

A New Reaction of Penta-co-ordinate Phosphorus Derivatives: the Formation of Phosphinates from an Oxazaphosph(v)ole and Carbonyl Compounds

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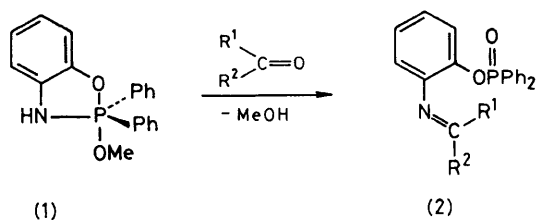
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Summary The oxazaphosph(v)ole (1) reacts with neat carbonyl compounds (aldehydes, ketones, and formamides) to give the phosphinates (2); in solution, a benzoxazole is formed in one case.

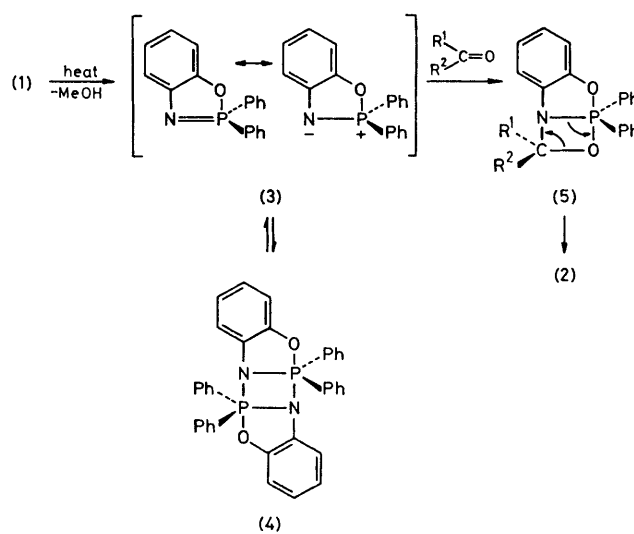
We have recently reported a convenient synthesis of oxazaphosph(v)oles [e.g. (1)],¹ and now report new reactions of these systems with a range of carbonyl compounds which



are unusual because they require a formal umpolung of one of the reactants, both of which are characteristically electrophilic. Other reactions of penta-co-ordinate phosphorus derivatives with carbonyl compounds are known,² but these processes either occur at an alternative site,³ or are initiated by prior thermolysis⁴ or tautomerism⁵ of the molecule.

Thus, treatment of the benzoxazaphosph(v)ole (1) with a neat carbonyl compound (dry, 4 molar excess) under the conditions shown in the Table, gives the phosphinates (2),† often in good to excellent isolated yield. In favourable cases, the yield (determined by ³¹P n.m.r.) is essentially quantitative. The reaction is apparently general for aldehydes, ketones, and formamides.

The formation of the phosphinates (2a–c) from amides is of particular interest because the latter are normally relatively unreactive. For these reactions, we propose the mechanism shown in Scheme 1, in which a prior elimination of methanol takes place to generate the reactive cyclic phosphine imine (3), which leads to (2) via a Wittig or Staudinger-type mechanism. The facile methanol elimination is readily understood if (1) is regarded as a phosphorus–nitrogen analogue of a hemiacetal.



SCHEME 1

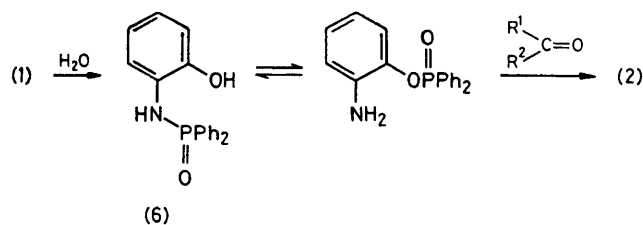
The following points support the mechanism. First, methanol (65%) is the major non-phosphorus-containing product. Secondly, thermolysis of the oxazaphosph(v)ole (1) in the solid state or in an inert solvent gives a quantitative yield of the well known⁶ diazadiphosphetidine (4), which is consistent with dimerisation of an intermediate phosphine imine. The existence of the diazadiphosphetidine–phosphine imine equilibrium (3) ⇌ (4) (cf. ref. 6) is established by independent thermolysis of (4) in dimethylformamide, which leads as expected to the phosphinate (2a) (59%). Finally, analogous reactions of cyclic phosphine imines with carbonyl compounds (e.g. aldehydes⁷ and ketones⁸) have been reported; the particularly high reactivity of the present example may be due to the vigorous conditions required to generate the phosphine imine (3) from (1) or from (4). This may also explain why the penta-co-ordinate intermediate (5) was not detected when the course of the reactions was monitored by ³¹P n.m.r. spectroscopy.

