Stereochemistry of Free-radical Oxidations at Trivalent Phosphorus

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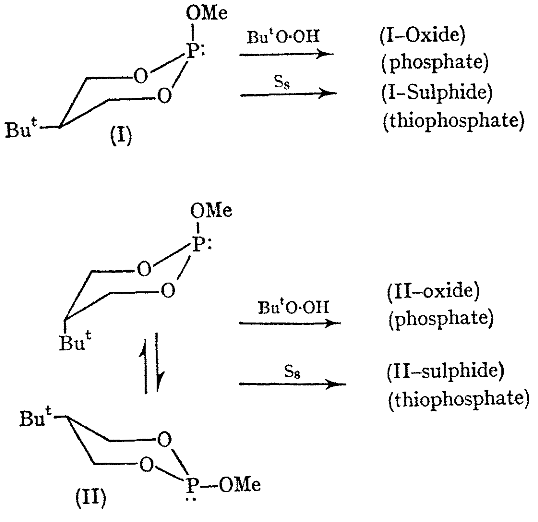
THE stereochemistry of reactions of numerous reagents with trivalent phosphorus has been studied, by use of optically active phosphines under conditions in which the phosphines are configurationally stable.[1] However, reactions of a strictly free-radical nature have not been studied stereochemically. We report the essentially stereospecific transfer of oxygen from t-butoxyl radical and sulphur from n-butylthiyl radical to give the oxide or sulphide with retention of configuration at phosphorus.

The phosphorus derivatives used were the geometrically isomeric (*cis–trans*) pair of t-butyl substituted six-membered ring cyclic methyl phosphites (2-methoxy-5-t-butyl-1,3,2-dioxaphosphorinans) (I) and (II) and the optically-active methyl-n-propylphenylphosphine.† Phosphites (I) and (II) have predominantly[2] the chair conformations shown. [The presence of an equilibrium amount of a flexible boat form of (II) cannot be excluded by our data.] The assignment of the configuration at C-5 is firm on ^1H n.m.r. grounds. However the configuration at phosphorus is uncertain. Verkade *et al.*[3] recently suggested a preferential axial orientation of the methoxy-group on phosphorus in a related six-membered ring phosphite. On this basis we tentatively assume that the methoxy-group occupies the axial position in phosphite (I), the more stable isomer. Knowledge of the absolute configuration at phosphorus is not essential to our argument.



t-Butoxyl radicals were generated thermally at 69° in deoxygenated MeCN with di-t-butyl hyponitrite[4] as radical source. n-Butylthiyl radicals were obtained by photolysis of n-butyl disulphide.[5] Results of reactions with varying ratios of the isomeric phosphites with t-butoxyl and n-butylthiyl radicals are given in Table 1, and compared to the results of the t-butyl hydroperoxide and S_8 oxidations of these compounds, reactions which are both usually assumed to proceed with retention of configuration at phosphorus.[6] Unless both the radical and non-radical reactions with the phosphites are forced by ring geometry to involve inversion, then the radical reactions of the cyclic phosphites also involve retention.

TABLE 1
Oxidation of isomeric phosphite mixtures

Reagent	Phosphite ratio (I) : (II)	Product ratios (I-oxide) : (II-oxide)
S_8	23:77	27:73
	89:11	92: 8
$Bu^nS{\cdot}SBu^n$ [a]	94: 6	95: 5
	92: 8	94: 6
	21:79	22:78
	12:88	15:85
$Bu^tO{\cdot}OH$	1 : 4	24:76
	9: 1	89:11
$Bu^tO{-}N{=}N{-}OBu^t$ [b] ..	15:85	21:79
	91: 9	96: 4

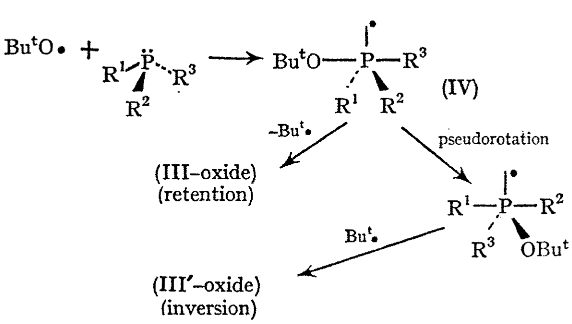
[a] 0·4—0·6M-phosphite, 0·30—0·38M-disulphide in deoxygenated MeCN at 3°.
[b] 0·3—0·4M-phosphite, 0·23M-hyponitrite in deoxygenated MeCN at 69°.

Similar experiments with optically active methyl-n-propylphenylphosphine showed that oxidation by hyponitrite and hydroperoxide gave the same optically active phosphine oxide in a stereospecific manner (Table 2).

TABLE 2
Oxidation of optically active phosphine[a]

Reagent	Rotations of product phosphine oxides	
$Bu^tO{\cdot}OH$[b]	−16·8 ± 0·2°	−16·5 ± 0·2°
$Bu^tO{-}N{=}N{-}OBu^t$ [c] ..	−16·4 ± 0·2°	−17·0 ± 0·2°

[a] Results with two independently prepared batches of optically active phosphine. Specific rotations on products recrystallized to constant rotation.
[b] 0·124M-phosphine, 0·414 M-peroxide in deoxygenated pentane at 0°.
[c] 3·0M-phosphine, 3·0M-hyponitrite in deoxygenated MeCN at 65°.



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† The phosphine was generated by $HSiCl_3$ reduction, (L. Horner and W. D. Balzer, *Tetrahedron Letters*, 1965, 1157) of the corresponding phosphine oxide prepared by the procedure of O. Korpium, R. A. Lewis, J. Chickos, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4842.

There is little doubt that the radical oxidation of the phosphine proceeds with retention of configuration at phosphorus.

Neither stereospecificity nor retention of configuration at phosphorus is a necessary requirement of reactions of this type as equilibration processes available to the phosphoranyl radical (IV), which may be involved, could lead to inversion Such an equilibration is shown below for a radical of assumed trigonal-bipyramidal geometry.[7] The absence of racemization does not rule out intermediates like (IV) in these cases if the lifetime of (IV) is short compared to the time required for pseudorotation.

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[1] For a review see W. E. McEwen, *Topics in Phosphorus Chemistry*, 1965, **2**, 1.

[2] J. H. Hargis and W. G. Bentrude, *Tetrahedron Letters*, 1968, 5365.

[3] D. W. White, G. K. McEwen, and J. G. Verkade, *Tetrahedron Letters*, 5369 (1968).

[4] H. Kiefer and T. G. Traylor, *Tetrahedron Letters*, 1966, 6163.

[5] C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.*, 1969, **81**, 1243.

[6] See Ref. 1, pp. 25, 26.

[7] E.p.r. measurements suggest trigonal-bipyramidal structure for $\cdot PCl_4$ and $MePCl_3$, G. F. Kokszka and F. E. Brinckman, *Chem. Comm.*, 1968, 349. P. W. Atkins and M. C. R. Symon, *J. Chem. Soc.*, 1964, 4363, found $PF_4\cdot$ to have geometry somewhat distorted from tetrahedral and to invert rapidly at room temperature.