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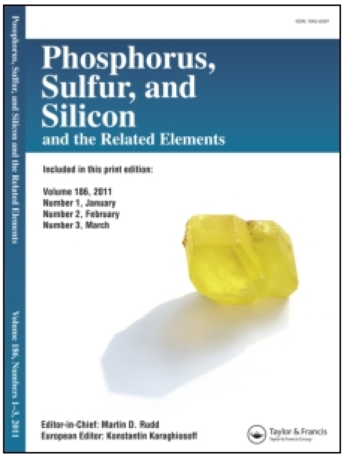

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Mikhael Pudovik; Rustem. Kamalov; Natalia Khailova; Ludmila Kibardina; Svetlana Terent'eva; Roza al'mianova

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Polyheterophosphacyclanes with Endocyclic P-C Bonds

MIKHAEL PUDOVIK, RUSTEM. KAMALOV,
NATALIA KHAILOVA, LUDMILA KIBARDINA,
SVETLANA TERENT'EVA and ROZA AL'MIANOVA

A.E. Arbuzov Institute of Organic and Physical Chemistry Russian Academy of Sciences, Kazan Scientific Centre, Kazan 420088, Russia

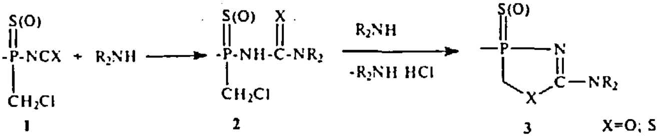
The methods of synthesizing of polyheterophosphacyclanes based onpolyfunctional organophosphorus compounds with chloromethyl groups and other structural fragments at the central atom were developed.

Keywords: polyfunctional organophosphorus compounds; heterocyclization; polyheterophosphacyclanes

Lately the development of organophosphorus chemistry has been characterized by a great interest in cyclic derivatives. On the whole they may be obtained by the phosphorylation of polyfunctional organic and organoelement substrates or by the intramolecular transformations of polyfunctional organophosphorus derivatives. Taking into consideration that five-membered phosphorus containing heterocycles are readily formed, we decided to use chloromethylphosphorus derivatives as a basis for synthesizing cyclic structures. For the preparation of polyfunctional chloromethylphosphorus derivatives four main approaches have been developed: a) the reactions of proton donor reagents (or their silylated derivatives) with chloromethylisocyanato or -isothiocyanatophosphonates(-phosphinates); b) the addition reactions of silylamidochloromethylphosphonates(-phosphinates) with unsaturated electrophilic reagents; c) the addition reactions of chloromethyldithio- or selenothiophosphonic(- phosphinic) acids to electrophilic reagents; d) the phosphorylation of polyfunctional organic and organoelement compounds by chloromethylchloro(thio)phosphonates (-phosphinates). Intermolecular transformations of such polyfunctional derivatives result in the formation of different cyclic structures.

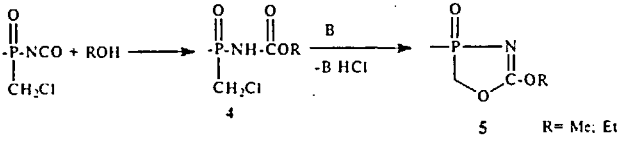
Iso(thio)cyanatochloromethylphosphonates(-phosphinates) **1** easily add one molecule of a secondary amine with the formation of phosphorylated urea(or thiourea). Under the influence of the second molecule of amine compounds **2** are converted into

1.3.4-oxa(thia)phospholines 3 [1]. The molecular structure of 2-amino-4-thioxo-4-phenoxy-1,3,4-thiazaphospholine was supported by the X-Ray analysis data. The molecules have an envelope conformation with the deviation of the carbon atom from the PNCS-plane on 0.455 A.

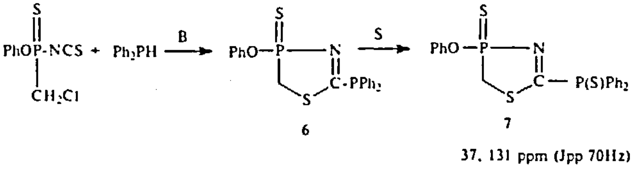


We have also found, that in some cases it is more appropriate not to use free amines, but their N-silylated derivatives. This type of addition reaction does not involve any base or solvent; there are also no stages of filtration and removal of solvent.

