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## Thermally Induced Gas Phase Phosphonylation of Arenes via Intramolecular Trapping of an Aryl Metaphosphate Moiety

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2-Aryloxy-1,3,2-dioxaphospholanes break down on pyrolysis in the gas phase by a mechanism best accounted for in terms of the formation of metaphosphate (ArOPO<sub>2</sub>) moieties, which rearrange to cyclic phosphonic monoesters via intramolecular insertion reactions, unless an abstractable β-hydrogen is present when a Chugaev-type reaction takes place to give a terminal alkene.

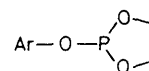
For the past several years attention in organophosphorus chemistry has focused largely on unusually hybridised species.<sup>1</sup> Of these, the most ephemeral are the metaphosphates for which comparatively little is known apart from the growing evidence of their ability to function as powerful electrophilic substitution agents,<sup>2</sup> especially in biochemical systems.<sup>3</sup> We have exploited this valuable property for the first time in synthesis, and report here that along the lines of our approach used to generate phosphonobenzene,<sup>4</sup> pyrolysis of 2-aryloxy-1,3,2-dioxaphospholanes (aryl phosphites) opens up a new and preparatively useful route to metaphosphate (ArOPO<sub>2</sub>) moieties which can be trapped intramolecularly to give access to otherwise difficult to obtain cyclic phosphonic monoesters of varying ring size. An important codicil to this procedure is that subsequent hydrolysis of the trapped products offers a new approach to the usually difficult process of direct phosphonylation of an aromatic nucleus.

The aryl phosphites (**1**) are easily prepared by simply mixing the appropriate phenol with equimolar amounts of 2-chloro-1,3,2-dioxaphospholane and Et<sub>3</sub>N in dry benzene, or alternatively by reaction of the phenol with PCl<sub>3</sub> and addition of an equimolar amount of ethylene glycol in the presence of Et<sub>3</sub>N. An isolation procedure consisting of filtration, removal of solvent, and distillation, gives the desired compounds in good preparative yields as colourless hygroscopic oils with the expected spectral properties.<sup>†</sup>

The conversion of the aryl phosphites (**1a–d**) into cyclic phosphonic monoesters is accomplished, in one step and good yields, by flash vacuum pyrolysis (f.v.p.). Thus, f.v.p. of (**1a**) at 700 °C and 0.001 mmHg gave the ester (**2**) in 50% yield as a colourless, hygroscopic solid [<sup>31</sup>P δ, (CD<sub>3</sub>)<sub>2</sub>SO, 27.16 p.p.m.]. The generality of the procedure is demonstrated by the preparation of the esters (**3**) [m.p. 203–204 °C; lit.<sup>5</sup>

200–203 °C; <sup>31</sup>P δ, (CD<sub>3</sub>)<sub>2</sub>SO, 6.04 p.p.m., 74%] from (**1b**), (**4**) [m.p. 211–215 °C; <sup>31</sup>P δ, (CD<sub>3</sub>)<sub>2</sub>SO, 8.4 p.p.m., 45%] from (**1c**), and (**5**) [m.p. 198–201 °C; <sup>31</sup>P δ (CD<sub>2</sub>Cl<sub>2</sub>) 29.79 p.p.m., 90%] from (**1d**).<sup>‡</sup> In all cases, ethylene is formed as a co-product, and it is assumed that the general reaction generates a highly electrophilic metaphosphate (ArOPO<sub>2</sub>) moiety which cyclises by an intramolecular C–H insertion reaction. Our attempts to isolate or intercept such species (with methanol) have so far failed.<sup>§</sup> Even in the case of (**1d**), having the steric protection of the very bulky 2,4,6-tri-*t*-butylphenyl group, the insertion of the metaphosphate moiety into the adjacent alkyl group to give (**5**) is apparently so fast and efficient that polyphosphates, which are the major products of monomeric methyl metaphosphate,<sup>6</sup> are not formed.

