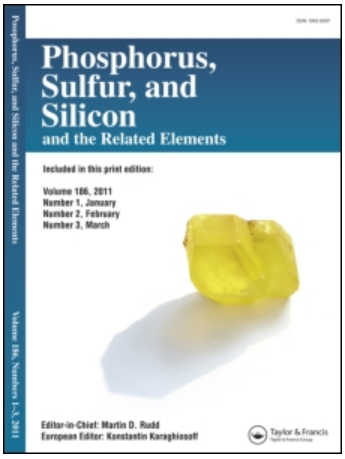

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DONOR-STABILIZED MONOMETAPHOSPHATES AS STARTING COMPOUNDS FOR PHOSPHORUS HETEROCYCLES

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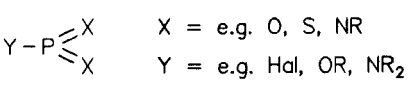
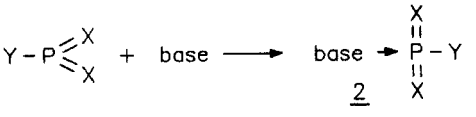
Abstract The reaction of donor-stabilized metaphosphoric acid derivatives like py*PX_2Y or Py_2*P_2S_5 with proton-active nucleophiles leads presumably to the intermediary formation of the corresponding monometaphosphate species which react via cyclo- or polyaddition to cyclic, and linear oligomeric or polymeric phosphorus compounds.

Derivatives of the monometaphosphoric acid belong to the group of $\sigma^3\lambda^5$ -phosphorus compounds:



1

These compounds are of different stability. Most of them are instable, and they are discussed as intermediates in elimination reactions of four-coordinated phosphorus compounds. Only when the substituents X and/or Y at the phosphorus atom are bulky groups the molecule is stable.[1] An other way of stabilization of **1** is given by the interaction with bases which act as donor molecules:

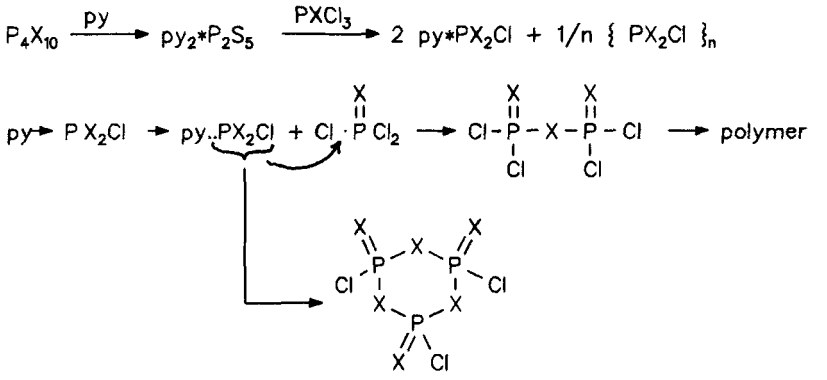


2

base = tert. aliphatic amines, N–heterocycles
tert. phosphines

Starting from compounds of the type **2** by thermic or chemical activation the reactive monomeric derivatives **1** can be generated.
So the $\sigma^3\lambda^5$-phosphoranes O_2PCl, S_2PCl and S_2PF has been generated by short-pathway thermolysis of the corresponding pyridine adducts **2a-c** (**a**: X=O, Y=Cl; **b**: X=S, Y= Cl; **c**: X=S, Y=F) and were characterized by photoelectron spectroscopy.[2,3]

More than 20 years ago on studying the reorganization between phosphorus chalkogenides, P_4X_{10}, and chalcogenophosphoryl trichlorides, $PXCl_3$ (X=O,S), we have found that this reaction occurs under relatively mild condition in the presence of catalytic amounts of pyridine.[4] Searching for the reason we could isolate the donor-stabilized monometaphosphoryl and thiophosphoryl chlorides Py^*PX_2Cl, respectively.[4,5] Also under these conditions these compounds act presumably as precursors for the chlorophosphoranes X_2PCl which react with the phosphoryl or thiophosphoryl chlorides under insertion into a P-Cl bond to oligomeric and polymeric phosphorus chlorides or by cyclization to the corresponding cyclic phosphorus chlorides mainly the trimeric compounds:



