

## Non-electrophilic Behaviour of Alkyl-substituted Metaphosphates in the Gas Phase: Formation of Alkenes by an Unusual 1,2-Methyl Shift induced by Hydrogen Abstraction—A Methyl Analogue of the Neophyl Ester Rearrangement

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Pyrolytic expulsion of ethylene from 2-neopentoxy-1,3,2-dioxaphospholane in the gas phase yields a virtually quantitative mixture of 2-methylbut-1-ene and its more stable isomer, 2-methylbut-2-ene in the ratio 2 : 1; this can be rationalised, using deuterium-labelling studies, as being formed from a thermally generated metaphosphate by a cyclic, concerted elimination reaction involving, as the key step, an unusual 1,2-methyl shift induced by competing  $\alpha$ - and  $\gamma$ -hydrogen abstraction reactions with loss of metaphosphoric acid.

Metaphosphates are renowned for their potent electrophilic properties both in biological systems<sup>1,2</sup> and aromatic substitution reactions (phosphorylation).<sup>3,4</sup> We report a different mode of behaviour whereby alkenes are formed from alkyl-substituted metaphosphates by a mechanistic process involving (i) hydrogen abstraction arising from the little recognised<sup>5</sup> basic properties of such species, followed by (ii) 1,2-methyl shift, like the Wagner–Meerwein rearrangement, albeit of the opposite polarity but concerted in nature.

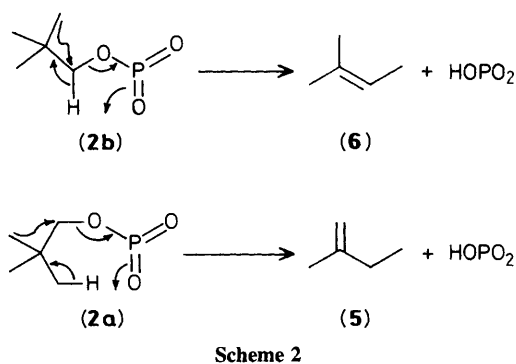
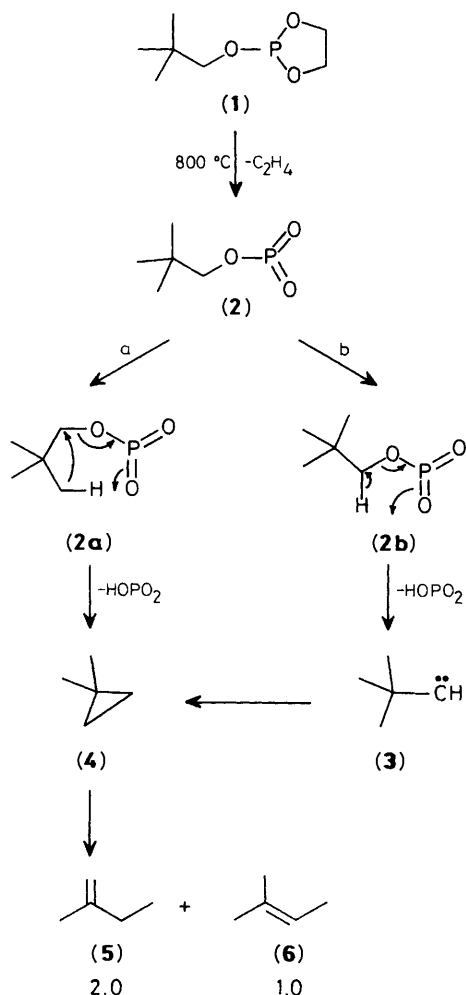
Thus, following the recent generation of aryl metaphosphates (ArOPO<sub>2</sub>) by thermal extrusion of ethylene from cyclic aryl phosphites,<sup>4</sup> gas-phase pyrolysis of 2-neopentoxy-1,3,2-dioxaphospholane (**1**) at 800 °C and 0.001 mmHg yielded a virtually quantitative mixture of 2-methylbut-1-ene (**5**) and its more stable isomer, 2-methylbut-2-ene (**6**) in the ratio 2 : 1. Both these alkenes can be envisaged as being formed from the thermally generated metaphosphate (**2**) by a combination of  $\alpha$ - and  $\gamma$ -hydrogen abstraction reactions as depicted in Scheme 1. This is supported by the isolation of a glassy solid whose <sup>31</sup>P n.m.r. spectrum showed characteristic signals at about  $\delta$  -11 and -23 for polymeric metaphosphoric acid.<sup>6</sup>

