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Phosphorus, Sulfur, and Silicon and the Related Elements

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Monocyclic and Fused 4-Imino(4-Oxo)-1,3,2-Diazaphospholanes and -Phosphorinanes. Synthesis and Some Properties

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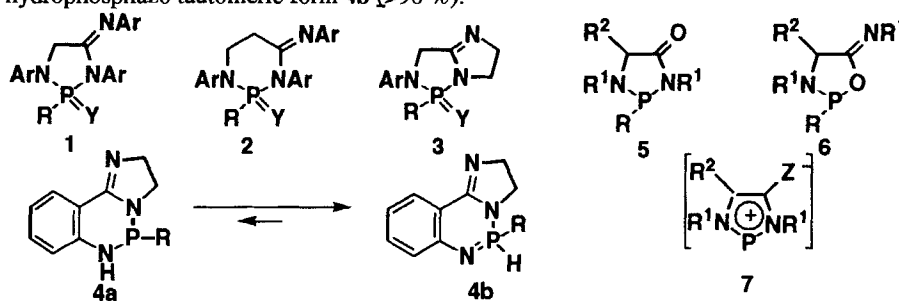
MONOCYCLIC AND FUSED 4-IMINO(4-OXO)-1,3,2-DIAZAPHOSPHOLANES AND - PHOSPHORINANES. SYNTHESIS AND SOME PROPERTIES

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In contrast to the great variety of well known phosphorus heterocycles with exocyclic C=O double bond the number of ones containing exocyclic C=N bond is unusually modest. We elaborated the convenient method of preparation of various N,P,N-heterocycles with exocyclic C=N bond (1-4) from the readily available corresponding amino acid amidines and appropriated dichlorides or diamides of phosphorus (III) acids. Rings' 1-3 with P(III) are easily converted into (thio)phosphoryl derivatives, while the direct phosphorylation of amino amidines by $RP(Y)Cl_2$ is unusually ineffective. Tricycles 4 - derivatives of 2-(2-amino phenyl)imidazoline - mainly exist in the more conjugated hydrophosphazo tautomeric form 4b (>90 %).



N,P,O-Heterocycles 6 with C=N bond together with concomitant N,P,N-isomers 5 are formed in the reactions of amino acid amides $R^1NHCHR^2C(O)NHR^1$ with $RPCl_2$. The course of preferential phosphorylation is strongly dependent on the nature of R, R^1 substituents in reagents. Decrease of $RPCl_2$ electrophility and increase of sterical hindrance on amide nitrogen are favoured to formation of 6. In the case of $R^1 = Ar$ or if $R^1 = Me$, $R = Cl$ only oxo-isomers 5 were obtained. EI mass-spectra of 2-chloro derivatives 1 ($Y = Cl$, i.e.p.) and 5 ($R^1 = R^2 = Me$) are indicative of these ones potential ability to be a potential precursors of the true phosphorus mezoionics such as 7 ($Z = NAr, O$). Mezoionic intermediate 7 ($Z = O$) was proposed to participate in a role of powerful oxidant in the reactions of chloride 5 with amines or HMDSNa.