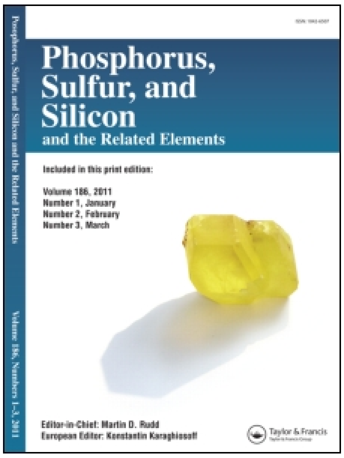

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ABSTRACTION *VERSUS* ELECTROPHILIC SUBSTITUTION: METAPHOSPHATE-MEDIATED REACTIONS IN THE GAS PHASE

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Abstract. Whereas arylmetaphosphates ($ArOPO_2$) tend to cyclise by intramolecular C-H insertion (phosphorylation) when generated in the gas phase, their alkyl-substituted counterparts exhibit non-electrophilic behaviour and give rise to alkenes by an unusual 1,2-methyl shift induced by a combination of hydrogen abstraction with concomitant elimination of metaphosphoric acid ($HOPO_2$).

We have already shown that 2-aryloxy-1,2,3-dioxaphospholanes (aryloxyphosphites) when subjected to thermolysis in the gas phase extrude ethylene (or butadiene) to generate highly electrophilic arylmetaphosphate species ($ArOPO_2$) which cyclise by intramolecular C-H insertion (phosphonylation) to produce cyclic phosphoric esters in a single step and good yields.[1] We now report that for analogous alkoxyphosphites thermal breakdown leads to a conspicuously different mode of reaction, whereby the metaphosphate intermediate rearranges with loss of metaphosphoric acid (HPO_3) to form alkenes exclusively.

For example, in the case of 2-neopentoxy-1,3,2-dioxaphospholane (1), thermal expulsion of ethylene at 800°C (0.001 mmHg) produces a virtually quantitative mixture of 2-methylbut-1-ene (4) and its thermodynamically more stable isomer, 2-methylbut-2-ene (3) in the ratio of 2.0:1. Also formed is a glassy solid identified from its

^{31}P n.m.r. signals at δ -11 and -23 as polymeric metaphosphoric acid. The reaction is most conveniently carried out in the apparatus described in FIGURE 1, in which a furnace A contains a silica tube B which may be packed with short lengths of silica tubing C. The presence of the silica tubing C reduces the minimum temperature required for complete decomposition of a compound in one pass by 50-100°C, and hence increases contact time. One end of the silica tube is fitted with an inlet tube D contained in an oven E. The other end of the silica tube is connected to a vacuum system by means of a U-tube trap F which is immersed in a liquid nitrogen bath G. In operation, the furnace A is pre-heated to the desired temperature, following which the oven E is heated to the sublimation point of the substrate, which is contained in the inlet tube D. The products of the reaction are collected in the trap F.

