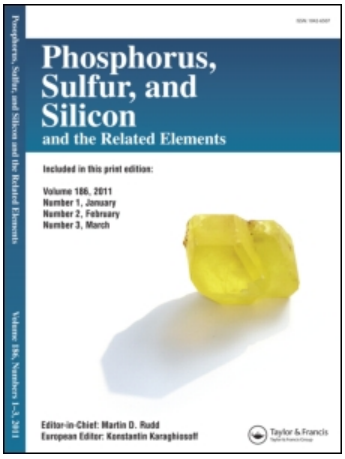

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COMMUNICATION

THERMOLYSIS OF PHOSPHONATES: PHOSPHONOFORMATE ESTERS

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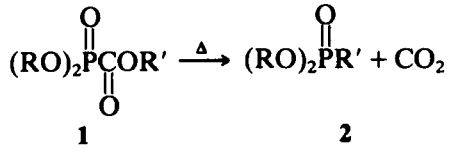
In the endeavour to develop new and facile methods for the generation of carbon-phosphorus bonds,[1] we have considered the pyrolysis of phosphonoformate esters **1**. These are structural analogues of chloroformates and chlorosulfites, both of which are useful in the preparation of alkyl chlorides by thermal decomposition.[2,3] An analogous process with **1** might be anticipated to yield the simple phosphonate **2** as illustrated in Equation (1).



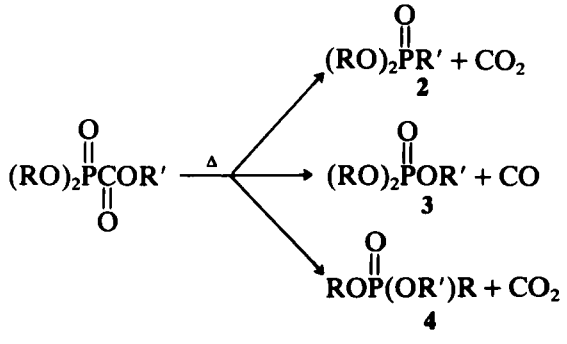
Equation 1

1 **2**

A recent report indicates this decomposition to occur in yields sufficient for the overall process to be of synthetic value.[4] However, preliminary work in this laboratory indicates the thermolysis of **1** to be more complex.

A series of phosphonoformate esters has been synthesized by the standard Michaelis–Arbuzov route.[5] These materials have been thermolyzed in the condensed phase. With several of the esters studied the "anticipated" product has indeed been found. However, in all instances at least one additional phosphorus product is found.

The thermal decomposition is summarized by Equation (2), at least two, and



Equation 2

TABLE I

Reagent	Temp	Time (h)	Yield [2]	Yield [3]	Yield [4]
R=R'=Me	295°C	6	75%	18%	—
R=Et; R'Me	295°C	8	49%	32%	trace
R=Et; R'=i-Pr	285°C	10	—	92%[a]	—
R=Me; R'=*i*-Pr	245°C	18	—	84%[a]	—
R=R'=Et	395°C	8	8%	79%	—
R=Et; R'=*i*-Bu	395°C	3.5	—	82%	—
R=Et; R'=2-Cl-Ethyl	400°C	6	—	86%	—
R=Me; R'=Bz	290°C	3	21%	18%	52%
R=Et; R'=Bz	255°C	12	33%	25%	6%

[a] Product isolated is a mixture of free acid and anhydride; the ester linkages pyrolyze under the reaction conditions.[6]

possibly three, competing pathways being involved. The experimental results for the series of phosphonoformates are listed in Table 1. Starting materials and isolated products exhibited ^{1}H (Varian EM-360A) and ^{31}P (IBM Bruker WP200SY) NMR and infrared (Perkin-Elmer 598) spectra in accord with the assigned structures and those previously reported. Quantification of yields of thermolyses was performed using both ^{1}H and ^{31}P NMR on samples containing added reference materials.

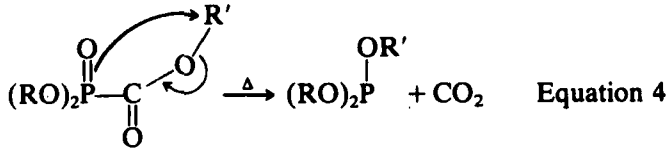
In two instances the formation of gaseous by-products was investigated by vapor phase chromatography. With trimethyl phosphonoformate (R=R'=Me) both carbon monoxide and carbon dioxide were found, the latter being observed in a five-fold excess compared to the former. With diethyl isobutyloxycarbonylphosphonate (R=Et, R'=*i*-Bu) carbon monoxide was observed to be the dominant vapor product, only a trace of carbon dioxide being found.

The significance of the carbon monoxide elision route appears to increase with substitution of the carboxylate ester function. It is completely dominant when a secondary ester is used. In no instance is it completely absent.

It is possible that the phosphonates **2** could arise directly as implied in Equation 2. However, the observation of additional phosphonate products in several instances opens another possibility. The most reasonable route for the formation of the "unanticipated" phosphonate products is *via* the thermal Michaelis–Arbuzov rearrangement of the corresponding phosphites (Equation 3). Similarly,

$$(RO)_2POR' \xrightarrow{\Delta} (RO)_2\overset{\overset{O}{\|}}{P}R' \qquad \text{Equation 3}$$

should such an intermediate be generated, the "anticipated" phosphonates could result simply *via* competitive rearrangement of one of the other alkyl ester linkages. Formation of the phosphites can be envisioned as occurring with elision of carbon dioxide as shown in Equation 4.



Equation 4

A further complication in the overall scheme is found with the thermolysis of a mixture of phosphonoformates. On thermolysis of a mixture of trimethyl phosphonoformate and diethyl benzyloxycarbonylphosphonate, both diethyl benzyl phosphate and dimethyl benzyl phosphate are found as products. This shows that intermolecular transfer of the carboxylate ester functionality is possible.

Clearly, the thermolysis of phosphonoformate esters is not a simple process. Further investigations are being performed to elucidate more clearly the processes occurring and to modify the reaction system in the hope of generating a system viable for synthetic applications.

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