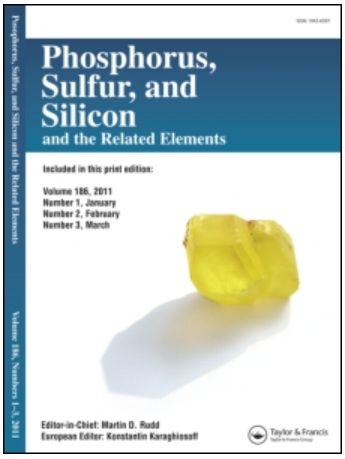

Phosphorus, Sulfur, and Silicon and the Related Elements

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Structural, Spectroscopic and Reactivity Studies on Phosphoric Amides

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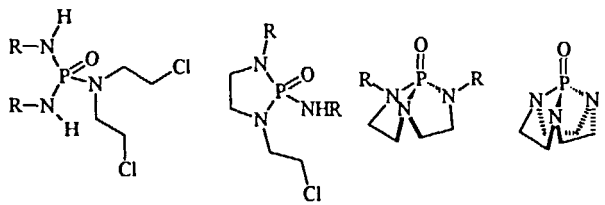
A series of non-cyclic, cyclic and bicyclic phosphotriamidates has been sythesized and their structure, NMR spectroscopic characteristics and their chemical reactivity are discussed.

Keywords: phosphoric amides; bond angles-NMR chemical shift relationship; nucleophilic cleavage; ring rearrangement; new heterocyclic systems

INTRODUCTION

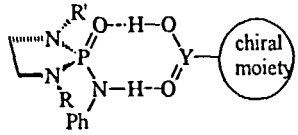
The following types of phosphoric triamides have been prepared and studied[1]:



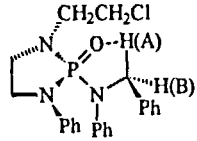
1 **2** **3** **4**

For some compounds, crystal structure was determined by X-ray diffraction and the molecular parameters (bond distances, bond angles and torsion angles) were correlated with the NMR (^{31}P, ^{15}N) spectroscopic properties. For some of the racemic products **2** X-ray diffraction revealed that the torsion angle O=P-N-H of the exocyclic amidate function is close to 0°, thus the function, acting as a hydrogen bonding acceptor (P=O) and donor (N-H), should be able to form a 1:1 complex with any hydrogen bonding acceptor/donor system of the general structure R-Y(O)OH. This conclusion was confirmed by recording ^{31}P NMR spectra of racemic **2** (R = Ph,

4-$MeOC_6H_4$) in the presence of optically active acids (mandelic, camphor-10-sulfonic). Signal separation (strongly solvent-dependent) was observed and interpreted as an evidence of the "chiral recognition" due to the formation of two diastereomeric hydrogen bonded complexes[2] :



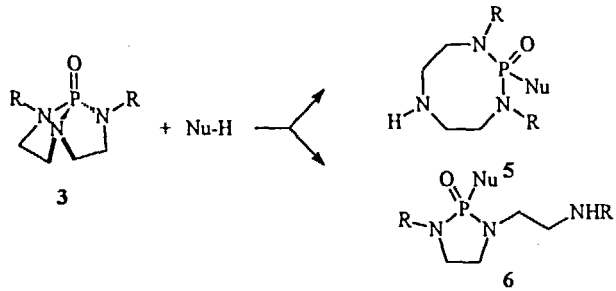
The hydrogen - bonding acceptor ability of the phosphoryl group was also demonstrated on the example of the N-benzyl triamidate **2a** for which a very large nonequivalence of the benzylic methylene hydrogens was observed in the ^1H NMR spectrum , corresponding to the *intramolecular* P=O...H-C hydrogen bond involving one of the methylene protons (H_A), as determined by the X-ray diffraction study of the substrate[3] :



2a

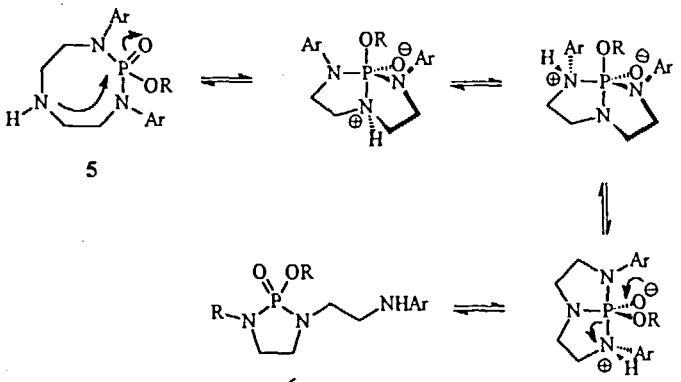
^{31}P NMR spectroscopy revealed that for the series **1** - **4**, each cyclization is accompanied by a powerful *deshielding* of the ^{31}P nucleus, leading to an unusually low field (98.0 ppm) value of δ_P for **4**. At the same time, X-ray diffraction studies showed systematic changes in the molecular parameters within the series, leading to a correlation between the δ_P values and the P-N bond distances or N-P-N bond angles. The correlation was discussed in terms of the hybridization changes at phosphorus due to the increasing degree of incorporation of P atom in the five-membered ring structures[4].

