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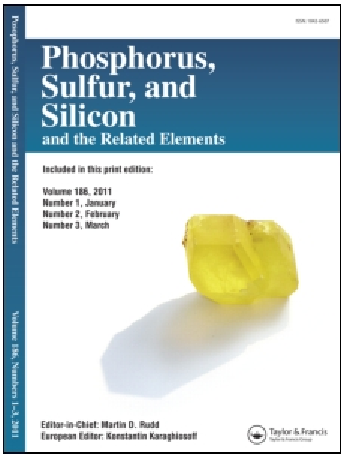

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Rearrangement and Fragmentation Reactions of α-Hydroxyiminophoshinates. On the Nature of the Metaphosphonate Intermediate Involved in Phosphonylations by α-Hydroxyiminophosphinate

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Rearrangement and Fragmentation Reactions of α-Hydroxyiminophosphinates. On the Nature of the Metaphosphonate Intermediate Involved in Phosphonylations by α-Hydroxyiminophosphinate

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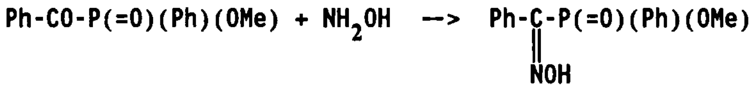
α-Hydroxyiminophosphonates are of interest on the one hand because of their potential to serve as metal chelators,[1] and on the other hand because they have been shown to act as phosphorylating agents.[2] As a consequence we have been studying the chemical and physical properties of various types of α-hydroxyiminophosphorus compounds.

Previously we reported that dimethyl (Z)-α-hydroxyiminobenzylphosphonate undergoes thermal fragmentation *via* a four-centered mechanism to nitriles and phosphates, while the (E)-isomer slowly rearranges to dimethyl N-benzoylphosphoramidate.[3]

On the other hand, (E)-methyl hydrogen α-hydroxyiminobenzylphosphonate was found to undergo fragmentation, in the presence of alcohols, to (mixed) phosphodiesters.[2] As the rate of fragmentation was independent of the structure of the alcohol, it was concluded that this reaction takes place by a dissociative mechanism which leads, in the first step, to monomeric methyl metaphosphate, which is then trapped by the solvent.[2]

In order to widen the scope of these reactions and to study their limitations, we undertook the comparative study of some α-hydroxyiminophosphinates. Dimethyl benzoylphenylphosphinate (2) was prepared by the Arbuzov reaction of dimethyl phenylphosphinite (1) with benzoyl chloride. Reaction of 2 with hydroxylamine gave the corresponding oximes (3) in the E:Z ratio of 9:1. The structure of (E)-3 was determined by X-ray crystallography.

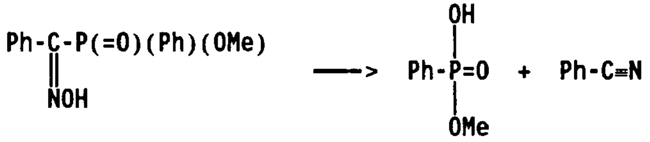
Examination of the two geometrical isomers of 3 revealed that their chemical properties are functions of their steric structures.



$$\mathrm{Ph\text{-}CO\text{-}P(=O)(Ph)(OMe)} + \mathrm{NH_2OH} \longrightarrow \mathrm{Ph\text{-}\underset{\underset{NOH}{\|}}{C}\text{-}P(=O)(Ph)(OMe)}$$

(2) (3)

Oxime (Z)-3 undergoes mainly thermal fragmentation to benzonitrile and to methyl hydrogen phenylphosphonate (4), similarly to the behavior shown previously by its phosphonate analog,[3] presumably by a four centered cyclic mechanism.



