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Polyhedron 24 (2005) 1855–1860
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On the reactions of chlorodithiophosphoric acid pyridiniumbetaine with polyfunctional nucleophiles. Part III: Reactions with monoalkylderivatives of thiosemicarbazide ☆,☆☆

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Received 17 February 2005; accepted 23 June 2005
Available online 8 August 2005

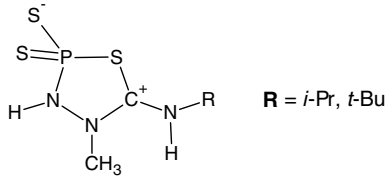
Abstract

Reactions of chlorodithiophosphoric acid pyridiniumbetaine, py · PS_2Cl (**I**) with monosubstituted thiosemicarbazide derivatives $RN(H)C(S)N(H)NH_2$, (R = methyl, ethyl), in acetonitrile media and in the presence of pyridine as an HCl acceptor were studied. New five-membered heterocyclic compounds were prepared, pyridinium salts of 4-methyl-3-sulfido-3,5-dithioxo-1,2,4,3λ^5-triazaphospholidine (**II**) and 4-ethyl-3-sulfido-3,5-dithioxo-1,2,4,3λ^5-triazaphospholidine (**III**). The substances **II** and **III** were completely characterized by ^{31}P NMR, FT-IR, Raman spectroscopies and their molecular structures were determined by the X-ray diffraction analysis.

Keywords: Five-membered heterocycle; Thiosemicarbazide; Chlorodithiophosphoric acid pyridiniumbetaine

1. Introduction

Chlorodithiophosphoric acid pyridiniumbetaine **I** (py · PS_2Cl) is a favourite starting substance for syntheses of many dithiophosphates. The reactions of **I** with primary and secondary amines were intensively studied [1–3] as well as reactions with aliphatic [4] and aromatic [4,5] bifunctional nucleophiles. These reactions led to the formation of various heterocyclic dithiophosphates containing five- or six–membered cycles, while the reaction of **I** with urea and its derivatives [6,7] led to the formation of new heterocyclic compounds of aza- or diazaphosphetidine types. The reactions of **I** with monosubstituted hydrazine derivatives provided heterocyclic compounds with 4–6 membered cycles [8]. It was found that structures of products were strongly influenced by the nature of organic substituents. Aliphatic substituents supported the formation of six-membered cycles while aromatic ones directed the reaction to five-membered cycles. Janča studied the reactions of **I** with disubstituted thiosemicarbazide derivatives of the type $R(H)NC(S)N(Me)NH_2$ (R = ^{i}Pr, ^{t}Bu) [9].



☆ Part I: On the reactions of chlorodithiophosphoric acid pyridiniumbetaine with diphenylthiourea (V. Novoměstská, J. Marek, J. Příhoda, Polyhedron 18 (1999) 2723).

☆☆ On the reactions of chlorodithiophosphoric acid pyridiniumbetaine with polyfunctional nucleofiles: Part II. Reactions with thiosemicarbazide derivatives (M. Janča, M. Nečas, Z. Žák, J. Příhoda, Polyhedron 20 (2001) 2823).

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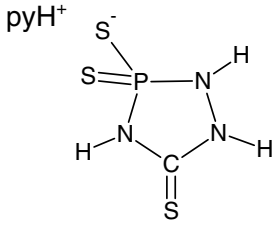
doi:10.1016/j.poly.2005.06.024

The composition of heterocyclic products was dependent on a number of factors. If triethylamine was present (as an acceptor of released HCl), the four-membered heterocyclic compounds of diazadiphosphetidine type with P–N–P–N rings were formed, while the compounds with five-membered P–N–N–C–S heterocycles were obtained in the reactions that were carried out in an absence of the HCl acceptor. It is worth to mention the molecular structure of the reaction product for its unusual structure where a three-coordinate positively charged carbon atom is present in the heterocycle. This positive charge is compensated by a negative charge on the exocyclic sulfur atoms.

A planar heterocyclic compound with the five membered P–N–C–N–N cycle, pyridinium salt of 3-sulfido-3,5-dithioxo-1,2,4,3λ^5-triazaphospholidine, was the product of the reaction between **I** and non-subsituted thiosemicarbazide [10] carried out in acetonitrile in the presence of pyridine.



This article deals with the study of reactions of chlorodithiophosphoric acid pyridiniumbetaine **I** (py · PS_2Cl) with 4-methyl- and 4-ethylthiosemicarbazide that can be considered potential four-functional nucleophiles. The formation of new heterocyclic compounds was expected.

2. Experimental

All reactions were performed under dry nitrogen in anhydrous solvents using conventional Schlenk techniques with the exception of preparations of thiosemicarbazide derivatives. All chemicals were used as supplied (Aldrich, Lachema). Solvents were dried by standard methods and were distilled prior to their use [11]. Chlorodithiophosphoric acid pyridiniumbetaine (**I**) [12] and thiosemicarbazide derivatives [13] were prepared according to the known procedures. The ^{31}P NMR spectra were measured in acetonitrile or pyridine using a Bruker AVANCE DRX 300 instrument and were referenced to H_3PO_4 (85%). The IR spectra were recorded in Nujol mulls on a Bruker IFS 28 spectrometer. The Raman spectra of solid samples were collected in Raman capillaries on a Bruker Equinox X55/S instrument (see Table 1).

Diffraction data were collected on a KUMA KM-4 κ-axis diffractometer equipped with CCD detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Because of the small absorption coefficients the absorption correction was neglected. All the structures were solved by direct methods and refined by full-matrix least-squares methods using anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms on N1 and N2 were refined isotropically; all other hydrogens were placed in calculated idealized positions and refined as riding. The software packages used were: XCALIBUR CCD system [14] for the data collection/reduction, and SHELXTL [15] for the structure solution, refinement, and drawing preparation (thermal ellipsoids are drawn at the 50% probability level). Lattice parameters and other crystallographic data for **II** and **III** are given in Table 2, selected bond lengths and angles in Table 3, and hydrogen bonding parameters in Table 4. The molecular structures are drawn in Figs. 1 and 2.

2.1. Reaction of py · PS_2Cl (*I*) with thiosemicarbazide derivatives

The solution of **I** was prepared in acetonitrile. Pyridine and the solid thiosemicarbazide derivative were added to obtain a 1:1:1 molar ratio of components (Table 1). The reaction mixture was stirred on a magnetic stirrer at ambient temperature for 48 h. The extent of the reaction was followed by ^{31}P NMR spectroscopy. A white solid product was precipitated in the course of the reaction. It was filtered off by a Schlenk frit and dried under vacuum. Further portions of the product were obtained after partially concentrating the filtrates.

2.2. Pyridinium salt of 4-methyl-3-sulfido-3, 5-dithioxo-1,2,4,3λ^5-triazaphospholidine (*II*)

White powder, yield: 93% (with respect to **I**). ^{31}P NMR (acetonitrile): δ 112.8 ppm, quartet, ^3J[P–H] = 8.63 Hz. IR: 3211 w, 3125 m, 3092 m, 3061 m, 3042 m, 2725 m, 1633 m, 1603 m, 1523 s, 1478 vs, 1457 vs, 1351 m, 1273

Table 1
Amounts of starting compounds and solvents used in the reactions

Product	4-Alkyl-thiosemicarbazide			py · PS_2Cl (g)	Acetonitrile (ml)	Pyridine (ml)	Yield (%)
		(g)	(mmol)				
II	methyl	0.50	4.76	0.997	40	0.39	93
III	ethyl	0.50	4.19	0.879	40	0.34	92