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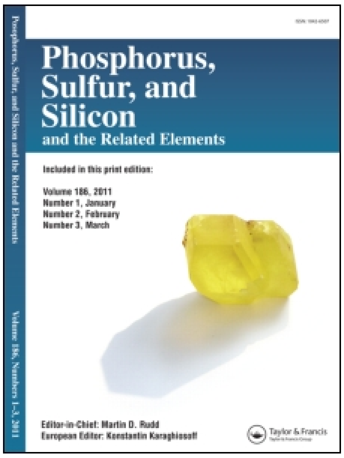

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The Syntheses and Binding Properties of the Novel Organophosphorus Calixarenes

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Phosphorylation of bromo, dialkylaminomethyl calix[4]resorcinarenes with various long chain aliphatic radicals with a number of P(III) derivatives i.e. triamido-and diamidophosphites, and polyhalogenides of P(III), P(IV) is described. A series of phosphoamide cavitands were obtained. Structures and properties of synthesized compounds were discussed on the basis of physical and quantum chemical methods.

Keywords: Phosphorylation; calix[4]resorcinarenes; carceplex; cavitands

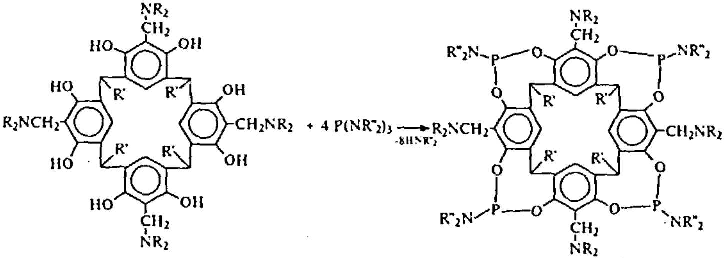
INTRODUCTION

Cyclodextrins, crown ethers and calixarenes are prominent in host-guest chemistry. Calixarenes and their derivatives can selectively involve both organic and inorganic guests. Bromo, dialkylaminomethyl calix[4]resorcinarenes are of the great interest because of their accessible synthesis,sufficient solubility and "bowl-like" conformation. The molecular design of new three-dimensional structures with calixaren as a basis can be achieved with the use of a wide range of reagents and methods of organophosphorus chemistry [1]. The purpose of this work is synthesis and investigation of new three-dimensional structures with three- and four-coordinated phosphorus which were obtaind on the basis of bromo, dialkylaminomethyl calix[4]resorcinarenes.

RESULTS

The phosphorylation of dialkylaminomethylated calix[4]resorcinarenes with P(III)-amides results in the formation of structures with cyclic phosphorus fragments fixed on the cavity rim [2,3], wtich are easily hydrolyzed.

It was found that hydrophosphoryl derivatives of the dialkylaminomethyl-calix[4]resorcinarene undergo two types of transformations depending on the type of substituent in dialkylamino groups: heterocyclization with elimination of 4 molecules of water and formation of phosphor(III)ylated cavitands or heterocyclization with elimination of 4 molecules of dialkylamine and formation cavitands with cyclic hydrophosphoryl groups [4].



(I)

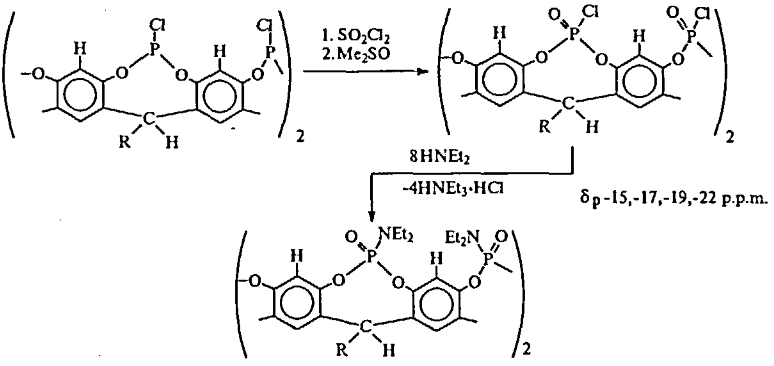
δ_P 139-143 p.p.m.

