

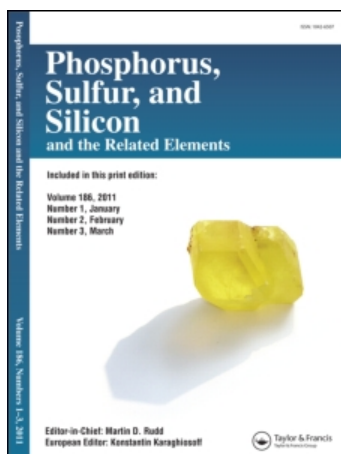
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Phosphorus-Hydrazine-Sulfur-Heterocycles

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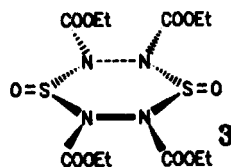
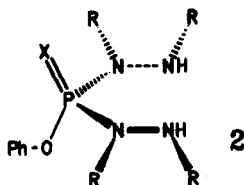
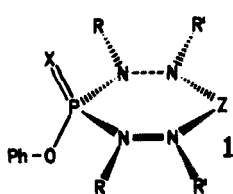
PHOSPHORUS-HYDRAZINE-SULFUR-HETEROCYCLES

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Abstract 2,6-Bis(ethoxycarbonyl)-3,5-dimethyl-4-phenoxy-4-thioxo-1-thia-2,3,5,6-tetraaza-4 λ^5 -phospha-cyclohexane and 2,6-Bis(ethoxycarbonyl)-3,5-dimethyl-1-oxo-4-phenoxy-4-thioxo-1 λ^4 -thia-2,3,5,6-tetraaza-4 λ^5 -phospha-cyclohexane are the first examples of six-membered phosphorus-hydrazine-sulfur-heterocycles. The λ^4 -thia-compound adopts a twist-conformation in solution.

Introduction. Phosphorus-hydrazine-heterocycles of type **1** can be prepared via the reaction of dihydrazido derivatives of phosphoric acid **2** with the corresponding dichlorides under HCl elimination [1-8].



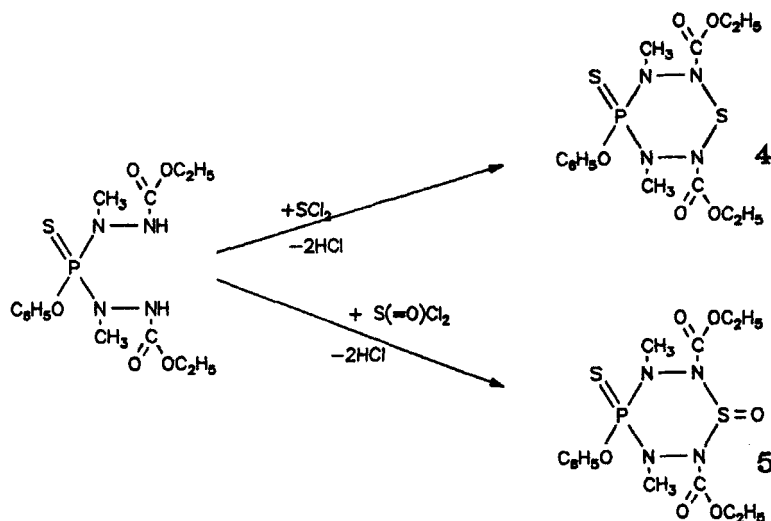
R, R' = Me, H X = O, S

1a: Z = SiMe_2 , SiPh_2 , $\text{P}(=\text{X})-\text{O}-\text{Ph}$

1b: Z = $\text{C}=\text{O}$; R = Me; R' = COOEt

N-unsubstituted dihydrazido derivatives of phosphoric acid react with thionylchloride, sulfurylchloride or sulfurdichloride under redox-decomposition. The synthesis of **3** showed that alkoxy-carbonyl-substituted hydrazido-compounds are sufficiently stabilized against oxidation [9].

Results and discussion. By introducing ethoxycarbonyl-groups into 2, we obtained an appropriate starting-material for the synthesis of 4 and 5.



Single crystal x-ray-analysis of 1b showed that the saturated ring-system has a twist-conformation [6]. ^1H -NMR- and ^{13}C -NMR-spectra of 5 reveal two doublets for two different N-methyl-groups and two signals for two different ethoxycarbonyl-groups at room temperature. This can be best interpreted assuming a twist-conformation of the ring. Temperature-dependent ^1H -NMR-spectra show, that the twist-to-twist interconversion $\underline{5a} \rightleftharpoons \underline{5b}$ is strongly hindered. Coalescence is observed at about 267 K. At higher temperatures only one doublet is observed for the protons of both N-methyl-groups. The energy of activation for the interconversion process can be estimated to be about 80 kJ/mol, a surprisingly high value.

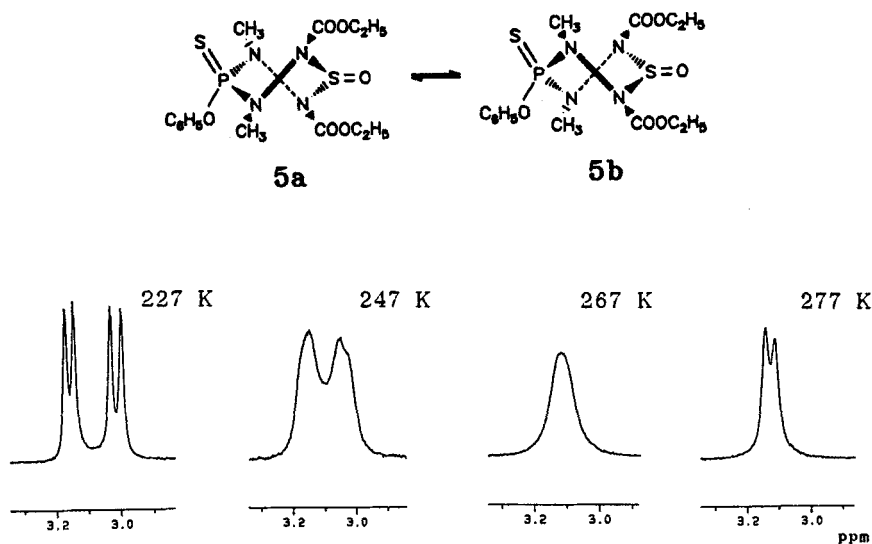


Fig. 1.: ¹H-NMR-spectra (270 MHz) of **5** at different temperatures. Only signals of N-methylprotons are shown.

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