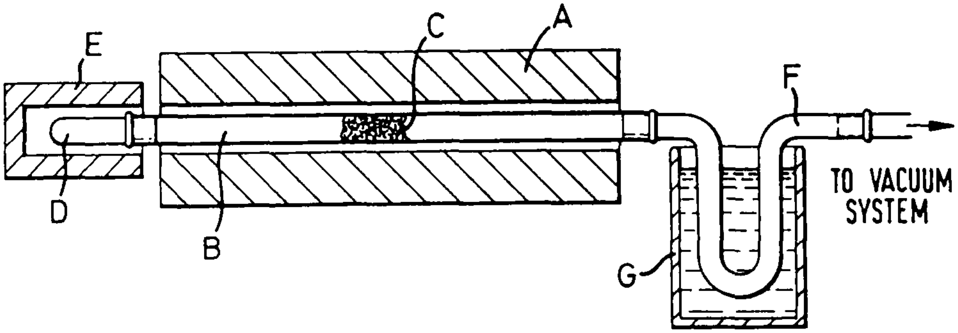
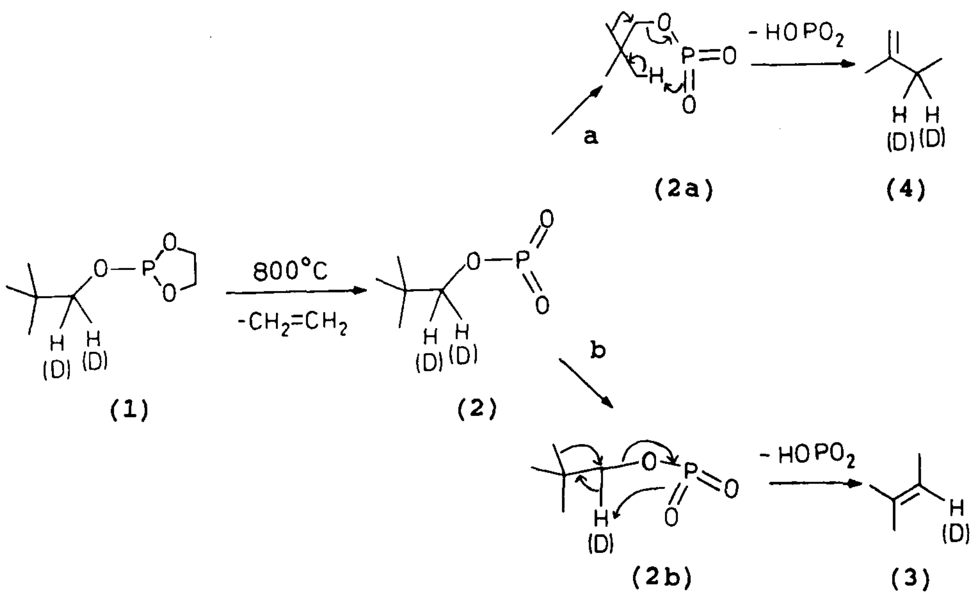


FIGURE 1

A mechanistic rationale for the formation of the foregoing products is outlined in SCHEME 1. The initial step involves competing abstraction of the α(minor)- and γ(major)- protons which in turn induces an unusual 1,2-methyl shift with concomitant elimination of metaphos-



SCHEME 1

phoric acid (HPO_3). This pathway is supported by deuterium-labelling studies in which thermolysis of α,α-(1)-d_2 under the same conditions produced (4)-d_2 and (3)-d_1 as the sole deuterium-containing products in the ratio of 3.8:1. This ratio represents a deuterium isotope effect (k_H/k_D) of 1.9 which is in keeping with other values obtained from gas-phase studies[2] where deuterium is lost in the rate-determining step (for path b in SCHEME 1). An alternative pathway previously envisaged by us[3] in which the metaphosphate intermediate (2) collapsed to the observed products *via* 1,1-dimethylcyclopropane was shown not to be the case by thermolysis of an authentic sample of the latter under the same conditions, when only small amounts of alkene (3) was formed compared to (4), together with substantial quantities of 3-methylbut-1-ene in the overall ratio of 1.0:7.1:4.0. Other control experiments also discounted any involvement of radical (or carbene) intermediates.[3]

The mechanistic transformation of (2) into (3) and (4) is reminiscent of the well-known Wagner-Meerwein rearrangement, albeit of the opposite polarity and concerted in nature. It is akin to the cyclic, concerted mechanism suggested to occur during the gas-phase thermolysis of neophyl esters[4], although in this process only a phenyl shift is observed and none of the alkenes are formed by methyl shifts. Our attempts to promote a 1,2-methyl shift by thermolysis of the corresponding neopentyl esters under similar conditions also failed. This inertness is in stark contrast to the rearrangement of (2) and reveals a new facet of metaphosphate chemistry until now known only for its powerful electrophilic properties.[5]

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