, and with tricrotyl phosphite and allyl diethyl phosphite.

Tri-3-butenyl phosphite reacts with ethoxyl or methyl radicals to give the phosphoranyl radicals (III; R = EtO or Me) and the cyclised radicals (IV; R = EtO or Me) which contain 5-membered (oxaphospholan) rings.



(IV)

However, t-butoxyl radicals gave only the corresponding phosphoranyl radical (III; R = Bu^tO), and no spectrum of a cyclised radical could be detected. This is presumably due to the steric effect of the bulky t-butoxy-group, coupled with the less favourable energetics for the formation of the oxaphospholan radicals (IV) compared with the oxaphosphetan radicals (*e.g.* II). Similar steric retardation of the intermolecular addition of spiro-tetra-alkoxyphosphoranyl radicals to olefins is apparent when the alkoxy-groups are tertiary.[5]

The phosphoranyl radicals from tri-4-pentenyl phosphite showed no detectable cyclisation.

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† The radical (II) is formally a Wittig intermediate[4] and as such might be expected to eliminate an allyl radical. We believe, however, that the major source of the allyl radicals is the β-scission of (I).

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

[2] A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 993; G. B. Watts, D. Griller, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 8784.

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

[4] E. Vedejs and K. A. J. Snoble, *J. Amer. Chem. Soc.*, 1973, **95**, 5778.

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