The Generation and Trapping of a Monomeric Aryldioxophosphorane ('Metaphosphonate')

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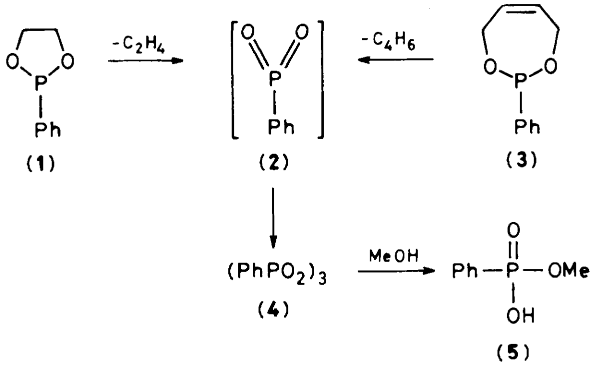
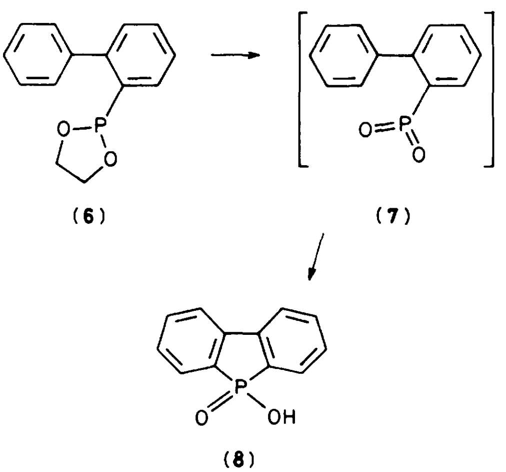
Gas phase pyrolysis of the cyclic phosphonite (**6**) generates a monomeric metaphosphonate (**7**) as evidenced by an intramolecular trapping reaction with the adjacent phenyl group to give 5-hydroxydibenzophosphole 5-oxide (**8**) in high yield.

Within the gamut of short-lived pentavalent phosphorus compounds with co-ordination number 3,[1] aryldioxophosphoranes ('metaphosphonates') are conspicuous by virtue of their pronounced tendency to oligomerise.[2] This property makes the current evidence for their detection very tenuous since until now trapping reactions have been conducted in solution, *e.g.* methanol,[3] resulting in products that are the same as those obtained by direct reaction with spontaneously formed oligomers.[4] We have now unambiguously detected such a species for the first time by thermal fragmentation of a cyclic phosphonite in the gas phase and its subsequent trapping by an intramolecular insertion reaction.

We observed that flash vacuum pyrolysis (F.V.P.) of 2-phenyl-1,3,2-dioxaphospholane (**1**) at 800 °C and 0.01 mmHg resulted in loss of ethylene and the essentially quantitative formation of a colourless, glassy solid which could also be obtained by extrusion of butadiene from the phosphonite (**3**)† under similar conditions. The identity of this extremely hygroscopic material was established as being principally the trimeric metaphosphonate (**4**) on the basis of analytical and mass spectral data, and by direct comparison of its ^{31}P n.m.r. spectrum with that of an authentic sample prepared by reaction between benzenephosphonic acid and benzenephosphonic dichloride.[4] Both spectra showed a resonance pattern between δ + 3.2 and − 1.1 consisting of at least six lines, the relative proportions of which were the same.





The formation of (**4**) could be interpreted as evidence for the generation of the postulated monomeric metaphosphonate (**2**), but attempts to intercept the latter by reaction with various cycloaddends, *e.g.* dimethyl acetylenedicarboxylate, tetracyanoethylene, 1,1-dicyanoethylene, and benzylideneaceto-

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† This compound was prepared in 34% yield from dichlorophenylphosphine and but-2-ene-1,4-diol by a method[5] similar to that described for compound (**1**). After distillation, (**3**) gave: b.p. 94—96 °C at 0.7 mmHg, satisfactory microanalysis as its sulphide, m.p. 69—70 °C; ^{1}H n.m.r. (CDCl$_3$) δ 4.0—4.5 (m, 4H), 6.45 (t, 2H, *J* 1 Hz), and 6.8—7.6 (m, 5H); ^{31}P n.m.r. (CDCl$_3$) δ + 160.1 p.p.m.

phenone, proved unsuccessful even when the vapourised reagent was introduced a short distance from the end of the pyrolysis zone. An apparent exception to these failures was the isolation of the monomethyl ester (**5**) of phenylphosphonic acid from trapping reactions with methanol. This we attribute to methanolysis of (**4**) rather than reaction with monomer (**2**).

Confirmation of the intermediacy of a monomeric metaphosphonate in these reactions was obtained indirectly by thermal fragmentation of 2(*o*-biphenylyl)-1,3,2-dioxaphospholane (**6**) [b.p. 110—115 °C at 0.05 mmHg; correct elemental analysis and expected ^{1}H n.m.r. data; ^{31}P n.m.r. ($CDCl_3$) δ + 164.3 p.p.m.], prepared from 2-bromobiphenyl as follows: conversion into the corresponding Grignard reagent followed by slow addition to a solution of PCl_3 in diethyl ether at −50 °C, and reaction of the resulting dichlorophosphine with ethylene glycol in the presence of triethylamine. When (**6**) was subjected to F.V.P. at 600—800 °C it was transformed almost quantitatively into 5-hydroxydibenzophosphole 5-oxide (**8**); (m.p. 252—255 °C; lit.[6] 253—257 °C; mixed m.p.‡ 250—254 °C), the anticipated product of intramolecular trapping of monomeric (**7**) by an adjacent phenyl ring. Since such a reaction requires the intervention of a powerful electrophile, we believe the formation of (**8**) from (**6**) constitutes a reliable diagnostic test for the existence of (**7**) as a true intermediate.

The present preparation of 5-hydroxydibenzophosphole 5-oxide (**8**), besides establishing the thermal fragmentation of cyclic phosphonites as a useful method for the generation of monomeric metaphosphonates, also illustrates the considerable potential of these highly reactive species in the synthesis of P-heterocycles.

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