The next topic discussed is the reactivity of the new heterocyclic system - the 1-oxo-2,8-disubstituted-2,5,8-triaza-1λ^5-phosphabicyclo[3.3.0]octane **3**. Nucleophilic cleavage of the amidate bond in **3** can follow two regioselectively different routes :



3 **6**

We have found that the regioselectivity of the alcoholysis of **3** (Nu-H = MeOH, EtOH, etc.) depends on the nature of substituents R and on the reaction conditions. For N-aryl substituted substrates (R = Ph, 4-MeOC$_6$H$_4$) the selectivity can be easily controlled by the pH of the medium: the reaction carried out in alcohol containing one mol-equivalent of HCl the eight-membered heterocyclic product **5** was exclusively formed, while in the alcohol/sodium alkanoate system only the five-membered 1,3,2-diazaphosphorinane product **6** was obtained. To our surprise however, the 1-oxo-1-alkoxy-2,8-diaryl-2,5,8-triaza-1λ^5-phosphacyclooctane **5** proved to be a rather unstable compound (it perfectly stable as a HCl salt or as a N-acyl derivative) which undergoes spontaneous (for **5**, R = Ph, Nu = EtO, in refluxing THF, $t_{½}$ = 4.7 h) rearrangement to the isomeric product **6**. To our knowledge this is a new type of a rearrangement of an eight- to a five-membered cyclic compound, and we propose the following mechanism for the rearrangement[5]:



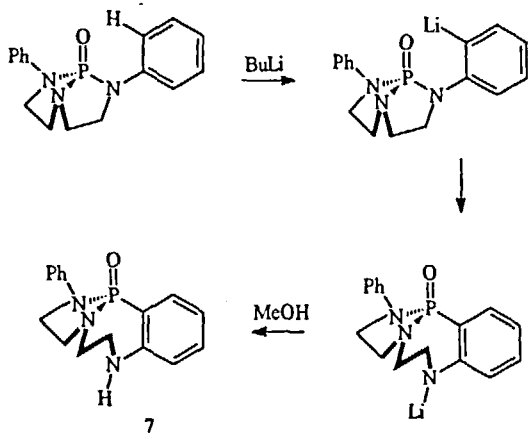
5

6

For substrates **3** with N-aliphatic substituents (**3**, R = Et, PhCH$_2$) solvolysis under acidic, as well as basic conditions yields only the triazaphosphaoctane product **5**. The eight-membered cyclic compounds are in this case also more stable and rearrange to the corresponding isomers **6** much more reluctantly than the N-aromatic derivatives. It seems therefore that several factors, such as the difference in the strain of the individual P-N bonds in **3**, the relative basicity of the N atoms, and the relative nucleofugality of the NHR groups in the ring-opening step, play a role in the nucleophilic cleavage of structure **3** and the reactivity of the products. The detailed mechanism of the reaction, also including nucleophilic reagents other than alcohols, is being currently studied.

The bicyclic substrates **3** demonstrated also another type of interesting reactivity, leading to the formation of new heterocyclic systems. When the N,N'-diphenyl derivative (**3**, R = Ph) was treated with BuLi in THF, followed by methanol, it was smoothly converted to a new, crystalline product which showed the ^{1}H NMR spectrum very similar to that of the substrate. X-ray diffraction analysis demonstrated that the product belongs to another bicyclic, heterocyclic system **7**, formed by the fusion of the five- and the seven-membered rings. The formation of product **7** is a

consequence of the *ortho*-metallation of one of the phenyl rings in **3**, followed by the 1,3-shift of phosphorus from nitrogen to the aromatic carbon. Such transformation was previously demonstrated in our Laboratory for simple N-aryl phosphoramidates[5] and is shown below for substrate **3** :



7

Our current investigation of he new heterocyclic system **7** aims in two directions. First, the acid-catalyzed solvolysis of **7** should lead, in analogy to the reaction of **3**, to a new, ten-membered heterocyclic system. Second, if **7** can undergo subsequent metallation/1,3-migration reaction, a new, bicyclic product should be obtained, consisting of two fused seven-membered heterocyclic rings. That product, in turn, when subjected to the nucleophilic cleavage of the remaining P-N bond, should yield yet another heterocyclic system, a twelve-membered cyclic structure incorporating one phosphorus and three nitrogen atoms in the ring. All those systems, because of the presence of the donor groups (nitrogens, the phosphoryl group, aromatic rings) and stereochemical restrictions introduced by the aromatic skeletons, may show interesting ligand properties.

Acknowledgments

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References

[1] H. Wan and T. A. Modro, *Synthesis*, 1227 (1996).

[2] H. Wan, A. M. Modro, T. A. Modro, S. A. Bourne, and L. R. Nassimbeni, *J. Phys. Org. Chem.*, **9**, 739 (1996).

[3] S. A. Bourne, X. Y. Mbianda, H. Wan, and T. A. Modro, *J. Mol. Str.*, in press.

[4] S. A. Bourne, X. Y. Mbianda, T. A. Modro, L. R. Nassimbeni, and H. Wan, *J. Chem. Soc. Perkin Trans.* **2**, 83 (1998).

[5] X. Y. Mbianda, T. A. Modro, and P. H. Van Rooyen, *Chem. Commun.*, 741 (1998).