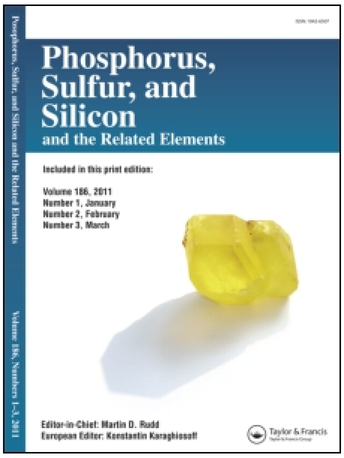

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From Gas Phase to Condensed Phase: Towards Metaphosphate Generation in Solution

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FROM GAS PHASE TO CONDENSED PHASE: TOWARDS METAPHOSPHATE GENERATION IN SOLUTION

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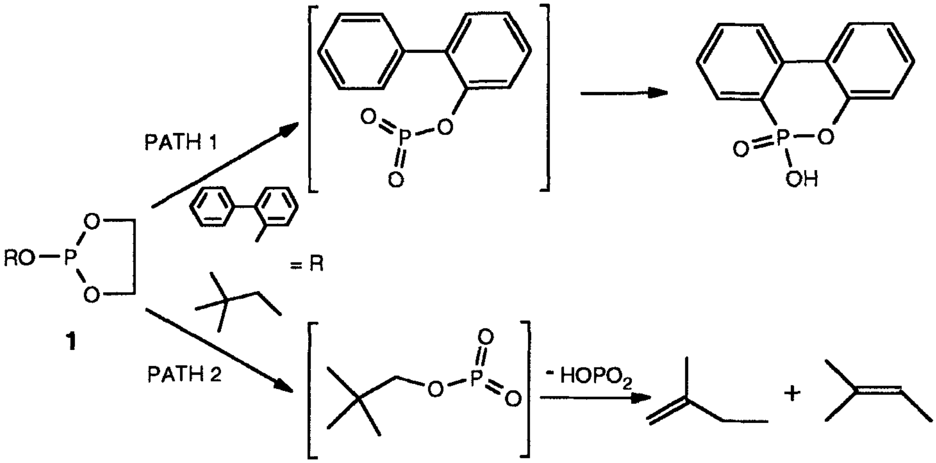
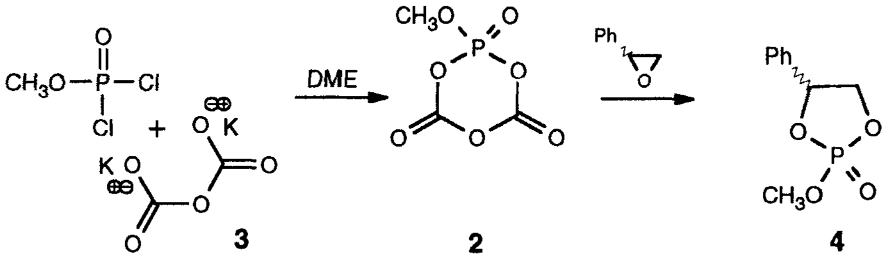
Abstract Based on attempts to generate methyl metaphophate in solution by thermal fragmentation of a cyclic pyrocarbonate phosphate, it has emerged that reaction of methyl dichlorophosphate with anhydrous potassium hydrogen carbonate serves as an alternative approach as proven by trapping with styrene oxide to form a 1,3,2-dioxaphospholane.

Our previous studies have shown that gas-phase pyrolysis of 2-substituted 1,3,2-dioxaphospholanes **1** generate highly electrophilic metaphosphate species by extrusion of ethylene. Depending upon the nature of the 2-substituent, the metaphosphate follows different reaction pathways, either by electrophilic substitution (path 1)[1] as shown in Scheme 1 or abstraction followed by elimination of metaphosphoric acid (path 2)[2].



SCHEME 1

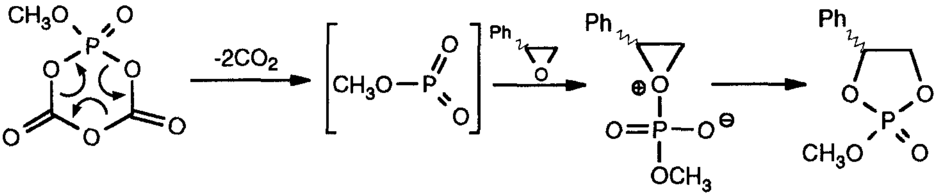
In a different and novel approach, aimed at producing metaphosphate species in solution, we have embarked on an investigation into the chelotropic breakdown of cyclic pyrocarbonate phosphates such as **2**. Our initial and tentative attempts to prepare **2** involved condensation of the di-potassium salt **3** (formed by hydrolysis of diethyl pyrocarbonate with potassium hydroxide at 0°C)[3] with methyl dichlorophosphate in anhydrous dimethoxyethane (DME) at 0°C (Scheme 2). On warming the reaction mixture to ambient temperature evolution of CO_2 occurred and a single phosphorus-containing product appeared at -13 ppm which gradually disappeared to be replaced by another product that resonated at -1 ppm.



