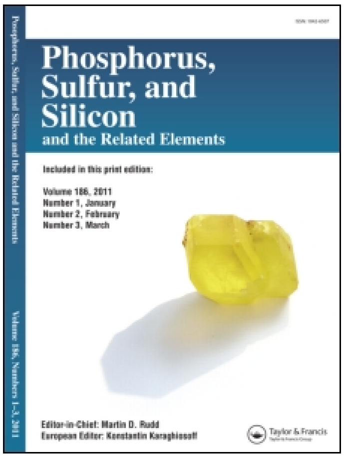

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Cyclic Elimination and Intramolecular Insertion Reactions of Thermally-Generated Monomeric Metaphosphoric Esters (Metaphosphates)

J. I. G. Cadogan[a]; Ian Gosney[b]; Peter M. Wright[b]
[a] B.P. Research Centre, Middlesex, England [b] Department of Chemistry, University of Edinburgh, Edinburgh, Scotland

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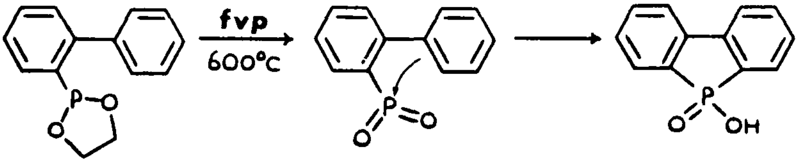
CYCLIC ELIMINATION AND INTRAMOLECULAR INSERTION REACTIONS OF THERMALLY-GENERATED MONOMERIC METAPHOSPHORIC ESTERS (METAPHOSPHATES)

J.I.G.CADOGAN
B.P.Research Centre, Chertsey Road, Sunbury-on-Thames,
Middlesex TW16 7LN, England

IAN GOSNEY AND PETER M.WRIGHT
Department of Chemistry, University of Edinburgh, West Mains
Road, Edinburgh EH9 3JJ, Scotland

Abstract 2-Aryl-1,3,2-dioxaphospholanes (aryloxyphosphites) decompose thermally in the gas phase with loss of ethylene to generate aryl metaphosphates which cyclise by intramolecular insertion (phosphonylation) or abstract a β-hydrogen to form a terminal alkene by loss of HPO_3.

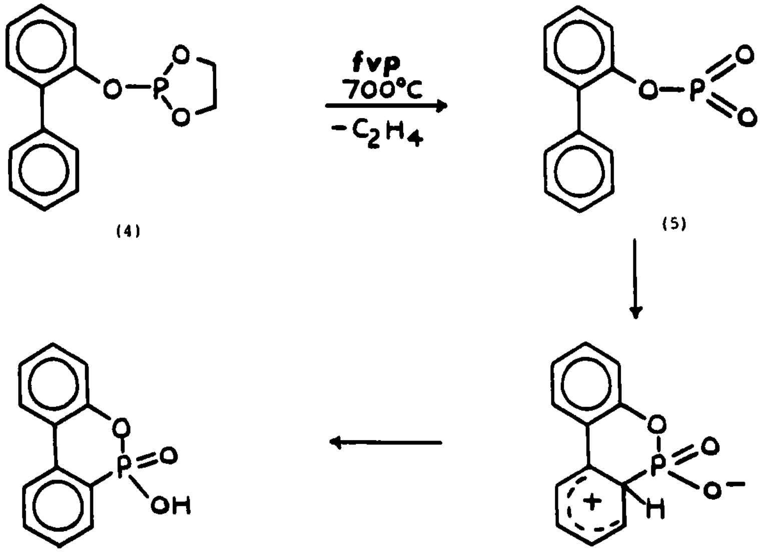
In the course of the currently intense interest in short-lived unusually co-ordinated phosphorus species, we found that thermolysis of cyclic phosphonites in the gas-phase under flash vacuum conditions provides a new and preparatively useful method for generating highly reactive metaphosphonate species [$ArPX_2$; X=O,S, or NAr].[1] Evidence as to the intermediacy of such species in these reactions came from the pyrolysis (600-800°C/3 torr) of the phosphonite (1) which is transformed almost quantitatively into 5-hydroxydibenzophosphole-5-oxide (3), the anticipated product of intramolecular trapping of the monomeric metaphosphonate (2) by the adjacent phenyl group.[2] We have now extended the scope of this



