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Synthesis of Phosphorus Heterocycles using the Donor-Stabilized Dithiomonometaphosphoryl Chloride as Preparative Tool

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The reactivity of the donor-stabilized monometaphosphoryl chloride $\text{Py} \Rightarrow \text{PS}_2\text{Cl}$ (**1**) versus multiple bond systems and organometallic compounds has been studied. Thus, on the reaction of **1** with diphenyl acetylene at elevated temperature the five-membered ring systems **2-4** are formed. In the first step probably cycloaddition of the intermediary liberated free monometaphosphoryl chloride PS_2Cl with diphenyl acetylene leads to the 1-thia-phosphacyclobut-3-ene **6**. This assumption will be supported by theoretical calculations. Attempts to eliminate one sulfur atom from the disulfide bridge in **2** result in the bicyclic ring system **5** besides a compound which is assumed to be **6**. The reaction of **1** with *tert*BuLi gives the dithiaphosphetane **7** whereas with $\text{NaN}(\text{SiMe}_3)_2$ the diazadiphosphetidine **8** is obtained.

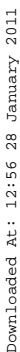
Keywords: Phosphorus heterocycles; dithiomonometaphosphoryl chloride; cycloaddition reactions

INTRODUCTION

As have been shown several years ago the donor-stabilized monometaphosphoryl chloride $\text{Py} \Rightarrow \text{PS}_2\text{Cl}$ (**1**, py = pyridine) can be used as a versatile reagent for preparing a large variety of derivatives of dithiophosphoric acid [1] as well as for the synthesis of phosphorus and

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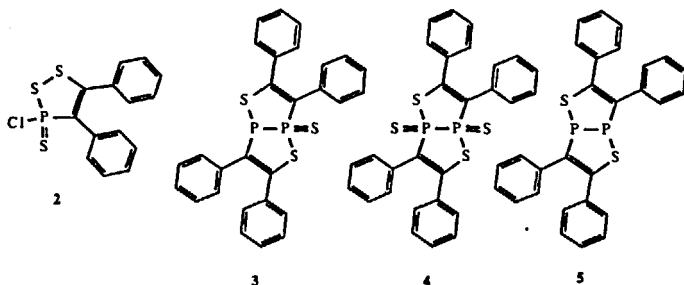


Recently we started to study the reactivity of $\text{Py} \Rightarrow \text{PS}_2\text{Cl}$ versus multiple bond systems and organometallic compounds, respectively.

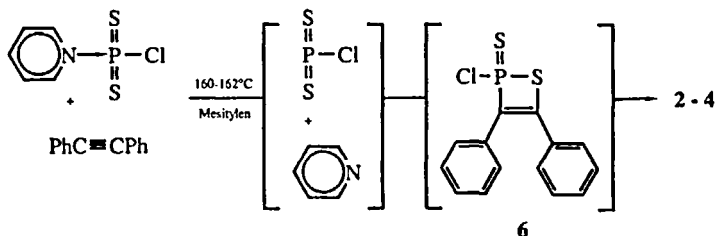
RESULTS AND DISCUSSION

Reaction of $\text{Py} \Rightarrow \text{PS}_2\text{Cl}$ (1) with diphenyl acetylene:

When 1 is reacting with diphenyl acetylene at higher temperatures in solution (boiling mesitylene, 160-162°C) surprisingly the different mono and bicyclic five-membered ring systems 2-4 could be isolated:



We assume that the first reaction step consists in a cycloaddition of the intermediary released dithiomonometaphosphoryl chloride PS_2Cl with diphenyl acetylene under formation of the 1-thia-2-phosphacyclobut-3-ene 6 which then in further steps under ring transformation reacts to the compounds 2-4:

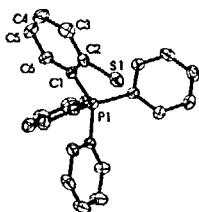


However, on experiments to eliminate one of the sulfur atoms from the disulfide bridge in **2** by reaction with triphenylphosphane instead of the expected intermediate **6** the bicyclic compound **5** has been obtained in 25% yield together with a compound ($d^{31}\text{P}$ 49 ppm) we could not isolate up to now. On careful repeating this experiment besides the signal of Ph_3PS (42 ppm) in the reaction mixture only the signal at 49 ppm is observed which we assign to the intermediate **6**. For related thioxo-phospha(V)-cyclobutenes the ^{31}P chemical shifts are found in the same region [3].

