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Synthesis of Novel Macrocyclic Ligands Containing Phosphoryl and Aminoacetal Fragments

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SYNTHESIS OF NOVEL MACROCYCLIC LIGANDS CONTAINING PHOSPHORYL AND AMINOACETAL FRAGMENTS

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GRAPHICAL ABSTRACT



R=C4H9(a), C6H13(b), OMe(c), OiPr(d)

Abstract A method for the synthesis of novel phosphorylated aminoacetals was developed. The latter are involved in Mannich reaction as amine component with calix[4]resorcinol and formaldehyde to form tetrasubstituted macrocycles containing four acetal groups and four phosphonate (phosphine oxide) fragments on the "upper" rim of molecule with high yields.

Keywords Aminophosphonate; aminophosphine oxide; calix[4]resorcinol; Mannich reaction

The development of methods for the selective synthesis of novel macrocyclic ligands is a key problem of organic and supramolecular chemistry. Macrocycles as well as calixarenes containing aminophosphoryl groups are of particular importance among these receptors.^{1,2} They exhibit various biological activities³ and are used as extragents of rareearth metals⁴ as well as transmitters in membrane extraction.^{2,5}

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In earlier investigations, we developed methods for the synthesis of tetrasubstituted calix[4]resorcinols containing aminophosphonate⁶ and aminoacetal^{7,8} groups on the upper rim of the molecule. These macromolecules are able to undergo chemical modification⁹ as well as to form supramolecular aggregates having catalytic activity in the hydrolysis of phosphonates,¹⁰ the complexation of Cu(II) and La(III) ions,¹¹ and the extraction of La(III) and Gd(III) ions.⁵

With the aim to synthesize macrocyclic polydentate ligands having phosphoryl fragments in addition to acetyl groups, we developed a method for a single-step synthesis of phosphorylated aminoacetals and investigated their reaction with formaldehyde and calix[4]resorcinol.

The synthesis of compounds **3a–d** was performed by the condensation of aminoacetal **1** with paraformaldehyd and dialkylphosphites (dialkylphosphinic acids) **2a–d** according to Kabachnik–Fields reaction (Scheme 1).

Scheme 1

As a result of the reaction of phosphorylated aminoacetals 3a-d with calix[4]resorcinol 4 and formaldehyde (Mannich reaction), new tetrasubstituted macrocycles 5a-d containing phosphine oxide (phosphonate) fragments with various substituents at the phosphorus atom on the "upper" rim of the molecule were obtained with the yields from 88 to 99%.



The presence of four phosphoryl and four acetal groups on the "upper" rim of compounds **5a--d** makes it possible to consider them as promising polydentate ligands.

The structure of the compounds synthesized was proved by ³¹P and ¹H NMR spectroscopy; the composition was confirmed by correct elemental analysis data.

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