Besides implicating the involvement of metaphosphate moieties, the present reactions are of some significance because they provide a new and powerful method for the



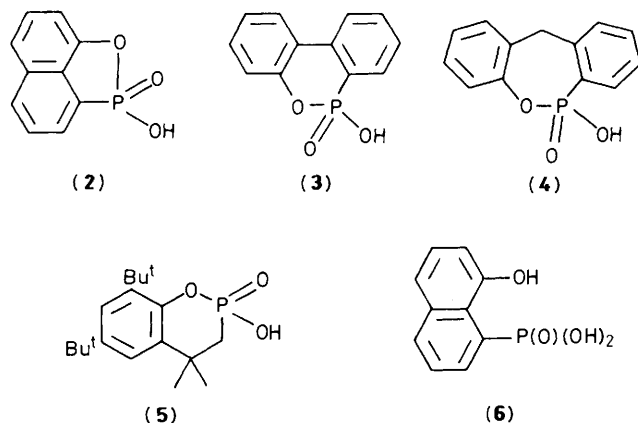
(1)

- a; Ar = α-naphthyl  
b; Ar = *o*-PhC<sub>6</sub>H<sub>4</sub>  
c; Ar = *o*-PhCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>  
d; Ar = 2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>  
e; Ar = 2-pyridyl-CH<sub>2</sub>CH<sub>2</sub>  
f; Ar = PhOCH<sub>2</sub>CH<sub>2</sub>

<sup>‡</sup> <sup>13</sup>C N.m.r. spectroscopy fully supported the structures, in particular by showing signal splitting for the direct attachment of P to C [e.g., (**3**) *J* 175.4 Hz, cf. *J* 183.2 Hz for PhP(O)(OH)<sub>2</sub>].

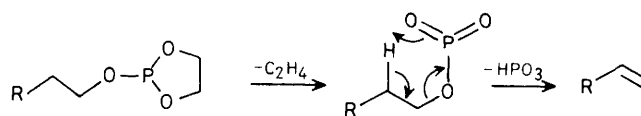
<sup>§</sup> Direct evidence in favour of metaphosphate intermediates in these reactions has come from the pyrolytic fragmentation of 2-methoxy-1,3,2-dioxaphospholane, which produced the same products in a trapping reaction with neat *N*-methylaniline, as those formed by authentic methyl metaphosphate.<sup>6</sup>

<sup>†</sup> All new compounds had correct analytical and mass spectroscopic characteristics: <sup>31</sup>P δ(CDCl<sub>3</sub>) 128.36 (**1a**), 129.56 (**1b**), 128.56 (**1c**), 136.31 (**1d**), 134.47 (**1e**), and 135.40 (**1f**) p.p.m. from 85% H<sub>3</sub>PO<sub>4</sub>.



phosphonylation of aromatic substrates. This process usually poses a difficult problem since known phosphonylating agents are not as a rule sufficiently electrophilic.<sup>7</sup> In this connection, it should be noted that aryl phosphonic acids can be obtained in the present context by subsequent hydrolysis of the trapped products. For example, in the case of (2), hydrolysis with saturated aqueous sodium hydrogen carbonate solution gives a virtually quantitative yield of the acid [(6); m.p. 242–246°C; <sup>31</sup>P δ, (CD<sub>3</sub>)SO, 19.07 p.p.m.] which is the product of formal phosphonylation of the original substrate 1-naphthol in the *peri*-position.

Finally, we report that for substrates with an abstractable β-hydrogen, the reaction follows a different pathway as shown by the pyrolysis (700°C and 0.001 mmHg) of (1e) and (1f) which are converted cleanly into 2-vinylpyridine and phenyl vinyl ether, respectively. These transformations are reminiscent of the Chugaev and closely related β-elimination reactions<sup>8</sup> and are best rationalised in terms of a metaphosphate intermediate that rearranges with loss of HPO<sub>3</sub>, Scheme 1. This is supported by the formation of a glassy solid with all the properties expected for polymeric metaphosphoric acid.



Scheme 1. R = pyridyl, (1e), or phenoxy, (1f).

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