(1) (2) (3)

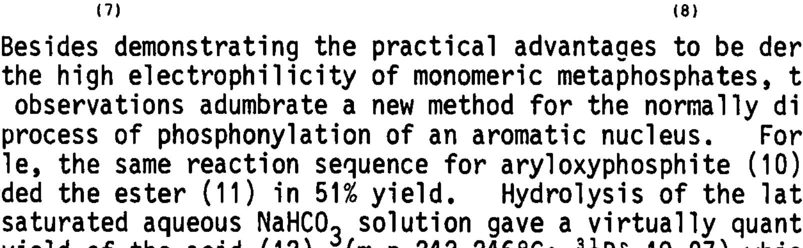
approach to the generation of monomeric metaphosphoric esters (metaphosphates) for which comparatively little is known apart from the growing evidence of their ability to function as powerful electrophilic substitution agents.[3]

Thus, pyrolysis of the aryloxyphosphite (4) at 700°C gave the cyclic phosphonic monoester (6) in 74% yield as a colourless solid (m.p.203-204°C; lit.[4] 200-203°C, $^{31}P\delta$ 6.04) by loss of ethylene.



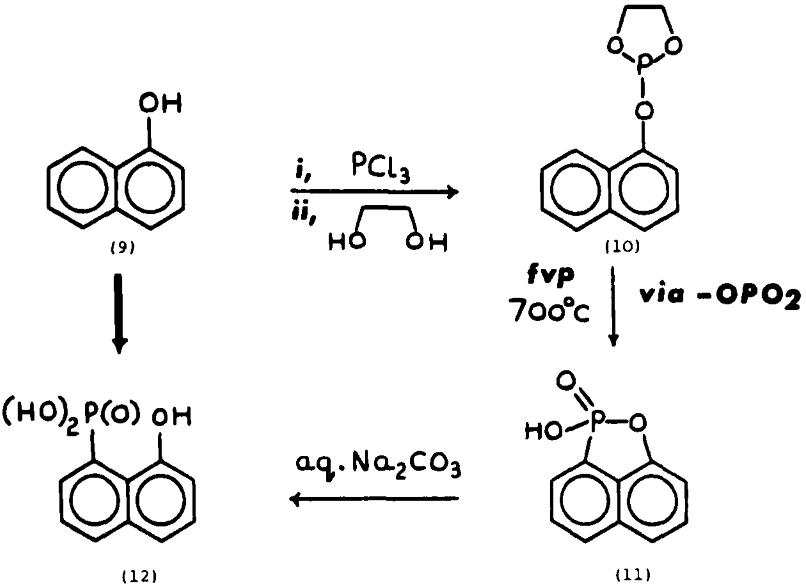
(4) (5) (6)

Similar pyrolysis of (7) resulted in the isolation of ester (8) (m.p.211-215°C, $^{31}P\delta$ 8.40, 45%). ^{13}C-n.m.r. spectroscopy fully supported the structures, in particular by showing signal splitting for the direct attachment of P to C [J175.4 and 174.0Hz, respectively, cf. J183.2Hz for PhP(O)(OH)$_2$] Formation of (6) and (8) by insertion of phosphorus into an aromatic C-H bond constitutes compelling evidence for the intermediacy of a monomeric aryl metaphosphate (ArOPO$_2$) moiety, *e.g.* (5) in these reactions.

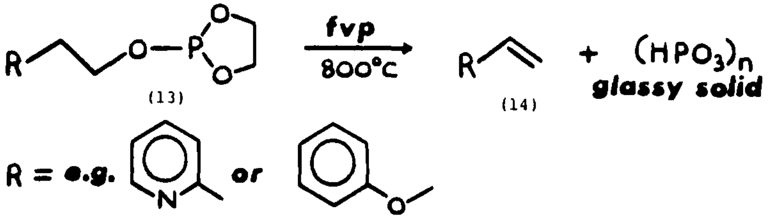


(7) (8)

