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Preliminary communication

MEMORY EFFECTS IN THE OXIDATION OF TRIALKYL PHOSPHITES BY ALKOXYL RADICALS

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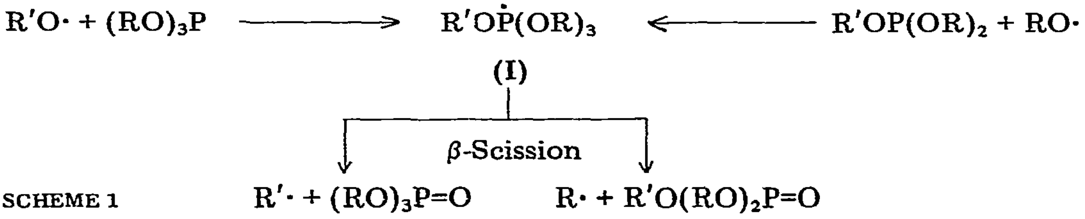
Summary

The alkyl radical products of β-scission of a cyclic tetraalkoxyphosphoranyl radical are independent of its source.

Trialkyl phosphites are readily oxidised by alkoxyl radicals to give trialkyl phosphates, the reaction proceeding by way of an intermediate tetraalkoxyphosphoranyl radical (I) which undergoes β-scission (Scheme 1) [1,2].



$$R'O\cdot + (RO)_3P \longrightarrow R'O\dot{P}(OR)_3 \longleftarrow R'OP(OR)_2 + RO\cdot$$

(I)

β-Scission

$$R'\cdot + (RO)_3P{=}O \qquad R\cdot + R'O(RO)_2P{=}O$$

SCHEME 1

There are reports that such oxidations which involve phosphoranyl radicals containing different alkoxy groups (Scheme 1) do [2] or do not [3] exhibit a "memory effect", that is the products are different [2] or the same [3] from the two pairs of reagents. The probable origin of a memory effect is shown in Scheme 2, for a particular system, and the three conditions which must be simultaneously fulfilled before such an effect may be detected are as follows:

(a) Phosphoranyl radical formation must be configurationally selective.
(b) β-Scission must be configurationally selective.
(c) Interconversion of the different configurational isomers must be slow compared with their rates of fragmentation.

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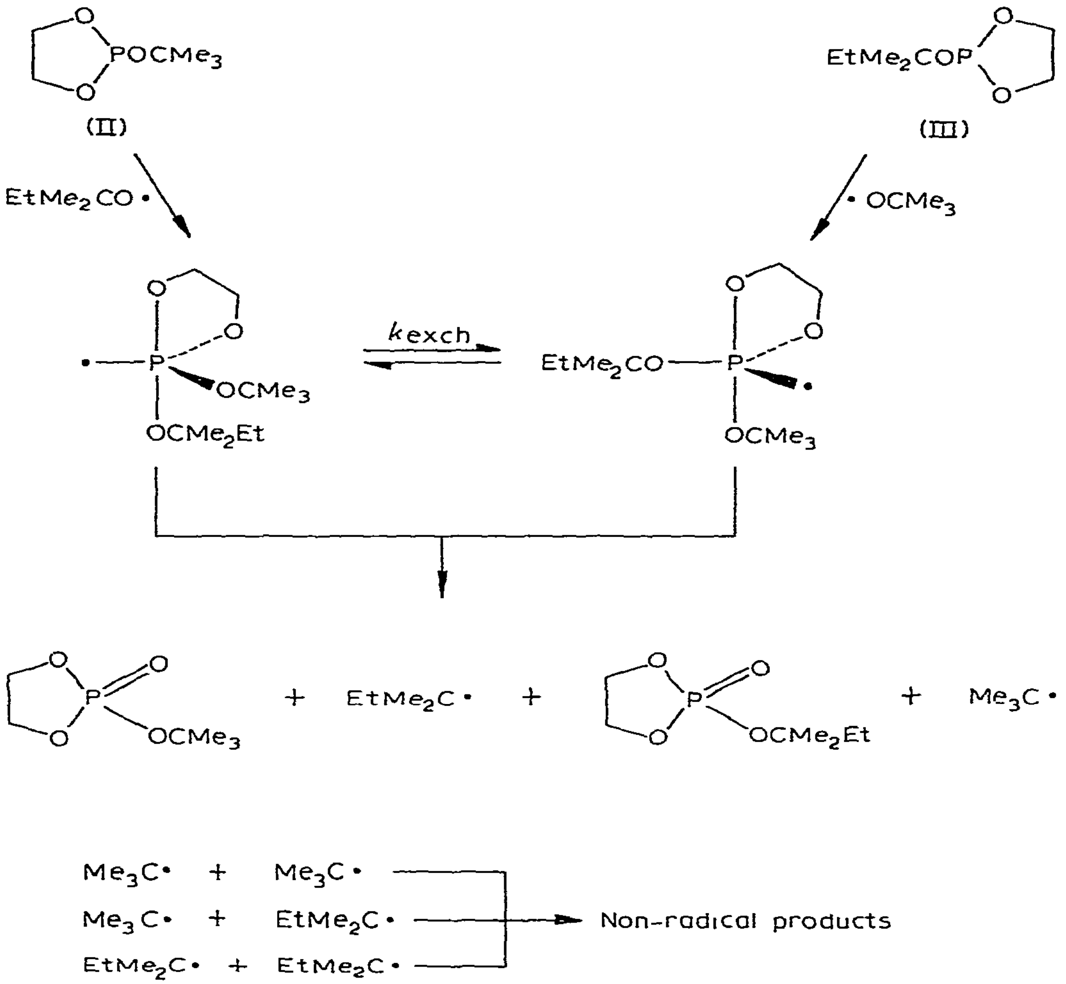

