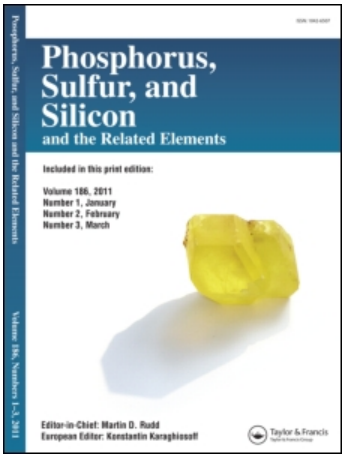

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FRAGMENTATION OF ACYLPHOSPHONATES—NEW PRECURSORS FOR DICOORDINATED PHOSPHORUS SPECIES†

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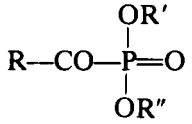
Acylphosphonic acids or methyl esters undergo acid catalyzed fragmentation to the corresponding carboxylic acids or methyl carboxylates, with the putative formation of phosphenous acid (HOP=O) or its ester.

Although dialkyl acylphosphonates (**1**) have been known for about forty years,[1] their dealkylated derivatives, namely acylphosphonic acids (**2**) and their monoesters, alkyl hydrogen acylphosphonates (**3**) are relatively little known. Specific compounds belonging to these classes have been prepared in order to study their biological properties and have been isolated as salts.[2–5] Characterization of free acylphosphonic acids and alkyl hydrogen acylphosphonates has not been previously described and their chemical and physical properties have not been reported.



1, R′ = R″ = alkyl
2, R′ = R″ = H
3, R′ = H, R″ = alkyl
4, R = phenyl, R′ = Me, R″ = H
5, R = phenyl, R′ = R″ = H
6, R = phenyl, R′ = R″ = Me

In this communication we wish to report a new acid catalyzed fragmentation reaction we discovered in the course of an exploratory study regarding the properties of acylphosphonic acids, and the corresponding monoesters.

Methyl sodium benzoylphosphonate was converted by acidification to methyl hydrogen benzoylphosphonate (**4**), which was characterized by means of spectroscopic methods. It exhibits in the IR spectrum bands at 3380 (broad), 1650, 1230, 1180 and at 1050–1030 cm^{-1}, and in the NMR spectrum (60 MHz, $CDCl_3$) δ 9.17 broad, 1 H; δ 7.54–7.28 m, 3 H; δ 8.23–8.10 m, 2 H; δ 3.83 d, (J = 11 Hz) 3 H). Heating this compound resulted in its quantitative conversion to methyl benzoate (92% isolated yield), which was found to be identical in all respects with an

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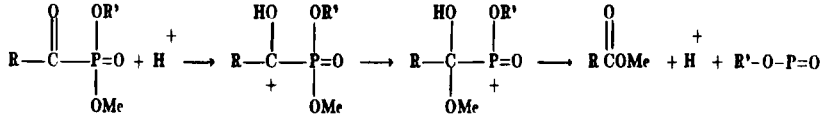
authentic sample. This seems to be a general reaction as indicated by the similar behaviour of other methyl hydrogen acylphosphonates (**3**, R = benzyl or n-hexyl) that also give the corresponding methyl carboxylates upon heating. Acylphosphonic acids behave analogously. Thus, benzoylphosphonic acid (**5**) (m.p. 210–213°C, IR, 3480 broad, 1650, 1230, 1180 cm) is converted by melting to benzoic acid in 30% yield, but the yield can be increased to 82% by the addition of *p*-toluenesulfonic acid.

In view of the thermal stability of acylphosphonate diesters it seemed reasonable to assume that the fragmentation of acids and the monoesters is acid catalyzed. To test this assumption dimethyl benzoylphosphonate (**6**) was heated in benzene in the presence of 10 mole% of *p*-toluenesulfonic acid monohydrate or boron trifluoride etherate, resulting in nearly quantitative conversion to methyl benzoate.

The stoichiometry of these fragmentation reactions requires the formation of phosphenous acid (HOPO) or its ester. The formation of PO_2^- in the thermal fragmentation of **4** and **5** could be shown by low resolution, negative ion, chemical ionization mass spectrometry, that showed peaks at $m/z = 63$.[6] Species of this type are rather scarce among the dicoordinated phosphorus derivatives that started appearing in the literature in recent years. Methyl phosphenite was previously assumed to be involved in the oxidation of alkyl phosphinates,[7] while thiophosphenous acid derivatives were recently trapped by cycloaddition with 2,3-dimethylbutadiene.[8]

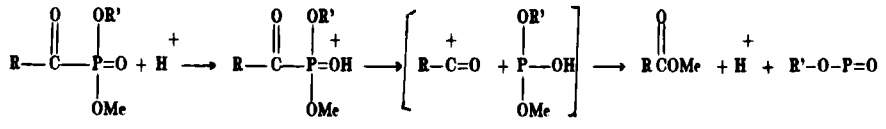
The mechanism of this fragmentation can be envisaged by assuming protonation of the carbonyl oxygen, creating electron deficiency upon the carbonyl carbon, which induces the transfer of a methoxy group from the phosphorus. The resulting intermediate then breaks down to products in the subsequent step (Scheme 1). In contrast to this, gas phase quantum mechanical calculations by



Scheme 1

MNDO[9,10] indicate that the preferred site of protonation in acylphosphonates is the P=O oxygen, and that the C—P bond breaks with zero activation energy in the P=O protonated intermediate, leading to acyl cation and phosphite, which then presumbably can give the products, by the transfer of a methoxy group (Scheme 2).

We presume that the fragmentation described in this communication, is not necessarily limited to acylphosphonates, and that analogous compounds, such as acylphosphinates and other acylphosphorus derivatives might behave similarly,



Scheme 2

with the generation of various types of dicoordinated phosphorus species. Experiments are underway to trap such dicoordinated phosphorus species by chemical means, and to characterize them by physical methods.

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