At temperatures above 115°C the five-membered ring **2** reacts under formation of the bicyclic system **4**.

The cyclic compounds **2-5** are completely characterized by elemental analysis, mass spectroscopy, ^{31}P -NMR, and X-ray structure analysis.

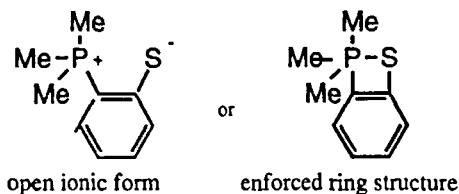
To get more knowledge about the expected stability of the reaction intermediate **6** some theoretical calculations were carried out. In the literature the formation of the similar four-membered P-S-ring 2,2,2-triphenyl-1,2,1⁵-benzothiaphosphetane via the reaction of pentaphenyl phosphorane with sulfur is reported [4]. Our attempts to repeat this experiment resulted in the only formation of the corresponding „open“ molecule **7** we have proved by X-ray structure determination:



7

Ab initio calculations for the open ionic form and the four-membered ring with methyl instead of phenyl rests showed that in this case the open form is the only stable molecule whereas the enforced ring structure is instable by about 84 kcal/mole compared with the acyclic compound (see next page). Contrary to this on ab initio calculations at the same level for molecules derived from the assumed intermediate **6** by substitution of the phenyl groups by hydrogen

and methyl, respectively, and even for **6** energy minima has been obtained. These results support the assumption that **6** should be the primary product of the cycloaddition reaction between the intermediary formed PS_2Cl and diphenyl acetylene.



Method ^a	R (P-S) [pm]	E [au]
open	317,32	-1090.31992
four-ring	217,32	-1090.18651
DE [kcal/mol]		83,72

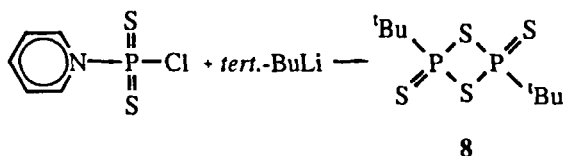
(^a) B3LYP/6-31G(d)//B3LYP/3-21Gä

Calculation of Energie//geometry optimization

Reaction of $\text{Py} \Rightarrow \text{PS}_2\text{Cl}$ (1) with organometallic reagents:

As we have found in detailed studies the reaction of **1** with organometallic compounds (*tert* BuLi; MeLi, PhLi, $\text{NaN}(\text{SiMe}_3)_2$) offers an alternative preparative way to dithiadiphosphetanes and diazadiphosphetidines, respectively.

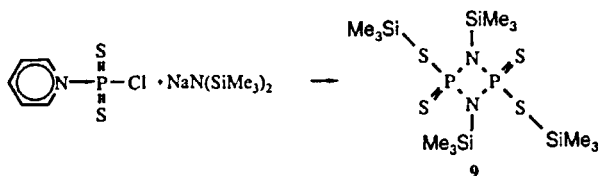
Thus, the reaction of *tert* butyl lithium with **1** in benzene at 50°C leads to the dithiadiphosphetane **8** in nearly quantitatively yield:



8 is characterized by elemental analysis, ^{31}P NMR, mass spectroscopy and X-ray structure. The structure data are quite normal for this type of compound. The P_2S_2 ring is planar.

On the reaction of **1** with $\text{NaN}(\text{SiMe}_3)_2$ probably in the first step the donorstabilized bis(trimethylsilyl) amide of the dithiomonometaphos-

phoric acid is formed which is followed by a trimethylsilyl group migration to one sulfur atom under formation of an imido derivative which is stabilized by [2+2] - cycloaddition yielding the diazadiphosphetidine **9**:



The diazadiphosphetidine is also completely characterized as the compounds described before.

In the following Table 1 the ^{31}P NMR data of all isolated compounds are summarized:

Table 1. ^{31}P NMR data (benzene; external standard 85% H_3PO_4)

Compound	^{31}P -chemical shift [ppm]
2	112.2
3	115.0 (d, $^1J_{\text{PP}} = 265 \text{ Hz}$; $\text{R}_2\text{P}-\text{PR}_2=\text{S}$)
	19.8 (d, $^1J_{\text{PP}} = 265 \text{ Hz}$; $\text{R}_2\text{P}-\text{PR}_1=\text{S}$)
4	64.8
5	84.3
8	54.4
9	66.4

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