TABLE. The formation of phosphinates (2) from the oxazaphosph(v)ole (1).

Compound	R ¹	R ²	T/°C	Reaction time/h	Yield/%	δ (³¹ P) (CDCl ₃)/p.p.m.
(2a)	H	NMe ₂	115–120	3	41	+30.2
(2b)	H	NC ₅ H ₁₀ ^a	120–130	2.5	61	+29.9
(2c)	H	NMePh	130–140	2	13	+30.5
(2d)	Ph	Ph	150–160	5	74	+30.4
(2e)	H	<i>p</i> -ClC ₆ H ₄	130–140	2	41	+30.8

^a Piperidino.

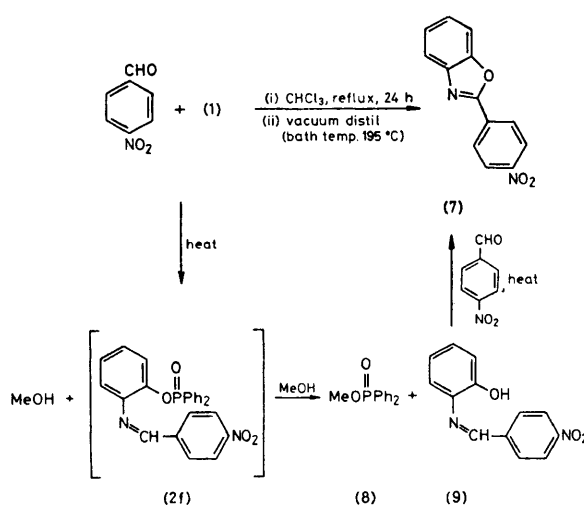
† All new compounds were characterised by their spectra and by elemental analysis.



SCHEME 2

Aldehydes and ketones may react with the oxazaphosph(v)ole (1) by a similar mechanism, though for these substrates we are unable to exclude an alternative pathway (Scheme 2). This involves the trivial *in situ* hydrolysis of the phosph(v)ole to the phosphinamide (6) followed by transphosphorylation and condensation of the free amino-group with the carbonyl compound. Independent treatment of the phosphinamide (6) with aldehydes or ketones leads to (2) under the conditions of the phosph(v)ole experiments; (6) remains unchanged in a similar control experiment with dimethylformamide.

Efforts to reproduce these reactions at a lower temperature in solution led to a novel transformation in one instance (Scheme 3), in which the oxazaphosph(v)ole was converted into an oxazole (7) (17%). Methanolysis of the phosphinate



SCHEME 3

(2f) to methyl diphenylphosphinate (8) (10%) and the phenol (9) is probably followed by oxidation of the latter by excess of *p*-nitrobenzaldehyde on work-up.

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¹ J. I. G. Cadogan, N. J. Stewart, and N. J. Tweddle, *J. Chem. Soc., Chem. Commun.*, 1978, 182.

² K. Burger in 'Organophosphorus Reagents in Organic Synthesis,' ed. J. I. G. Cadogan, Academic Press, New York, 1980, ch. 11.

³ F. Ramirez, H. J. Kugler, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, 1968, **33**, 1185, and references therein.

⁴ K. Burger and K. Einhellig, *Chem. Ber.*, 1973, **106**, 3421.

⁵ A. R. Hands and A. J. H. Mercer, *J. Chem. Soc. C*, 1968, 2448.

⁶ A. Schmidpeter and J. Lubert, *Phosphorus*, 1974, **5**, 55; H. B. Stegmann and G. Bauer, *Synthesis*, 1973, 162.

⁷ A. Schmidpeter, W. Zeiss, D. Schomburg, and W. S. Sheldrick, *Angew. Chem.*, 1980, **92**, 860; *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 825.

⁸ W. S. Sheldrick, D. Schomburg, A. Schmidpeter, and T. von Criegern, *Chem. Ber.*, 1980, **113**, 55.