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

Felix D. Sokolov a, Damir A. Safin a,*, Nail G. Zabirov a, Alexander Yu. Verat a,
Vasiliy V. Brusko a, Dmitry B. Krivolapov b, Ekaterina V. Mironova b, Igor A. Litvinov b

a Department of Chemistry, Kazan State University, Kremlevskaya Street 18, 420008 Kazan, Tatarstan, Russia
b Arbusov Institute of Organic and Physical Chemistry, Arbuzov Street 8, 420088 Kazan, Tatarstan, Russia

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Abstract

The reaction of bis-thiourea o-C6H4[NHC(S)NHP(S)(Oi-Pr)2]2 (1) with iodine, KOH and CICH2C(O)OCH3 leads to O,O-diisopropyl-1,3-dihydro-2H-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]2, has been synthesized. Bis-thiourea [CH2NHC(S)NHP(S)(Oi-Pr)2]2 (6) forms a stable potassium salt, which oxidation by iodine leads to a product of heterocyclization, O,O-diisopropyl-[(diisopropoxyphosphorothio)amino]carbonothioyl]imidazolidine-2-ylideneamidothiophosphate (8), in which one of the thiourea fragments is kept.

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1. Introduction

N-Thiophosphorylated thioureas are of interest as complexing agents [1,2] and precursors for synthesis of heterocycles, containing exocyclic phosphoryl 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 α,β-positions in a molecule, it is reasonable to expect interesting transformations leading to cyclic structures.

Herein we report the structure and properties of cyclic guanidinates: 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 complexion 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-2H-benzimidazol-2-ylideneamidothiophosphate (2)

Path b: A suspension of anhydrous K2CO3 (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 K2CO3 precipitate was filtered off and the solvent was removed in vacuo. The residue was recrystallized from