R=CH_3, C_2H_5, C_3H_7.
R'=CH_3, C_2H_5, C_3H_7, C_6H_{13}, $C_{11}H_{23}$.
R''=CH_3, C_2H_5.

The interaction of dialkylaminomethylated calix[4]resorcinarene with tetraalkyldiamidoalkylphosphites proceeds with formation of sault type product (initial calixarene with alkylphosphoric acid).

The interaction of calix[4]resorcinarenes, bearing aliphatic radicals of different length, with phosphorus trichloride proceeds in different manner, depending on reaction conditions. When 1:8 (calixarene : PCl_3) ratio have been used the cyclic hydrophosphoryl cavitands have been obtained. In the presence of a base (1:8:3 calixarene : PCl_3 : triethylamine) the final products are cyclic chlorophosphites. They don't react with trichlorophosphorus thiooxide, but may be easily oxidized into P(IY)-derivatives by sulfurylchloride or dimethylsulphoxide.

As a result of quantum calculation , it was shown that length of P - Cl bond in cyclic chloro P(III) derivatines of calix[4]resorcinarenes is much more shorter as compare with chloro P(III) phosphosines. This fact explanes the anomal chemical shift of cyclic chloro P(III) derivatines of calix[4]resorcinarenes in NMR ^{31}P spectra (127 - 129 p.p.m.).

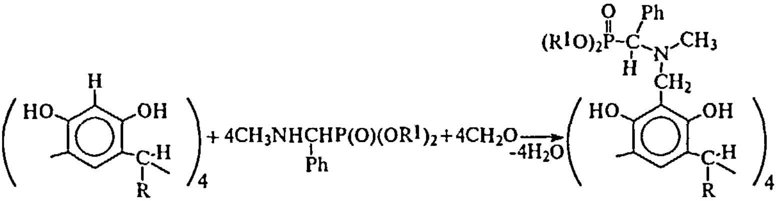


R= C_5H_{11}, C_6H_{13}, $C_{11}H_{23}$.

δp -14,-15 p.p.m.

Unlike phosphorus trichloride the phosphorylation of calixarenes with trichlorophosphorus oxide proceeds with the formation only linear compouds. Depending on the calixarene - trichlorophosphorus oxide ratio two or four dichlorophosphate groups can be introduced into the molecule of calixarene. When heated they are'nt converted into cyclic derivatives. Acording NMR ^{31}P spectra the complicated mixture of different phosphorus containing compounds have been formed.

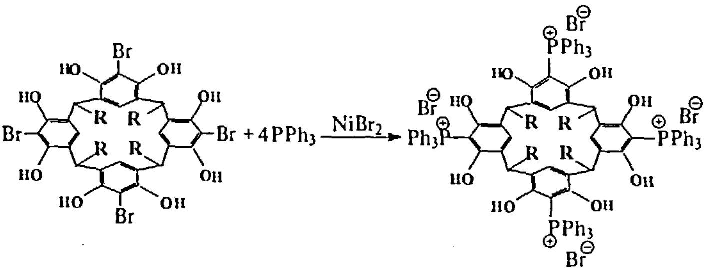
New C-phosphorylated alkylarylaminomethyl cavitands have been obtained as a result of the reaction of calix[4]resorcinarenes, α-aminophosphonates, phormaldehide in the 1:4:4 ratio [5].



R=CH_3, C_3H_7. R^1=CH_3, C_2H_5.

δp 21-24 p.p.m.

The new type phosphonium salts has been obtained as a result of phosphorylation of brom derivatives of the calix[4]resorcinarenes with thriphenylphosfine in the presence of catalytic amounts of $NiBr_2$ [6].



R=CH_3, C_6H_{13}.

δ_P 24-26 p.p.m.

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