Thus, the reaction of P_4S_{10} with $POCl_3$ in the presence of pyridine in a molar ratio P_4S_{10} : $POCl_3$: pyridine = 1 : 7 : 0,16 corresponding the formal equation

$$P_4S_{10} + 7\,POCl_3 \longrightarrow 5\,P_2OS_2Cl_4 + \{\,PO_2Cl\,\}$$

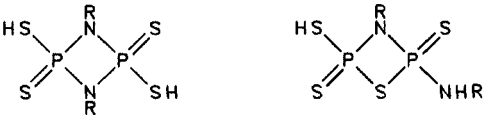
leads to a liquid reaction mixture and a glassy product which correspond 91% and 9% of the weighing loss, respectively. Fractional distillation resulted in the following distribution of compounds (Table I)

TABLE I

Compounds	%P referred to total P
$PSCl_3$	35,8
$P_2OS_2Cl_4$, $P_2O_2SCl_4$ (+oligomers)	24.5
$P_3O_3S_3Cl_3$ (+ polymeric chlorides)	27.1

Py^*PS_2Cl (**2b**) reacts with primary amines under intermediary formation of imido dithioxophoshoranes

which can be stabilized by [2+2] cycloaddition yielding diaza or azathiaphosphetidines.[6,7]



Whether the P_2N_2- or the P_2NS-ring system is formed mainly depend on the rest R which influenced both, the basicity of the amine and also the steric conditions at the ring system. Thus, it was found that the tendency of formation of azathiaphosphetidines increases with the basicity of the used amine as well as with the size of the rest R.

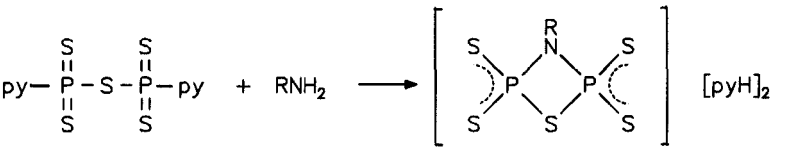
Another remarkable example of the influence of steric factors on the ring size of the formed heterocyclic compounds was found on the reaction of **2b** with monosubstituted hydrazines. Depending on the bulkiness of R the formation of four-, five-, or six-membered P-N heterocycles has been observed.[8]

More complicated is the course of reaction starting from the oxygen derivative **2a**.

Both, the reaction with primary amines and the reaction with alcohols lead to a mixture of oligomeric and polymeric phosphoric acid derivatives. Even alcohols with a bulky group like adamantanol do not react to the corresponding donor-stabilized alkoxy phosphorane, py^*PO_2OR, as it was observed already on the reaction of **2b** with e.g. ethanol.

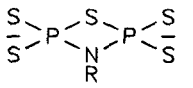
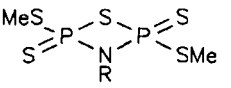
Based on the NMR spectrum we assume that the reaction of 1-adamantanol with **2a** leads to a mixture of linear trimeric and bicyclic compounds.

Starting from the dimeric metaphosphoric acid derivative **3** and primary amines or substituted hydrazines it is also possible to prepare phosphorus-nitrogen heterocycles. So, **3** reacts with sterical hindered primary amines under formation of an symmetrical azathiadiphosphetidine:

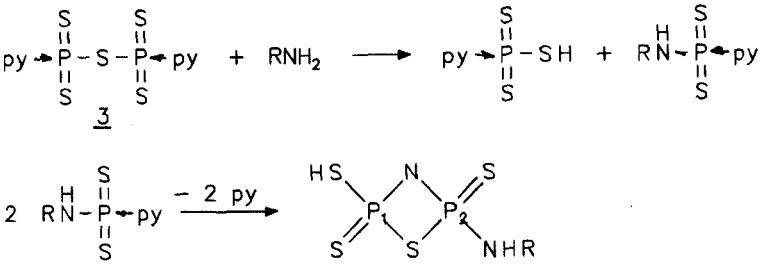


3 **4**

TABLE II ^{31}P NMR of P_2NS rings [ppm]

R		
4a: t-bu		61,98/61,11 (cis/trans)
4b: mesityl	84,66	74,64
4c: 2,6-diisopropyl-phenyl	77,41	
4d: HN-t-bu	82,89	60,06

In the case of the reaction of 2,6-diisopropylphenyl amine with **3** beside the symmetrical compound **4c** also the unsymmetrical azathiaphosphetidine is formed. This means that partially according to the following equation the P-S-P bond was cleaved:



R = 2,6-diisopropylphenyl $^{31}P_1$ 78,15 ppm J_{P-P} 19,25 Hz
$^{31}P_2$ 51,67 ppm

Then a monometaphosphate derivative is formed which reacts under [2+2] cycloaddition forming the unsymmetrical azathiaphosphetidine.

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