$$\mathrm{Ph\text{-}\underset{\underset{NOH}{\|}}{C}\text{-}P(=O)(Ph)(OMe)} \longrightarrow \mathrm{Ph\text{-}\overset{\overset{OH}{|}}{\underset{\underset{OMe}{|}}{P}}{=}O} + \mathrm{Ph\text{-}C{\equiv}N}$$

(Z)-3 (δP=25.6 ppm) (4) (δP=19.6)

In contrast, heating of (E)-3 caused it to undergo a facile Beckmann rearrangement to the N-phosphonylated amide 5. The structure of 5 was determined by X-ray crystallography.

$$\mathrm{Ph\text{-}\underset{\underset{HON}{\|}}{C}\text{-}\overset{\overset{OMe}{|}}{\underset{\underset{Ph}{|}}{P}}{=}O} \longrightarrow \mathrm{Ph\text{-}CONH\text{-}\overset{\overset{OMe}{|}}{\underset{\underset{Ph}{|}}{P}}{=}O}$$

(E)-3 (δP=30.4) (5) (δP=18.0)

Reaction of (E)-3 with sodium iodide in refluxing acetone yielded the dealkylated product, sodium (E)-α-hydroxyiminobenzylphenylphosphinate (6).

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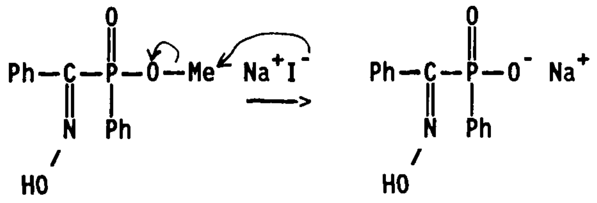
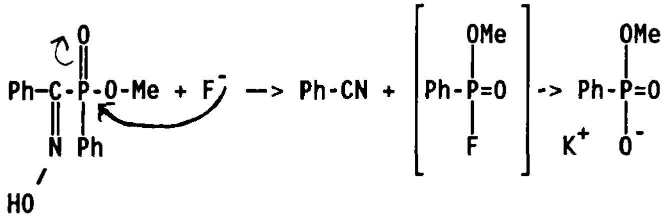


(E)-3 (δP=30.4) (E)-6 (δP=15.5)

In contrast, reaction of (E)-3 with potassium fluoride proceeded by attack upon the phosphorus and led to C-P bond fission.



(E)-3 (δP=30.4) δP=17.1

When (E)-6 was dissolved in alcohols containing hydrogen chloride, the formation of alkyl hydrogen phenylphosphonates was observed along with the formation of benzonitrile. In another experiment the fragmentation of (E)-(7) was examined in a mixture composed of methanol and 2-propanol in a 1:1 molar ratio. In this experiment the formation of two products, namely methyl hydrogen phenylphosphonate (9, R = Me) and 2-propyl hydrogen phenylphosphonate (9, R = i-Pr) was observed in the ratio of 3:2. This result is interpreted in terms of a dissociative type mechanism in which (E)-α-hydroxyiminobenzylphenylphosphinic acid [(E)-(7)] decomposes in the first step to benzonitrile and phenylphosphonic anhydride (phenylmetaphosphonate, 8) which is subsequently trapped

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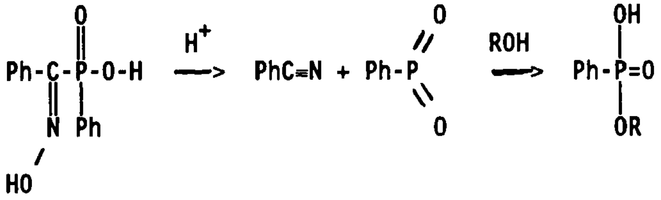
by the solvent. This assumption is further supported by the formation of t-butyl hydrogen phenylphosphonate (9, R = t-Bu), when (E)-(7) was allowed to fragment in t-butyl alcohol.[2]



(7) (δP=22.5)

(8)

(9)

R	δP-31
Me	19.6
2-Pr	15.7
t-Bu	11.6

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