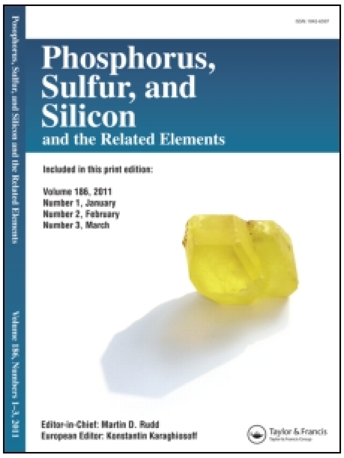

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Development of the Synthesis Methods of Polyheterophosphacyclanes with Endocyclic P-C Bond on the Basis of Functionalized Alkylphosphonates (-Phosphinates)

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Development of the Synthesis Methods of Polyheterophosphacyclanes with Endocyclic P–C Bond on the Basis of Functionalized Alkylphosphonates (-Phosphinates)

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We developed a new approach to the synthesis of saturated and unsaturated phosphoruselementocontaining heterocycles was developed; we based it on the addition reactions of various proton nucleophiles (amines, silylamines, alcoholes, mercaptanes, aminoalkylphosphonates, phosphines, CH-acides, etc.) to the halogenmethylphosphonylated isocyanates or isothiocyanates. Intermediate compounds of these reactions (phosphorylated ureas, thioureas, urethanes, thiouretanes, acylamides, etc.) are easily transformed into phosphorus containing cyclic structures.

Keywords Addition reactions; intramolecular cyclization; polyheterophosphacyclanes; posphorylated iso(thio)cyanates; proton nucleophiles

INTRODUCTION

We have developed new approach to the synthesis of polyheterophosphacyclanes with endocyclic P-C bond. It is based on the reactions of intramolecular cyclization of polyfunctional phosphonates (-phosphinates), where phosphorus atom is connected with halogenalkylgroups and other structural fragments (ureas, thioureas, thiouretanes, thioamides etc.). Such compounds can be easily obtained by the addition of proton nucleophiles to chloromethylphosphonylated (-phosphinilated) isocyanates or isothiocyanates **1**. In most cases polyfunctional P(IV) derivatives **2** in the presence of a base undergo

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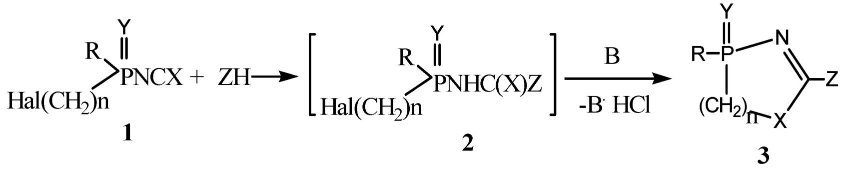
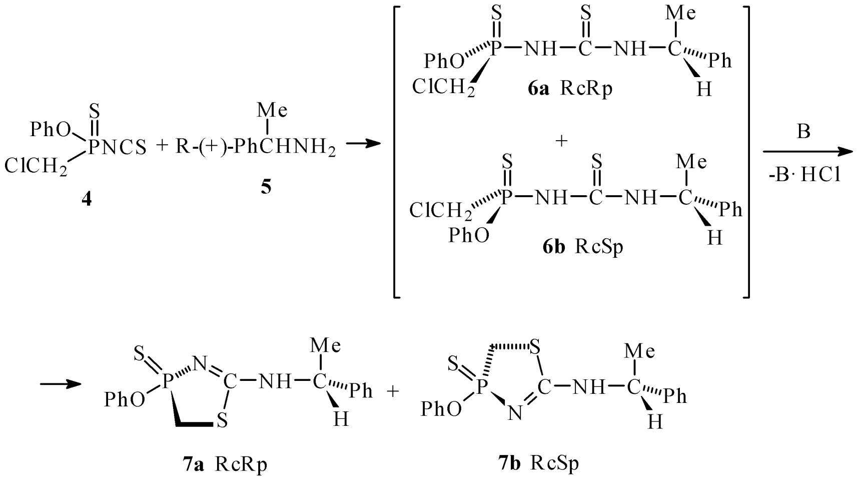
intramolecular cyclization to afford unsaturated cyclic structures with endocyclic P—C bond **3**.



n= 1; 2 X=O; S Y= O; S Z= NH_2; NHAlk; $NAlk_2$; SR; PPh_2 Hal= Cl; Br

SCHEME 1

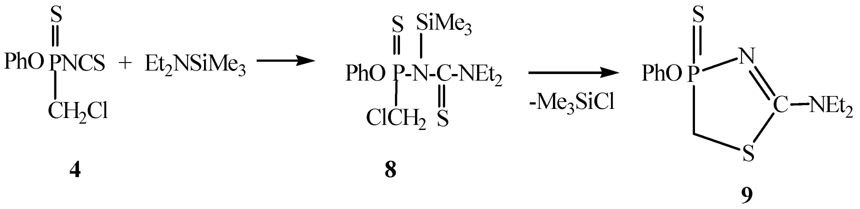
The interaction of isothiophosphonate **4** with (*R*)-(+)-(1-phenyl)ethylamine 5 proceeds stereoselectively and results in the formation of a mixture diastereomers of 2-(1-phenyl)ethylamino-4-thioxo-4-phenoxy-1,3,4-thiazaphosphol-2-ines **7a** (δ_P120.03) and **7b** (119.73) in 19:81% ratio. The predominant diastereomer **7b** was isolated in pure state with 32 % yield. As far as optically active amine (Lancaster, 98%, $[\alpha]_D^{20}$+29) was used in the reaction, both diastereomers 7a and 7b are homochiral and differ one from another only by the configuration of the phosphorus atom. X-Ray investigation was undertaken to determine the absolute configuration of chiral centers on phosphorus atoms in enantiomer pairs of diastereomers **7a** and **7b**.



SCHEME 2

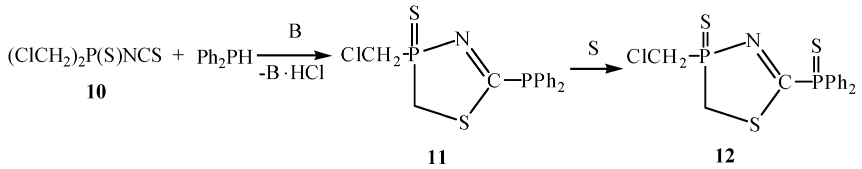
It appeared that the configuration of carbon and phosphorus atoms in these compounds is the opposite. So, the preferred binding with the enantiomer possessing the opposite configuration of the chiral center takes place in the course of the reaction of chiral isothiocyanate **4** with amine **5**.

It appeared that the reaction of silylated diethylamine with phosphorylated isothiocyanate **4** proceeds easily to form silicon containing phosphorylated urea **8**, which is easily cyclized with the elimination of trimethylchlorosilane to give 1,3,4-oxazaphospholine **9**. In a number of cases using of silylated derivatives of amines instead of free amines has some advantage. This approach does not require employment of a solvent and a base; the stages of the filtering and removal of the solvent are excluded



SCHEME 3

The reaction of diphenylphosphine with bis (chloromethyl)isothiocyanatophosphinate **10** proceeds with the formation of addition product which is converted into 1,3,4-thiazaphospholine **11**. The addition of sulfur to compounds 11 gives rise to thiazaphospholine 12.



SCHEME 4