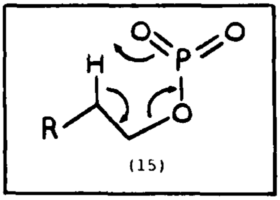
Besides demonstrating the practical advantages to be derived from the high electrophilicity of monomeric metaphosphates, these novel observations adumbrate a new method for the normally difficult process of phosphonylation of an aromatic nucleus. For example, the same reaction sequence for aryloxyphosphite (10) afforded the ester (11) in 51% yield. Hydrolysis of the latter with saturated aqueous NaHCO$_3$ solution gave a virtually quantitative yield of the acid (12) (m.p.242-246°C; $^{31}P\delta$ 19.07) which is the product of formal phosphonylation of the starting substrate naphth-1-ol (9) in the *peri*-position.



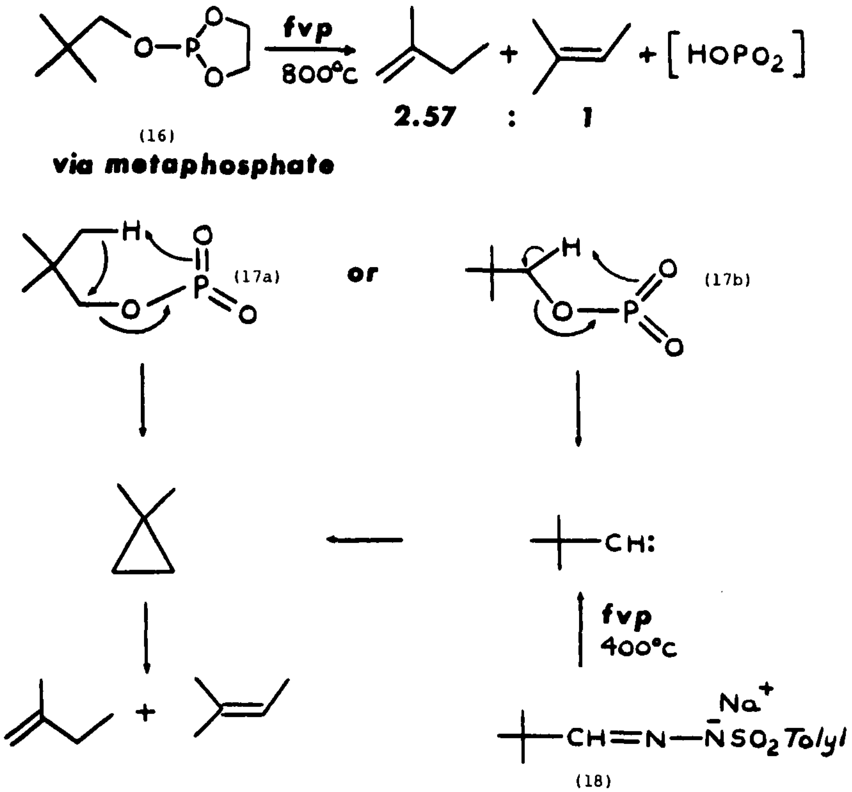
A somewhat different result akin to the Chugaev reaction is observed when the aryloxyphosphite contains an abstractable β-hydrogen, *e.g.* (13). Ethylene is extruded, but the metaphosphate intermediate (15) rearranges with loss of HPO_3 to give a terminal alkene (14) in good yield. This mechanism is fully supported by the concomitant formation of a transluscent glassy solid with the properties of polymeric metaphosphoric acid.



β-elimination via metaphosphate



In the case of the neopentoxy compound (16) pyrolysis yields a mixture of 2-methyl but-1- and -2-enes in the ratio of 2.57:1. At this stage, the mechanism of the reaction is not clear, but a pathway is envisaged whereby the metaphosphate intermediate (17) collapses to products *via* 1,1-dimethylcyclopropane which is formed either directly, or from *t*-butylcarbene as evidenced previously by us[5] upon pyrolysis of the tosylhydrazone salt (18). An alternative mechanism involving cleavage of (16) to produce a neopentyl radical can be ruled out since generation of the latter by pyrolysis of bis-neopentyl oxalate gives rise to 2-methyl but-1-ene and 1-methyl propene as the only products.



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