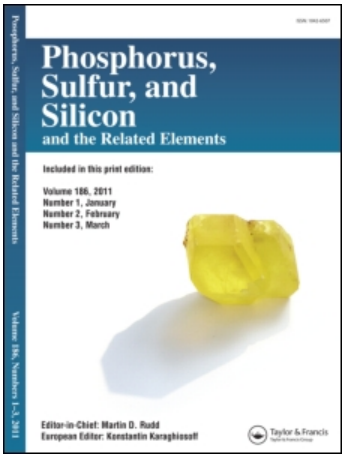

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STRUCTURE AND REACTIVITY OF 2-HYDROXYIMINOBENZYL-2-OXO-4,4,5,5-TETRAMETHYL[1,3,2]DIOXAPHOSPHOLANES

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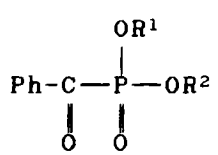
Abstract The reaction of 2-benzoyl-2-oxo-4,4,5,5--tetramethyl [1,3,2] dioxaphospholane (3) with hydroxylamine yields the corresponding E oxime (E-4) and benzonitrile (5), which arises from fragmentation of the Z oxime via an intramolecular attack of the N-OH on the phosphorus.

In the course of our research on acylphosphonates and their oximes, we found that acylphosphonic acids 1 ($R^1 = R^2 = H$) and their monoesters (1, R^1 = Me, R^2 = H) undergo thermal fragmentation to carboxylic derivatives, with the putative involvement of low coordination phosphorus species.[1] This fragmentation reaction has been extended to dimethyl esters of acylphosphonic acids (1, $R^1 = R^2$ = Me), when it was shown that the otherwise stable diesters undergo fragmentation to methyl carboxylates in the presence of acids.[2]



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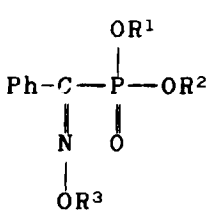

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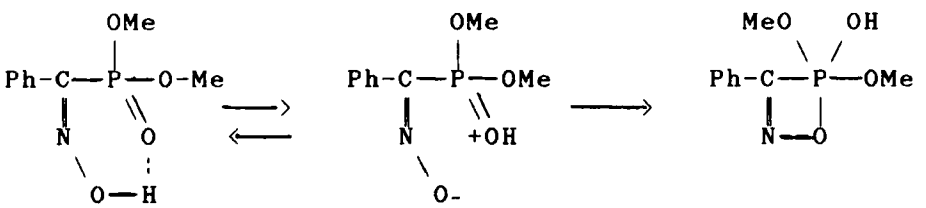
In addition to this, we have studied the structures and chemical properties of oximes derived from acylphosphonic acids and mono and diesters. We found that treatment of dimethyl benzoylphosphonate with hydroxylamine gives dimethyl α-hydroxyiminobenzylphosphonate (2, R^1 = R^2 = Me, R^3 = H) as a mixture of geometrical isomers in the E/Z ratio of 5/4, as evidenced by P-31 nmr and X-ray crystallography.[3] This mixture of isomers undergoes thermal fragmentation with preferential reaction of the Z isomer leading to dimethyl hydrogen phosphate ($\delta^{31}P$ = 0.42 ppm, septet) as main product and tetramethyl pyrophosphate ($\delta^{31}P$ = -13.5 ppm), as a minor product, in addition to the formation of benzonitrile (5).[3]

The methyl ether of the (Z) oxime (2, R^1 = R^2 = R^3 = Me) undergoes fragmentation slowly in refluxing trimethylbenzene to benzonitrile (92%) and trimethyl phosphate (85%) as the only phosphorus containing product. In contrast, the (E) oxime ether was absolutely stable under these conditions.[3] These results were rationalized by assuming a preequilibrium of (Z-2, R^1 = R^2 = Me, R^3 = H) with a zwitterionic intermediate via an intramolecularly hydrogen bonded species followed by a nucleophilic attack by the oxime oxygen on the phosphorus, leading to a 4-membered cyclic intermediate, which then decomposes to products (Scheme 1). Such



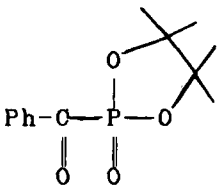
Scheme 1

preequilibrium is not possible in the case of oxime ether (R^3 = Me).

