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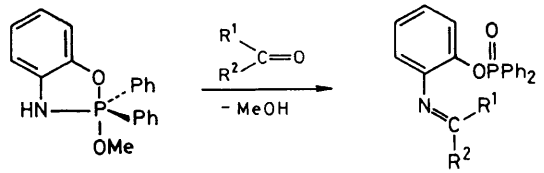
Summary The oxazaphosph(v)ole (**1**) reacts with neat carbonyl compounds (aldehydes, ketones, and formamides) to give the phosphinates (**2**); in solution, a benzoxazole is formed in one case.

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

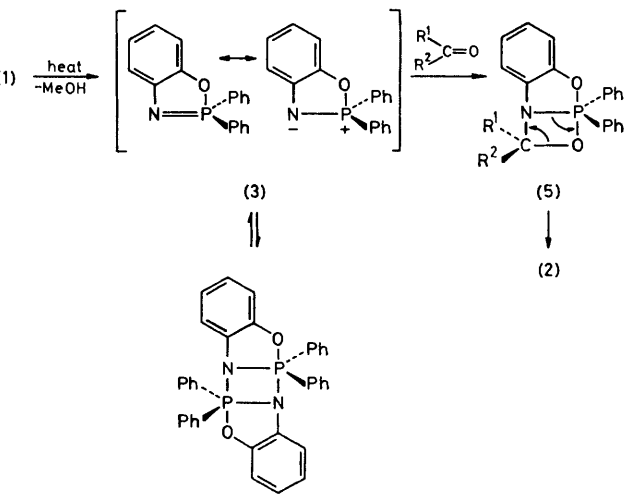


(1) (2)

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 thermolysis[4] or tautomerism[5] 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 ^{31}P 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

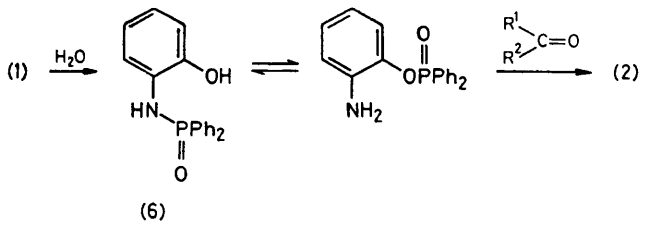
The following points support the mechanism. First, methanol (65%) is the major non-phosphorus-containing product. Secondly, thermolysis of the oxazaphosph(v)ole (**1**) in the solid state or in an inert solvent gives a quantitative yield of the well known[6] diazadiphosphetidine (**4**), which is consistent 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.* aldehydes[7] and ketones[8]) 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 ^{31}P 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_5H_{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	*p*-ClC_6H_4	130—140	2	41	+30·8

[a] Piperidino.

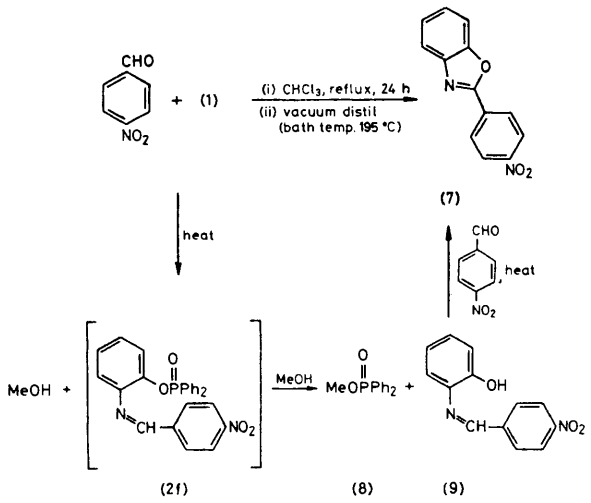
† All new compounds were characterised by their spectra and by elemental analysis.



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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