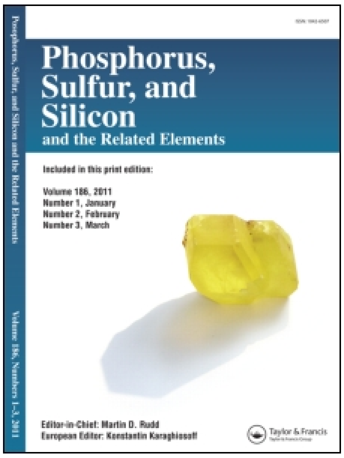

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Monocyclic and Fused 4-Imino(4-Oxo)-1,3,2-Diazaphospholanes and - Phosphorinanes. Synthesis and Some Properties

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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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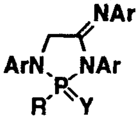
In contrast to the great variety of well known phosphorus heterocycles with exocyclic C=O double bond the number of ones containing exocyclic C=N bond is unusually modest. We elaborated the convenient method of preparation of various N,P,N-heterocycles with exocyclic C=N bond (**1**-**4**) from the readily 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 %).



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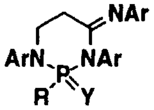

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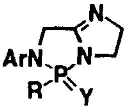

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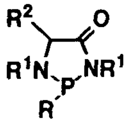

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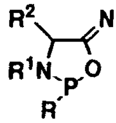

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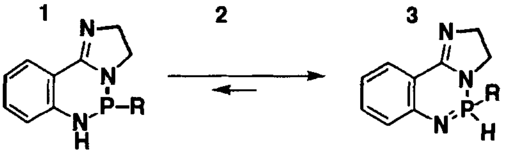
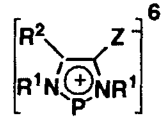


4a **4b**



7

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= l.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.