

Reactions of P_4S_{10} and $pyPS_2Cl$ with N,N' -diphenylurea and N,N' -diphenylthiourea

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Abstract

The reaction of P_4S_{10} (**1**) with N,N' -diphenylurea $(PhNH)_2CO$ (**2**) results in new heterocyclic compounds: the pyridinium salt of 1,3-diphenyl-2-sulfido-2-thioxo-1,3-diaza- $2\lambda^5$ -phosphetidine (**3**) (with a P–N–C–N cycle) and the pyridinium salt of 1,4-diphenyl-2,5-disulfido-2,5-dithioxo-1,4-dithiadiazia- $2\lambda^5,5\lambda^5$ -diphosphinane (**4**), containing the (P–S–N)₂ cycle and the cyclic thiophosphates $[pyH]_2[P_2S_8]$ (**5**), $[pyH]_2[P_2S_7]$ (**6**) and $[pyH]_3[P_3S_9]$ (**7**). A similar reaction, but carried out with N,N' -diphenylthiourea $(PhNH)_2CS$ (**8**), leads to the formation of **4** and **6**. $pyPS_2Cl$ (**9**), used as an alternative starting material, also yields compounds **3**, **4**, **5**, and further $[pyH][PS_2Cl_2]$ (**10**) and S_8 after reaction with **2**. Compound **3** reacts with $Pd(CH_3COO)_2$, with the formation of the complex $[Pd(Ph_2N_2COPS_2)_2]$ (**11**). The crystal structures of **3** and **7** were determined by single-crystal X-ray diffraction.

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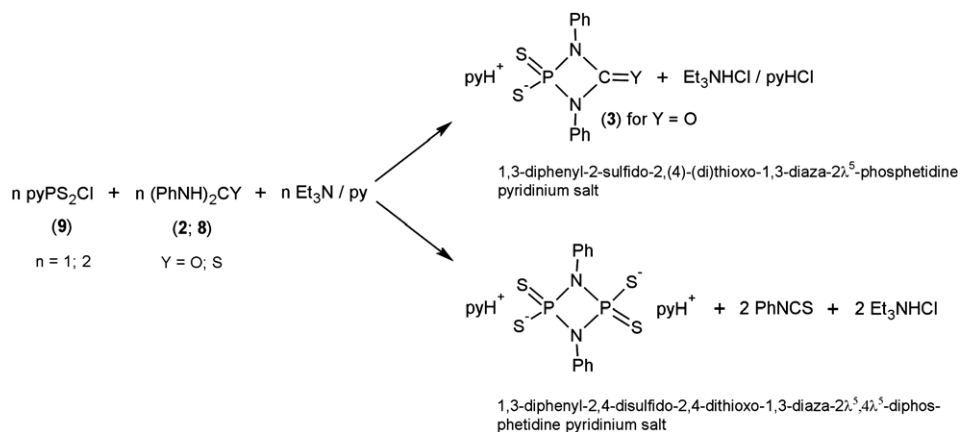
1. Introduction

Phosphorus pentasulfide, P_4S_{10} (**1**) is a very important starting material for the syntheses of many linear phosphorus and sulfur containing compounds, but has been used less extensively for the preparation of cyclic compounds containing the exocyclic PS_2 group [1,2], as compared with $pyPS_2Cl$ (**9**). Commercially available P_4S_{10} usually contains lower phosphorus sulfides, P_4S_9 , P_2S_5 , P_2S_4 , that can also arise upon prolonged storage or thermal decomposition of this compound [3], and the reactive units $[PS_2]$ [3], $[PS_3]$ and elemental sulfur can also be found among the decomposition products. The existence of the anion $py[PS_3]^-$ has been described as a product of the reaction

between **9** and H_2S [4]. The formation of the $[PS_2]$ unit is also assumed in many reactions of **9** with nucleophilic reagents [5–14,31]. Thus these units and elemental sulfur can participate in the formation of various compounds containing the exocyclic PS_2 group.

