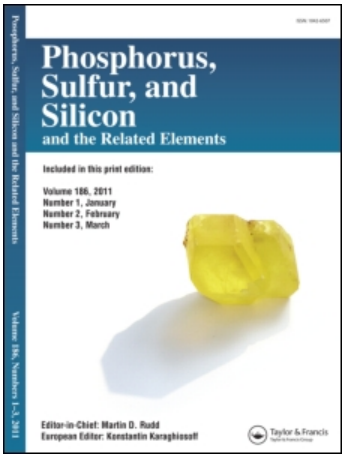

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The New Type of Calix[4]Resorcines Bearing Phosphonates and Phosphonium Fragments at The Lower Rim

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Two approaches to the synthesis of calix[4]resorcines bearing phosphonates and phosphonium fragments at the lower rim were elaborated. One of the approaches based on methodology for synthesis of octols by fourfold condensation of 4-substituted benzaldehydes with resorcinol and its derivatives. The calixaren matrix was used as a starting material for functionalization in another method. Both approaches based on the reaction of phosphorylation of arylhalides by the derivatives of P(III) acids in the presence of Ni(II) compounds. Phosphorylated calyx[4]resorcines were further modified at the upper rim with amine groups.

Keywords Calix[4]resorcinols; derivatives of P(III) acids; phosphorylation; condensation

INTRODUCTION

The modification of calixarenes by the introduction of phosphorus–containing groups has attracted considerable attention during the past years. Depending on the phosphorus-containing fragments those mycrocycles can possess interesting properties such as physiological activity, complexing ability towards transition metals.

RESULTS AND DISCUSSION

Calix[4]resorcines are phenolic macrocyclic compounds and readily available from resorcinols and aldehydes.[1] The present work deals with

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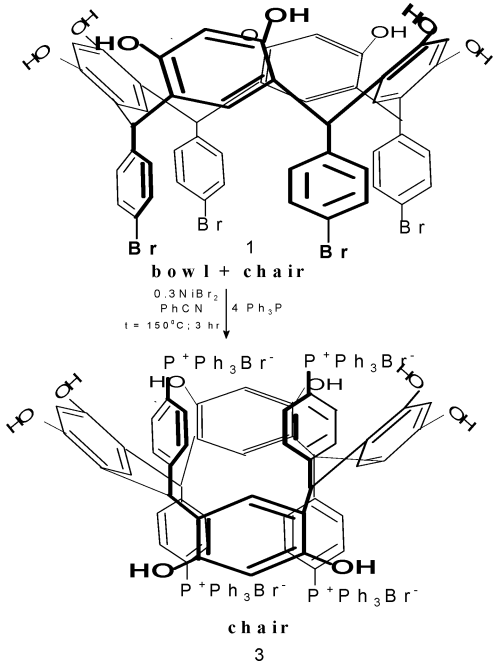
synthetic methodology, that allows the preparation of calyx[4]resorcines bearing phosphonates and phosphonium groups at the aromatic fragments disposed at the lower rim. Two approaches were elaborated: using the calixarene matrix as the starting material and the fourfold condensation of 4-phosphorylated benzaldehydes with resorcinol. Both approaches based on the reaction of phosphorylation of arylhalides by the derivatieves of P(III) acids in the presence of Ni(II) compounds. The method of phosphorylation of arylhalides was work out on the simple aromatic systems.[2–6]

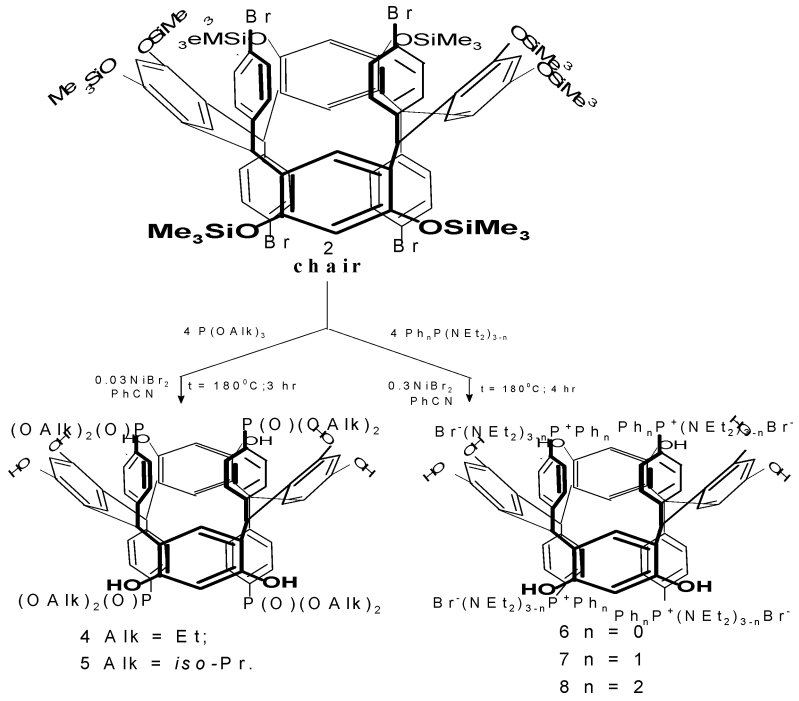
When calixarene matrix was used as the starting material, the calyx[4]resorcine **1** was employed[7] in conformations *bowl* and *chair*. As phosphorylating reagents PPh_3, $P(OEt)_3$, $P(O\textit{iso}Pr)_3$, $Ph_nP(NEt_2)_3$ (n = 0–2) were used. In order to avoid the decomposition of P(III) derivatives the hydroxyl groups of calixarene **1** were protected with trimethylsilil groups using hexamethyldisilazane. It was found that only isomer in conformation *chair* undergoes O-sililation and gives **2**.

