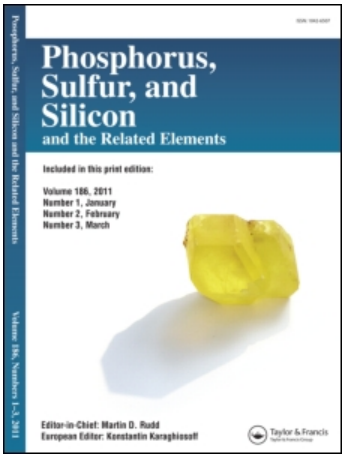

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Inherently Chiral Phosphoruscontaining Calix[4]Arenes

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Inherently chiral phosphoruscontaining calix[4]arenes with asymmetrical placement of substituents at the macrocyclic lower rim (phenolic oxygen atoms) as well as with asymmetrical superposition of substituents at the upper rim (para-positions of benzene rings) and at the lower rim have been synthesized. The key steps of the synthesis are O,O-phosphorotropic rearrangements of 1,3-distally disubstituted calix[4]arenes into 1,2-proximal isomers induced by strong bases.

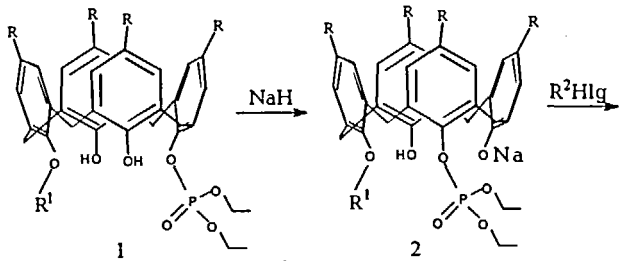
Keywords: calixarenes; chirality; organophosphorus compounds; phosphorotropic rearrangements

INTRODUCTION

The design of highly selective artificial receptors based on calixarenes[1] is an intensively developing area of supramolecular chemistry[2], within which the synthesis of chiral calixarenes is a promising method for obtaining "host" molecules capable to enantio- or diastereo-selective recognition[3]. These were first obtained by functionalization of calixarenes by chiral reagents[4], but recently a new approach based on asymmetric placement of achiral substituents on the upper[5] or lower[6] rims of the

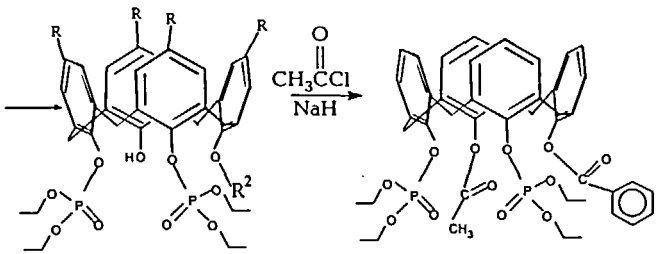
calix[4]arene macrocycle has been developed. The latter allows the macrocyclic cavity to be fixed in one of four possible conformations: cone, partial cone, 1,2-alternate, 1,3-alternate. Here, the synthesis of inherently chiral phosphoruscontaining calix[4]arenes based on O,O-phosphorotropic rearrangements of 1,3-distally disubstituted calix[4]arenes into 1,2-proximal regioisomers induced by strong bases is discussed.

The inherently chiral calix[4]arenes **2** (R^1=Et), **3** and **4** were synthesized in good yields by successive treatments of 1,3-disubstituted calixarenes **1**[7-8] with sodium hydride (or butyl lithium) and the electrophilic reagents.



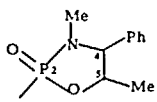
1 2

R = H, t-Bu; R^1=Et, P(O)(OEt)$_2$



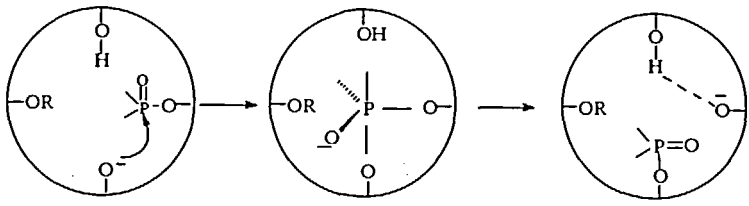
3 4

R^2= $CH_2C(O)OCH_3$, C(O)Ph,



(2S, 4S, 5R)

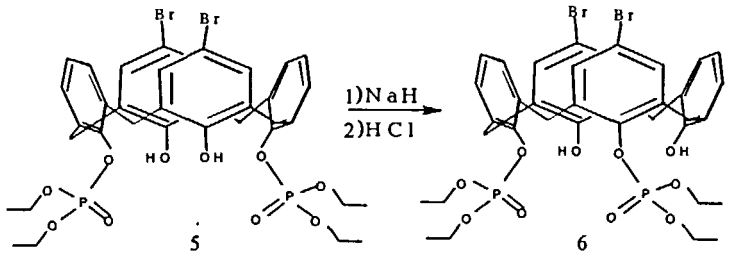
The key step of these syntheses is phosphorotropic rearrangement **A→C** brought about by advantageous spatial orientation of the phenolate anion oxygen for intramolecular nucleophilic attack at the phosphorus atom[9]. Phosphorane **B** is intermediate of this process.



A **B** **C**

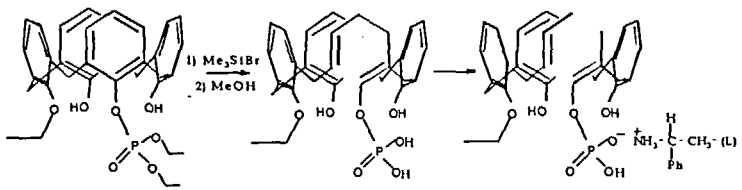
The phosphorotropic rearrangement is good tool for synthesis of calix[4]arenes with chirality induced by asymmetrical superposition of substituents at the lower and the upper rims of macrocycle.

Chiral calix[4]arene **6** with two diethoxyphosphoryl groups at proximal positions of the lower rim and two bromine atoms at the distal positions of the upper rim has been obtained in result of the migration of the phosphoryl group of dibromocalixarene **5** from the distal position to the proximal one induced by sodium hydride[10].



5 **6**

Described syntheses of the inherently chiral calixarenes **2-4** and **6** lead to racemic mixture of two enantiomeric forms which were separated by chiral HPLC method (analytical variant). Diastereomers **3,9** were synthesized for the preparative separation which is in progress now.



7 8 9

Acknowledgments

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