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## Phosphorus, Sulfur, and Silicon and the Related Elements

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# Phosphito- and Amidophosphitocavitands

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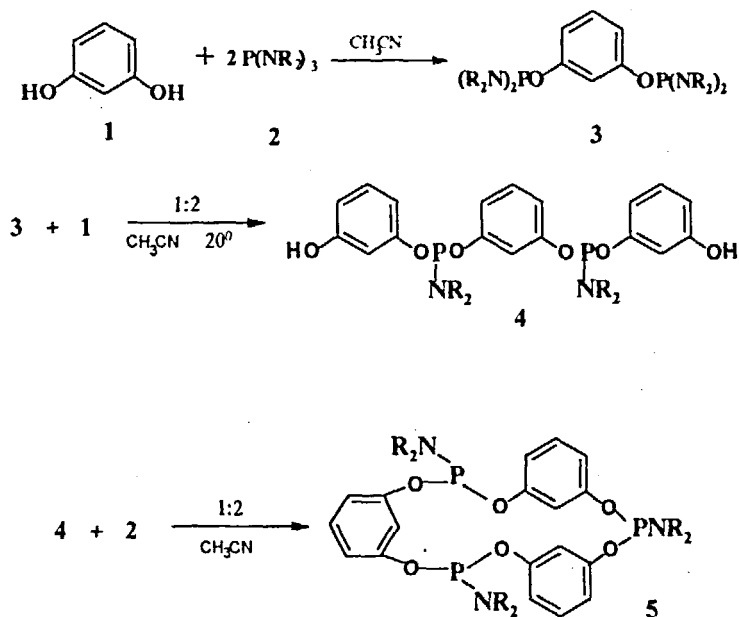
On the basis of resorcinol and resorcinolcalixarenes new approaches for the synthesis of phosphorus-containing macroheterocycles with an internal cavities were developed.

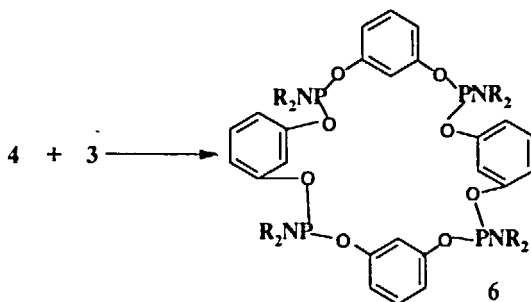
**Keywords:** resorcinol; calixarenes; triamides of phosphorous acids

## INTRODUCTION

Two approaches were used for the synthesis of phosphorus-containing macroheterocycles with an internal cavity. An approach was based on the molecular assemblage method using diatomic phenols (resorcinol was principally studied) and triamides of phosphorus acids. In our work, this approach was applied to the synthesis of a new class of phosphorus-containing crown-ethers with regularly alternating arylene fragments and phosphorus acid residues in their molecules.

The tactics of the synthesis involved a combination of reactions starting from resorcinol (1) and hexaalkyltriamides of phosphorous acid (2). At the first stage, this combination was used for obtaining linear oligonuclear intermediates with active peripheral groups. The final stage of the synthesis involved cyclization with the use of the phosphamide method:

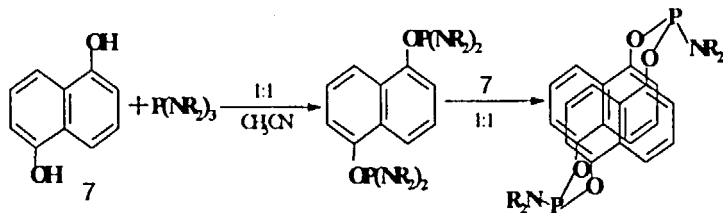




$R = \text{CH}_3, \text{C}_2\text{H}_5$

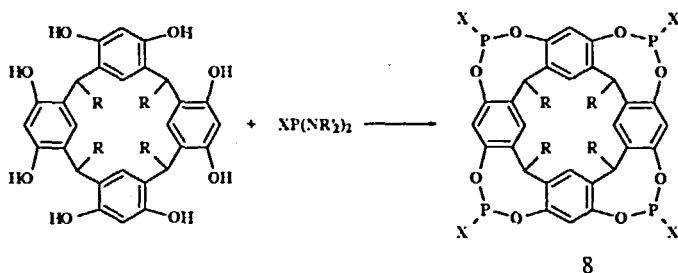
The identities and structures of intermediates and final products were controlled by means of NMR spectroscopy and X-ray diffraction analysis.

Systems based on 1,5-dihydroxynaphthalene were obtained in a similar way:



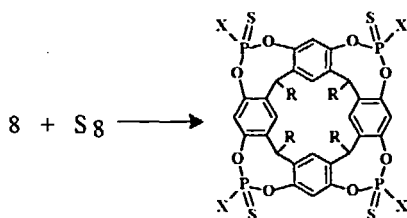
The oxidation of compounds that had been obtained and their complexation with metals were also studied.

The second approach was based on the modification of resorcinolcalixarenes by di- and triamides of phosphorous acid. By this means, we were successful in obtaining conformationally rigid structures that provided a first example of sterically individual phosphocavitands.



The reaction is of great synthetic value. So, conjugates of phosphocavitands with steroids and sugars were obtained using this reaction. We revealed the effect of radical R on the rate and efficiency of phosphorylation that was also of great importance. This result was explained by the regulation of conformational transformations in the initial calixarenes.

The chemical compositions and structures of the compounds obtained were studied by means of NMR spectroscopy and X-ray diffraction analysis. Relying on these data, we performed stereospecific reactions with phosphatide cavitands, for example:



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