In the reaction of **1** in conformations *bowl* and *chair* with PPh_3 only isomer in conformation *chair* yields the calyx[4]resorcine **3** with four triphenylphosphoniophenyl groups (Scheme 1).



SCHEME 1

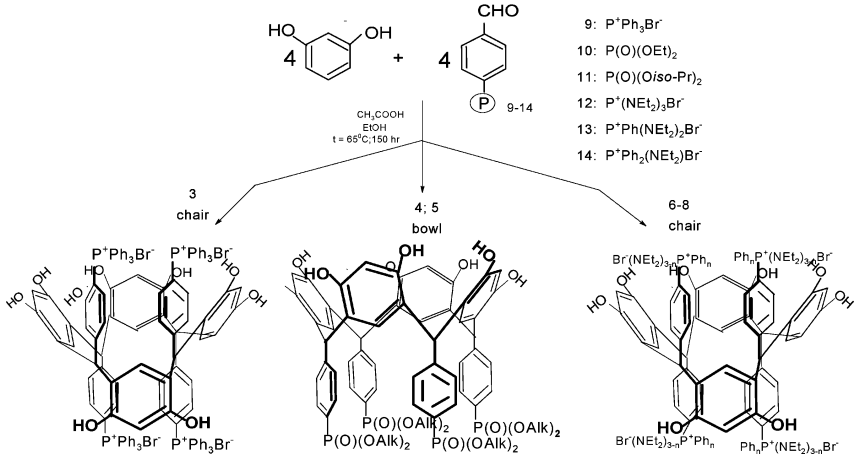
The reaction of **2** with $P(OEt)_3$, $P(OisoPr)_3$ and $Ph_nP(NEt_2)_3$ (n = 0–2) leads to corresponding phosphorylated calyx[4]resorcine **4–8** with eight phenolic groups (Scheme 2). We believe that introduction of phosphorus-containing groups to **2** leads to hydrolytic unstability of intermediate O-sililated derivatieves.



SCHEME 2

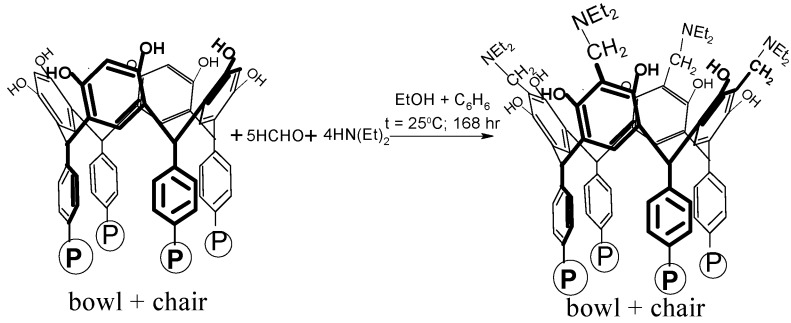
For the purpose of preparation of phosphorylated calyx[4]resorcines via methodology for synthesis of octols by fourfold condensation of 4-phosphorylated benzaldehydes with resorcinol, the number of phosphorus-substituted benzaldehydes were synthesized.[8] With success the 4-phosphorylated benzaldehydes **9–14** were used in condensation with resorcinol (Scheme 3). The calyx[4]resorcines bearing four triphenylphosphoniophenyl groups **3** and four aminophosphoniophenyl groups **6–8** were isolated in conformation *chair*. The products **4, 5** derived from condensation of **9, 10** with resorcinol were found to exist in conformation *bowl*.

Conformers *bowl* and *chair* could be easily distinguished by their characteristic ^1H- and ^{13}C-n.m.r. pattern.



SCHEME 3

Mannich reaction of **3–8** with diethylamine and formaldehyde in an alcoholic-benzene solution leads to tetra aminomethyl derivatives **15–20** (Scheme 4) in corresponding conformations.



SCHEME 4

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