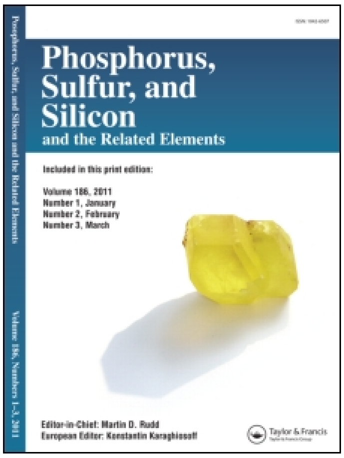

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SHORT COMMUNICATION
A NOVEL BASE-CATALYZED FRAGMENTATION OF ALIPHATIC ACYLPHOSPHONATES

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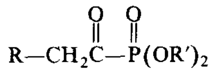
Attempts to prepare alkali metal enolates from aliphatic acylphosphonates result in fragmentation and subsequent formation of dialkyl 1-(dialkylphosphoryloxy)alkylphosphonates **2**.

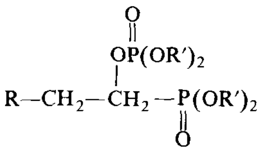
Acylphosphonates have been the subject of some attention lately.[1-9] However, interest in these compounds was focused only upon nucleophilic reactions on the carbonyl group, resulting in C—P bond cleavage in some cases. Water,[1] alcohols,[2] thiols[3] or amines[4] reacting with acylphosphonates lead to such cleavage, while hydroxylamine[5] and hydrazine derivatives[6] yield azomethine type products. The reaction with sulfur ylides seems unique among the nucleophiles: Diethyl acetylphosphonate **1a** treated with some sulfur ylides forms diethyl 1-(diethylphosphoryloxy)ethylphosphonate **2a** together with varying proportions of enolphosphates.[8] The formation of **2a** was rationalized by a mechanism involving the respective sulfur ylide.[8]

a, R = H, R′ = Et
b, R = H, R′ = Me
c, R = Me, R′ = Et
d, R = Me, R′ = Me



$$R\text{—}CH_2\overset{\overset{\displaystyle O}{\|}}{C}\text{—}\overset{\overset{\displaystyle O}{\|}}{P}(OR')_2$$

1



$$R\text{—}CH_2\text{—}\overset{\overset{\overset{\displaystyle O}{\|}}{OP(OR')_2}}{\overset{|}{CH_2}}\text{—}\underset{\underset{\displaystyle O}{\|}}{P}(OR')_2$$

2

In view of reports concerning the facile reduction of acylphosphonates to aldehydes,[9] we were interested in examining acylphosphonates as potential precursors of aldehydes in synthesis, and therefore initiated a program for the preparation and the study of properties of enolates derived from aliphatic acylphosphonates. However, it soon became apparent that upon treatment of acylphosphonates with base in tetrahydrofuran in inert atmosphere (lithium diisopropylamide at $-70°C$ or sodium hydride at $-20°C$ or $0°C$) followed by acid quenching, workup and distillation, products of type **2** are isolated in yields of approximately 50%.[10] We propose to rationalize the formation of **2** by assuming the formation of carbanion **3**, its fragmentation to ketene[11] and the phosphite anion **4**. It is well known that **4** adds

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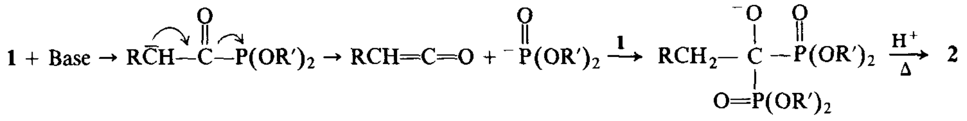
to the carbonyl of acylphosphonates resulting in the eventual formation of products of type **2**.[12]



$$\mathbf{1} + \text{Base} \rightarrow \underset{\mathbf{3}}{\text{RCH}-\overset{O}{\overset{\|}{C}}-\text{P(OR')}_2} \rightarrow \text{RCH}{=}\text{C}{=}\text{O} + \underset{\mathbf{4}}{{}^{-}\overset{O}{\overset{\|}{P}}\text{(OR')}_2} \xrightarrow{\mathbf{1}} \text{RCH}_2-\underset{O=P(OR')_2}{\overset{^{-}O}{C}}-\overset{O}{\overset{\|}{P}}\text{(OR')}_2 \xrightarrow[\Delta]{H^+} \mathbf{2}$$

3 **4**

It seems reasonable to assume that formation of **2** in the reaction of **1** with sulfur ylides[8] may also be rationalized by the same mechanism, and there is no need to invoke sulfur ylides as playing any role in this reaction.

Further work is in progress to define conditions that will allow the use of phosphonates as precursors of aldehyde-enolates.

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10. Compound **2a** showed infrared and nmr spectral properties identical in all respects with those published.[11] Compounds **2b**–**2d** possess physical, analytical and spectral properties fully consistent with their structure.
11. We have not been able to find direct evidence for the formation of this product.
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