

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

Polyhedron 25 (2006) 3611–3616



POLYHEDRON

[www.elsevier.com/locate/poly](http://www.elsevier.com/locate/poly)

# Synthesis, structure and properties of novel *N*-thiophosphorylated derivatives of 1,3-dihydro-2*H*-benzimidazol-2-imine and imidazolidine-2-imine

Felix D. Sokolov<sup>a</sup>, Damir A. Safin<sup>a,\*</sup>, Nail G. Zabiroy<sup>a</sup>, Alexander Yu. Verat<sup>a</sup>,  
Vasiliy V. Brusko<sup>a</sup>, Dmitry B. Krivolapov<sup>b</sup>, Ekaterina V. Mironova<sup>b</sup>, Igor A. Litvinov<sup>b</sup>

<sup>a</sup> Department of Chemistry, Kazan State University, Kremlevskaya Street 18, 420008 Kazan, Tatarstan, Russia

<sup>b</sup> Arbusov Institute of Organic and Physical Chemistry, Arbuzov Street 8, 420088 Kazan, Tatarstan, Russia

Received 2 June 2006; accepted 11 July 2006

Available online 1 August 2006

## Abstract

The reaction of bis-thiourea *o*-C<sub>6</sub>H<sub>4</sub>[NHC(S)NHP(S)(*Oi*-Pr)<sub>2</sub>]<sub>2</sub> (**1**) with iodine, KOH and ClCH<sub>2</sub>C(O)OCH<sub>3</sub> leads to *O,O'*-diisopropyl-1,3-dihydro-2*H*-benzimidazol-2-ylideneamidothiophosphate (**2**) formation. The complex of the potassium salt of compound **2** with 18-crown-6, having the composition [K(18-crown-6)L], has been synthesized. Bis-thiourea [CH<sub>2</sub>NHC(S)NHP(S)(*Oi*-Pr)<sub>2</sub>]<sub>2</sub> (**6**) forms a stable potassium salt, which oxidation by iodine leads to a product of heterocyclization, *O,O'*-diisopropyl-(1-[(diisopropoxyphosphorothio)amino]carbonothioyl)imidazolidine-2-ylidene)amidothiophosphate (**8**), in which one of the thiourea fragments is kept.  
© 2006 Elsevier Ltd. All rights reserved.

**Keywords:** Heterocycles; Crown-ether; Crystal structures; Phosphorylated derivatives; Thioureas

## 1. Introduction

*N*-Thiophosphorylated thioureas are of interest as complexing agents [1,2] and precursors for synthesis of heterocycles, containing exocyclic phosphorylic groups. Thus, a number of reactions with their participation, leading to phosphor-containing iminothiazolidines, iminooxazolidines and thiophosphoryl(phosphonyl)aminothiozoles, have been reported [3–5]. With the presence of two thiourea fragments occupying  $\alpha,\beta$ -positions in a molecule, it is reasonable to expect interesting transformations leading to cyclic structures.

Herein we report the structure and properties of cyclic guanidates: imidazol-2-imine and imidazolidin-2-imine, synthesized by cyclization of bifunctional *N*-thiophosphorylated thioureas. Guanidine derivatives of this kind

attract attention as antifilarial agents [6] and as ligands for metal binding [7,8]. Their alkali metal salts are important as intermediates for the synthesis of complexes with d- and f-elements. Organic analogues of the synthesized compounds show complexation properties towards Cr(III), Hg(II), V(IV), Co(III), Ni(II), Pd(II), Cu(II), Zn(II), Sn(II) and Sn(IV) cations [7b,9,10].

## 2. Experimental

### 2.1. Synthesis of *O,O'*-diisopropyl-1,3-dihydro-2*H*-benzimidazol-2-ylideneamidothiophosphate (**2**)

*Path a:* Yield: 80%. M.p. 218 °C [11].

*Path b:* A suspension of anhydrous K<sub>2</sub>CO<sub>3</sub> (1.38 g, 10 mmol), 18-crown-6 (0.1 g, 0.38 mmol as a catalyst) and bis-thiourea **1** (1.47 g, 2.5 mmol) in benzene solution (50 mL) was stirred at room temperature for 2–3 days. Then the K<sub>2</sub>CO<sub>3</sub> precipitate was filtered off and the solvent was removed in vacuo. The residue was recrystallized from

\* Corresponding author. Tel./fax: +7 843 2543734.

E-mail addresses: [felix.sokolov@ksu.ru](mailto:felix.sokolov@ksu.ru) (F.D. Sokolov), [damir.safin@ksu.ru](mailto:damir.safin@ksu.ru) (D.A. Safin).