In contrast to dimethyl α-oxyiminophosphonates mentioned above, that are stable at ambient temperature, the oximes derived from α-hydroxyiminobenzylphosphonic acid (2, $R^1 = R^2 = R^3 = H$) and its monomethyl ester (2, R^1 = Me, $R^2 = R^3 = H$) undergo spontaneous fragmentation at room temperature to benzonitrile and monomeric metaphosphate and have been shown to serve as phosphorylating agents.[4]

Following these discoveries, in order to widen the scope of our studies, we synthesized a number of related acylphosphonic derivatives to gain more information regarding the relationship between structure and reactivity in this type of compounds. In this paper we wish to describe results obtained from the study of a five membered cyclic acylphosphonate.

Arbuzov reaction of 2-methoxy-4,4,5,5-tetramethyl [1,3,2] dioxaphospholane with benzoyl chloride gave 2-benzoyl-2-oxo-4,4,5,5-tetramethyl [1,3,2] dioxaphospholane (3) in 70% yield which exhibited the expected spectral properties. In ^{31}P nmr it gave a signal at 17.0 ppm. The treatment of 3 with hydroxylamine gave a single oxime 4 (≈ 13%, $\delta^{31}P$ = 23.0 ppm) in addition to benzonitrile (5, ≈44%), 4,4,5,5-tetramethyl [1,3,2] dioxaphospholane-2-oxide (6, ≈35%, $\delta^{31}P$ = 18 ppm J = 722 Hz), 2-hydroxy-4,4,5,5-tetramethyl [1,3,2] dioxaphospholane-2-oxide (7, ≈38%, $\delta^{31}P$ = 14.9 ppm), and a number of acyclic phosphorus containing products (total of 14%, $\delta^{31}P \approx 0$ ppm). The structure of the oxime 4 was determined as E by X-ray crystallography. (See Figure 1).



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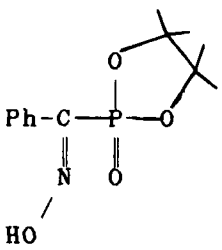
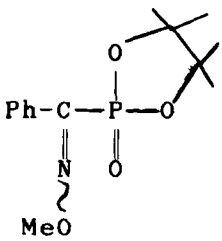


E-4



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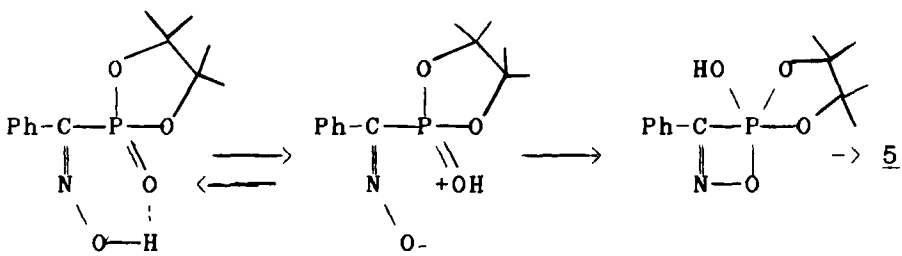
The absence of Z-isomer in the oxime product 4 and the relatively high yield of benzonitrile are rationalized by assuming that the Z-4 oxime is the predominant kinetic product in the reaction of 3 with hydroxylamine. However, while in the acyclic oximes 2, the Z isomer is stable at r.t. or at most it may undergo isomerization to E-2, the cyclic Z-4 undergoes extremely facile fragmentation via the route shown on scheme 2. The driving force for this fragmentation is the strain of the five membered ring[5] that makes the phosphorus



8

Scheme 2

highly electrophilic and susceptible to nucleophilic attack by the oxime oxygen through which the phosphorus is converted into the strain-free pentacoordinated intermediate 8, which is then decomposed rapidly with the formation of benzonitrile. To test this mechanistic scheme, we reacted 3 with methoxylamine. This

reaction gave both isomers of the two oxime O-methyl ethers (E-9, 13% and Z-9, 8%) in addition to 26% of 6, and 53% of ring-opened products, but no benzonitrile. The formation of both oxime ether isomers, E and Z-9, provides support to our assumption regarding the initial formation of Z-4, and that it indeed it is the source of benzonitrile in the reaction of 3 with hydroxylamine.

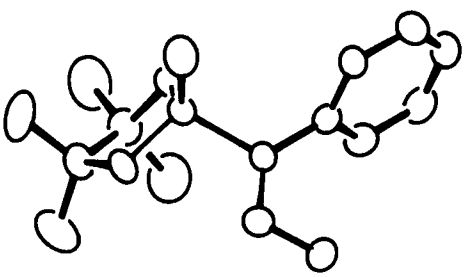


Fig. 1 X-ray structure of 4

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