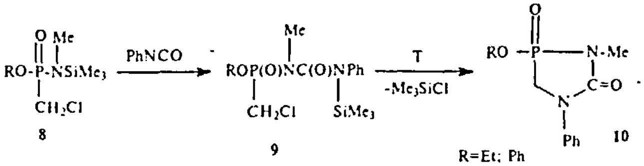
It has been shown that at room temperature isocyanatochloromethylphosphonates(-phosphinates) readily add one molecule of alcohol with the formation of N-phosphorylated uretanes 4, which were first separated and then characterized. In the presence of a base they are converted into five membered unsaturated heterocycles - 2-alkoxy-1.3.4-oxazaphospholines 5. Compounds 4 were also obtained by the reaction of chloromethylchlorophosphonates(-phosphinates) with alkyluretanes.



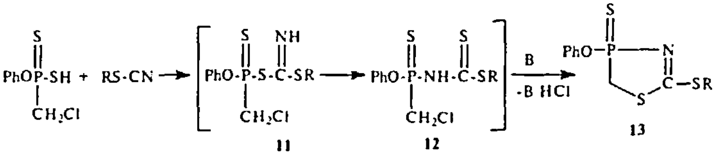
The addition of diphenylphosphine to chloromethylisocyanatothiophosphonate gives rise to the heterocycle 6, involving four- and three coordinated phosphorus atoms. Since this compound is rather unstable, it is converted into the final product 7 by adding elemental sulfur [2].



The phosphorylation of heptamethyldisilazane by O-phenyl(ethyl)chloromethylchlorophosphonates results in the formation of appropriate silylamidochloromethylphosphonates 8. Their interaction with phenylisocyanate proceeds with the formation of the addition product **9**, which is cyclized into 1,3,4-diazaphospholidine-2-on **10** [3].

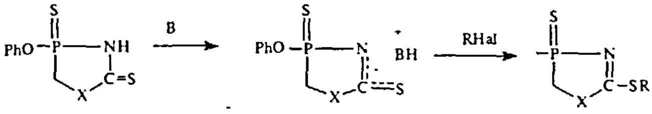


One more method of synthesizing heterocycles with endocyclic P-C bonds involves the reactions of chloromethyldithia(selenothia)phosphonic acids with electrophilic reagents. We tried to obtain chloromethyldithia- or selenothiaphosphonic acids by treatment of chlorophosphonates with sulfur hydride or seleno hydride in the presence of a base. But we failed in separating these acids into their pure state and further they were used without special purification. The treatment of chloromethylchlorothiophosphonates by sulfur hydride in the presence of alkylthiocyanate and a base make it possible to obtain 1,3,4-thiazaphospholine **13**. Being formed at the first stage phosphonic acid is added to alkylthiacyanate with the formation of the addition product **11**. Its isomerization into N-thiophosphorylated dithiocarbamate **12** followed by cyclization under the influence of a base gives rise to the final product **13** [4].



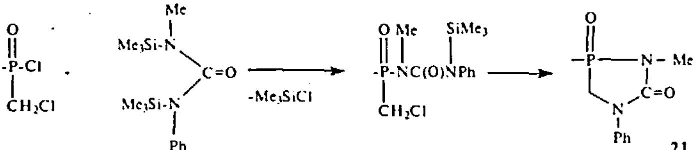
According to the X-Ray analysis data the molecule of thiazaphospholine **13** has an envelope conformation with the deviation of the C-5 atom from the PNCS plane on 0.323 A. The length of the chemically unequivalent S^2C^1 and S^2-C^2 bonds is approximately the same (1.785 and 1.786).

The reaction of chloromethylselenothiophosphonic acid **14** with bis(thiocyanato)methane makes it possible to obtain a new 5-membered saturated Se,N,P-containing heterocycle - 1,3,4-selenazaphospholine **15**. The cyclic compounds **16** exhibit acidic properties. In the presence of a base they form salt-type compounds **17**, which become 1,3,4-thia(seleno)phospholines **18** when treated by alkylhalide.



16 17 18 X=S; Se

Different heterocyclic systems can also be obtained by the phosphorylation of polyfunctional organic and organoelement compounds. The reaction of chloromethylchlorophosphonates with disilylated urea **19** results in the formation of phosphorylated urea **20** , followed by its cyclization with intramolecular alkylation of the nitrogen atom by a chloromethyl group and the formation of heterocycle **21** [5].



19 20 21

We have also shown, that the reaction of chloromethylchlorophosphonates with N,O-bis(trimethylsilyl)acetamide is accompanied by the elimination of acetonitrile and finally results in chloromethylsiloxyphosphonate [6].

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