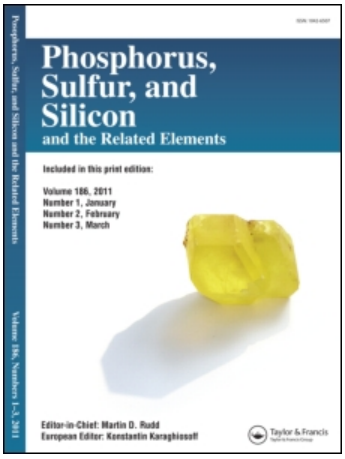

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SYNTHESIS AND BINDING PROPERTIES OF PHOSPHORUS-CONTAINING CALIXARENES AND CALIXRESORCINARENES

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Abstract Full and regioselectively phosphorylated calix-[4]arenes and calix[4]resorcinarenes were synthesized by Nickel catalyzed Arbuzov reaction of para-bromosubstituted calixarenes as well as by reaction of the hydroxyl-derivatives with chlorophosphates. Stereochemistry, chemical transformations, and complexation of the titled phosphorus-containing macrocycles were examined.

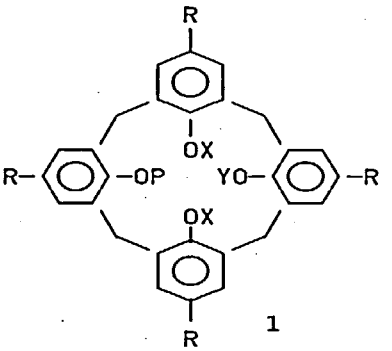
INTRODUCTION

Calix[4]arenes and calix[4]resorcinarenes due to their original bowl shaped molecular architecture are versatile starting material for design of novel 'host' molecules capable to separation of metal cations and particularly neutral organic molecules[1]. Continuing our studies of phosphorus-containing macrocycles[2] we have synthesized and investigated a number of calixarenes and calixresorcinarenes functionalized with exocyclic phosphoryl groups. This presentation summarizes methods of phosphorylation of titled macrocycles as well as properties of the compounds obtained.

SYNTHESIS OF PHOSPHORYLATED MACROCYCLES

Nickel catalyzed Arbuzov reaction of para-bromosubstituted calixarenes as well as interaction of polyoles with chlorophosphates or system dialkylphosphite/Et_3N/CCl_4 were used for synthesis of full and regioselectively substituted

upper-rim and lower-rim phosphorylated macrocycles 1,2 [3-5]. By subsequent treatment of the dialkoxyphosphorylderivatives of calixarenes and resorcinarenes with trimethylbromosilane and methanol the water-soluble hydroxyphosphorylderivatives 1,2 (P = $P(O)(OH)_2$) were obtained[6]. Mannich reaction of the tetraphosphorylated resorcinarenes 2 (R = $P(O)(OAlk)_2$, X = Y = H) leads to bis aminomethyl derivatives 2 (Y = CH_2-NRR').



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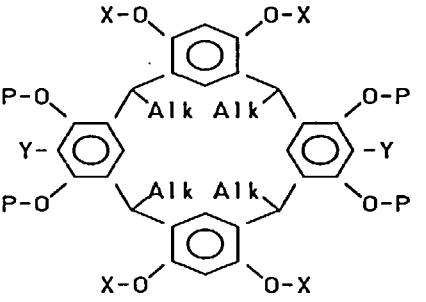


2

a R = $P(O)(OAlk)_2$, $P(O)Ph_2$; X = Y = P = Alk, H

b R = H, t-Bu; P = X = Y = $P(O)(OAlk)_2$, $P(O)(OH)_2$

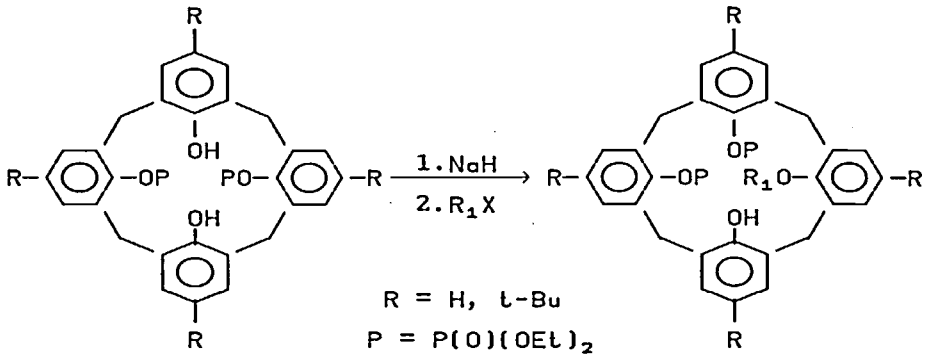
c R = H, t-Bu; X = H; P = Y = $P(O)(OAlk)_2$, $P(O)(OH)_2$

d R = H, t-Bu; Y = H; P = X = $P(O)(OAlk)_2$

a P = X = $PO(OAlk)_2$, $P(O)(OAr)_2$; Y = H

b P = $PO(OAlk)_2$, $P(O)(OAr)_2$, $P(O)(OH)_2$; X = H, C(O)Me, SO_2-BENZO-15-CROWN-5; Y = H, CH_2-NMe_2, CH_2-NH-PROLINE-l

Chiral calix[4]arenes 3[7] were synthesized with good yields by one-pot procedure consisted in successive treatment of 1,3-bis(diethoxyphosphoryl)calix[4]arenes 1c[5] (P = Y = $PO(OEt)_2$, X = H) (*cone* conformation) with sodium hydride and benzoyl chloride or methylmonobromoacetate. The key step of this process is the O,O-phosphorotropic rearrangement conditioned by advantageous spatial orientation of the phenolate anione oxygen for the intramolecular nucleophilic attack of phosphorus atom.



1c 3

STEREOCHEMISTRY

Two steroisomeres *cone* (all up benzene rings orientation) and *1,2-alternate* (two up and two down neighbouring rings orientation) were isolated in the case of diphosphate 1c[4] [R = t-Bu, X = H, P = Y = $(EtO)_2PO$]. All other di-, tri- and tetraphosphorylated calixarenes 1 exist in *cone* conformation. Spatial structure and conformational stability of the conformers were examined by NMR and X-Ray analyses. The *cone* conformers are stereochemically rigid, in contrast to which the *1,2-alternate* one is flexible.

The NMR spectra as well as X-Ray analyses have confirmed that all phosphorylated calix[4]resorcinarenes 2 exist in a *boat* conformation where two opposite benzene rings (nonsubstituted in case of tetraphosphates) are coplanar to the main plane of a molecule and two others are perpendicular to it. As follows from the data of ^1H NMR spectra, the conformational mobility of the phosphorylated calix[4]resorcinarenes 2 depend on the nature of the substituents placed at the upper rim of macrocycle as well as solvent nature[8].

COMPLEXATION

All phosphoryl groups of the tetraphosphorylated calix-

arenes 1b [P = X = Y = $(EtO)_2PO$] are conveniently preorganized for complexation of a metal cations, particularly for lithium one. Stability constants in tetrahydrofuran solutions are 5.43 for lithium, 4.40 for sodium and 3.89 for potassium.

Calix[4]resorcinarene 2 [P = $P(O)(OH)_2$, X = H, Alk = C_5H_{11}] forms complexes with aromatic molecules (toluene, xylenes, anysole, phenol, phenylalanine etc.) in water solutions. The constant of association of the tetraphosphoric acid 2 with phenol is 1.5 and with phenylalanine is 75 M^{-1}.

ACKNOWLEDGMENTS

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