At first, it was presumed that abstraction led to 1,1-dimethylcyclopropane (**4**), either directly (path a) or *via* t-butylcarbene (**3**) by insertion (path b), followed by rearrangement to the observed alkenes. However, pyrolysis of an

authentic sample of 1,1-dimethylcyclopropane (**4**) under the same conditions produced not only very little of alkene (**5**) compared to (**6**), but also substantial quantities of 3-methylbut-1-ene in the overall ratio 1 : 7.1 : 4.<sup>8</sup> This disproved conclusively the notion that 1,1-dimethylcyclopropane (**4**) was involved as an intermediate in the pyrolytic conversion of (**1**) into products, although the possibility remained that t-butylcarbene (**3**) under the 'hot' conditions served as the sole precursor to the observed alkenes, even though at 500 °C in the gas phase it is known<sup>9</sup> to form 1,1-dimethylcyclopropane (**4**) exclusively. That this is not the case was shown by the independent generation of t-butylcarbene from the pyrolysis of the sodium salt of t-butylmethylenetoluene-*p*-sulphonylhydrazide<sup>9</sup> at 800 °C, when a similar plethora of alkenes was formed, together with 1,1-dimethylcyclopropane, which is not observed as a product from (**2**).

The further possibility of a free-radical pathway *via* the neopentyl radical could also be ruled out since the generation of the latter by pyrolysis of bis-neopentyl oxalate<sup>10</sup> at 800 °C produced a different mixture of alkenes consisting of 2-methylpropene and 2-methylbut-1-ene in the ratio of 1.2 : 1.

A mechanistic pathway which would account for the sole formation of reaction products (**5**) and (**6**) is shown in Scheme 2 and involves a 1,2-methyl shift induced by competing abstraction of both  $\alpha$ - and  $\gamma$ -hydrogens by the -OPO<sub>2</sub> moiety



[see arrows in (2a) and (2b)]. Support for the intermediacy of (2) and its subsequent decomposition by the pathway outlined above was obtained from the pyrolysis of  $[\alpha, \alpha\text{-}^2\text{H}_2]$ -(1) which gave isotopically pure  $[\text{}^2\text{H}_2]$ -(5) and  $[\text{}^2\text{H}_1]$ -(6) as the sole products, confirmed by  $^1\text{H}$  and  $^2\text{H}$  n.m.r. studies. The ratio of  $[\text{}^2\text{H}_2]$ -(5) to  $[\text{}^2\text{H}_1]$ -(6) was found to be 3.8:1, which represents a deuterium isotope effect of the order of 1.9, in line with other values reported<sup>11</sup> for gas-phase studies involving loss of deuterium in the rate-determining step (for path b).

In light of the evidence for the conversion of (2) into products by the concerted mechanism depicted in Scheme 2, the question remains as to the timing of the vicinal methyl shift. Our results point to initial abstraction of hydrogen,



which in turn induces the methyl shift in a process that is akin to the Wagner–Meerwein rearrangement accompanying gas-phase pyrolysis of neopentyl chloride.<sup>12</sup> In this instance, heterolysis of the carbon–chlorine bond is presumably of more importance and accounts for the preference of an incipient ion-pair type of transition state. The representation of a cyclic, concerted transition state for the rearrangement of (2) (Scheme 2) without any charge development is similar to that suggested to occur during the pyrolysis of neophyl esters (including acetate and carbonate),<sup>13</sup> but significantly only phenyl migration products are observed and none of the alkenes formed resulted from a methyl shift. Our attempts to induce a 1,2-methyl shift by pyrolysis of the corresponding neopentyl esters also failed; at 800 °C both the acetate and carbonate passed through the furnace unchanged whilst at higher temperatures decomposition occurred. This behaviour is strikingly different from the facile rearrangement of (2) and reveals a new facet of metaphosphate chemistry, hitherto renowned only for its powerful electrophilic qualities. This new aspect is further demonstrated here by the thermal fragmentation of 2-(3,3-dimethyl-2-butoxy)-1,3,2-dioxaphospholane, which affords a quantitative mixture of 2,3-dimethylbut-2-ene, 3,3-dimethylbut-1-ene, and 2,3-dimethylbut-1-ene by a combination of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -hydrogen abstraction reactions, respectively, coupled with a 1,2-methyl shift (for  $\alpha$ - and  $\gamma$ -products).

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