SCHEME 2

When the same reaction was repeated in the presence of styrene oxide at 0°C, the peaks at -13 ppm and -1 ppm were not observed, but instead a closely matched pair of peaks at +16.83, 17.03 ppm appeared and grew in intensity as the reaction proceeded to completion. Comparison with an authentic sample, prepared by the condensation of 1-phenylethanediol and methyl dichlorophosphate in the presence of pyridine at 0°C, confirmed the identity of the product formed to be a diastereomeric mixture of 2-methoxy-4-phenyl-1,3,2-dioxaphospholane-2-oxide **4**. This observation is in keeping with a similar trapping reaction by Quin and co-workers[4] following generation of ethyl metaphosphate by thermal fragmentation of an oxaphosphabicyclo[2.2.2]octene derivative and provides compelling evidence for the intermediacy of metaphosphate in the foregoing reaction.

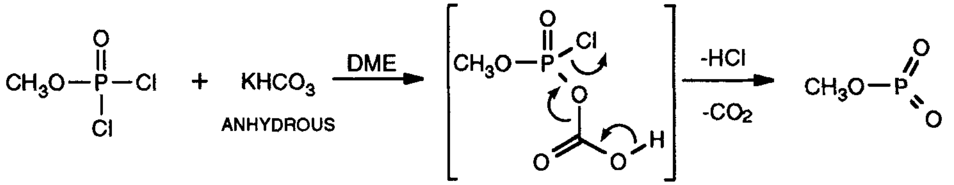
A plausible mechanism for the formation of **4** is outlined in Scheme 3 and can be ascribed to the intervention of methyl metaphosphate **5** arising from decomposition of its pyrocarbonate precursor upon warming to room temperature. In an attempt to shed further mechanistic light on the mode of reaction in the final step, the trapping reaction was repeated with optically pure (R)-styrene oxide but the same diastereomeric mixture was obtained. This result ruled out the possibility of rearrangement of **6** to **4** in a *single step* otherwise only the RR-isomer would have been observed. Instead, it pointed to ring-opening *via* a stabilised carbocation with bond rotation, or an entirely different mechanism involving direct attack by the metaphosphate species (in its charge-separated form) on the styrene oxide with inversion of configuration.



2 **5** **6** **4**

SCHEME 3

Initially we attributed the peaks observed at -13 and -1 ppm in our first experiments (Scheme 2) to trimeric and dimeric condensed forms of **5**, but it was recognised that terminal phosphoryl groups in chains appear at about -10 to -12, while signals for phosphoryl units in chains or cycles resonate at about -23 to -26 ppm[5]. The true identity of these products was revealed by comparison with the literature report by Satterthwait and Westheimer[6] on the thermal decomposition of methyl 2-butenylphostonate which extruded butadiene to form *sym*-di-methylpyrophosphate (-13 ppm) and methyl phosphonic acid (-1 ppm), apparently *via* the intermediacy of methyl metaphosphate. The origin of these products clearly requires the involvement of water and this finding led us to re-examine the nature of our supposed precursor pyrocarbonate **2**. These studies established that during its attempted preparation, decomposition of the di-potassium salt occurred *in situ*, despite careful precautions, to afford potassium hydrogen carbonate! Indeed when an anhydrous sample of the latter was condensed with methyl dichlorophosphate in the presence of styrene oxide, formation of **4** occurred exclusively in keeping with the intermediacy of methyl metaphosphate as shown in Scheme 4 and its subsequent trapping (*vide supra*). Intriguingly, we have now managed to prepare the di-sodium analogue of **3**, [$\nu_{C=O}$ 1610 cm^{-1}; FAB-MS (M$^+$+1) 150.96199, $C_2HNa_2O_5$ requires 150.96200] subsequent treatment of which with methyl dichlorophosphate yields the cyclic pyrocarbonate phosphate **2** (-17 ppm) whose chemistry will be described later.



SCHEME 4

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