Many heterocyclic compounds containing the exocyclic PS_2 group were prepared by reactions of **9** with various mono- [15], di- [14] and polyfunctional nucleophiles [5–9,11,13], e.g., thiosemicarbazide [5,6] and urea [7,8] derivatives. Reactions of **9** with monosubstituted thiosemicarbazide compounds of the type $RNHC(S)NHNH_2$ ($R = Me, Et$) [5], carried out in the presence of pyridine, led to the formation of five-membered P–N–C–N–N heterocycles, whereas the reaction with disubstituted $RNHC(S)N(Me)NH_2$ ($R = ^iPr, ^tBu$) yields different reaction products, depending on the reaction conditions [6]. In the presence of triethylamine, the triethylammonium salt of 1,3-diaza- $2\lambda^5,4\lambda^5$ -diphosphetidine with a four-membered

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Scheme 1.

P–N–P–N cycle was formed, whereas the pyridinium salt of 1,3,4-triaza-2λ⁵-phospholane with a five-membered P–N–N–C–S cycle was prepared in the absence of a HCl acceptor.

The reaction of **9** with urea leads to the formation of the cyclic ammonium salt of 4,6-dioxo-2-sulfido-2-thioxo-1,3,5-triaza-2λ⁵-phosphinane [7]. The reaction of **9** with *N,N'*-diphenylthiourea, (PhNH)₂CS (**8**), yields, in the presence of triethylamine and depending on the reaction temperature, two different heterocyclic compounds containing P–N–C–N and P–N–P–N cycles [8] (see Scheme 1).

The reaction of pyPS₂Cl (**9**) with (PhNH)₂CO (**2**), as well as reactions of phosphorus pentasulfide (**1**) with **2** and **8** had not been studied as yet. Therefore they became the subject of our investigation in this work.

2. Results and discussion

2.1. Reaction of P₄S₁₀ (**1**) with *N,N'*-diphenylurea (**2**)

The course of the reactions between **1** and nucleophilic reagents has commonly the character of nucleophilic reduction in which, depending on the reaction conditions, a wide variety of compounds arise [11,12].

The reaction of **1** with **2** was carried out in acetonitrile and in the presence of pyridine in the molar ratio 1:4:4. A number of reaction products arose in the course of the

reaction. The composition of the reaction mixture was followed by ³¹P NMR spectroscopy. The integral rates of all resonance signals presented in the ³¹P NMR spectrum are shown in Table 1. Compound **13**, containing unexpectedly an oxygen atom in the molecule, is probably the product of partial hydrolysis of sulfur containing precursors. Yellow needle crystals were also formed at the same time and they were assigned to the previously undescribed compound **7**.

2.2. Reaction of P₄S₁₀ (**1**) with *N,N'*-diphenylthiourea (**8**)

This reaction was carried out in a similar way to that described above. Yellow crystals were formed after 15 min heating. The resonance signals, which were found in the ³¹P NMR spectrum of the reaction mixture, are mentioned in Table 1. After cooling the reaction mixture, the solvent was partially evaporated in vacuum at ambient temperature, the solid was filtered off and rinsed with acetonitrile. The ³¹P NMR spectrum of this solid, dissolved in acetonitrile, proved that the solution contained only compound **4**.

2.3. Reaction of pyPS₂Cl (**9**) with *N,N'*-diphenylurea (**2**)

The reaction between **9** and **2** (1:1) was carried out in acetonitrile solution in the presence of pyridine as a HCl acceptor. At first, the reaction mixture was refluxed for

Table 1
Identified ³¹P NMR signals in the studied reaction mixtures

Compound	δ (ppm)	Reaction partners			
		P ₄ S ₁₀ + (PhNH) ₂ CO		P ₄ S ₁₀ + (PhNH) ₂ CS	pyPS ₂ Cl + (PhNH) ₂ CO
		Reflux (2 h) (%)	After standing 3 months (20 °C) (%)	Reflux (20 min) (%)	Reflux (1.5 h) (%)
3	88.1	89	83		9
4	109.1	4	1	94	4
5 [16]	120.3	7	1		1
6 [16]	130.4		7	4	
10 [18]	84.0				25
12 [17]	87.4		1	2	
13 [16]	32.1		7		

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