SCHEME 2

TABLE 1

OXIDATION OF 2-ALKOXY-1,3,2-DIOXAPHOSPHOLANS BY t-ALKOXYL RADICALS

Reagents[a,b]	Product radicals[c] $[Me_3C\cdot]/[EtMe_2C\cdot]$ (−20°C)	Rate constant[d] for β-scission at −20°C (s^{-1})
II + $EtMe_2CO\cdot$	0.83 ± 0.04	$(1.6 \pm 0.4) \times 10^4$
III + $Me_3CO\cdot$	0.81 ± 0.04	$(1.8 \pm 0.4) \times 10^4$

[a] Continuous UV irradiation of cyclopropane solutions of the phosphite and the appropriate dialkyl peroxide in the spectrometer cavity. [b] Only one, and the same, phosphoranyl radical signal was apparent in both cases: either the isomers are interconverting rapidly on the ESR time scale or their spectra are indistinguishable because of overlapping lines. [c] The ratio $[Me_3C\cdot]/[EtMe_2C\cdot]$ was independent of the source within experimental error between −70 and −20°C. Interpretation is simplest at the higher temperatures when the phosphoranyl radical concentration is negligible. [d] First-order rate constant for decay of the ESR signal of the phosphoranyl radical when photolysis was interrupted, extrapolated from measurements at lower temperatures.

Using ESR spectroscopy we have attempted to detect memory effects in an oxidation involving the intermediacy of a cyclic phosphoranyl radical (Scheme 2) for which the number of low-energy isomers is limited to two by the constraint that the five-membered ring must bridge apical and equatorial sites [4]. The results are given in Table 1.

The phosphite oxidation exhibits no memory effect within experimental accuracy. Although it is likely that both phosphoranyl radical formation and β-scission are configurationally selective processes [2,4], the magnitude and direction of this selectivity is uncertain at present. The most likely reason for the complete loss of "memory" is that ligand exchange in the phosphoranyl radical intermediate is rapid compared with its β-scission. Apical and equatorial ligands of similar apicophilicity appear to undergo rapid exchange [4,5] (k_{exch} = 10^7-10^9 s^{-1} at −20°C) and it is unlikely that memory effects will be detectable in most phosphite oxidation reactions, except possibly in a system involving a phosphoranyl radical which undergoes β-scission extremely rapidly [2].

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