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Phosphorus-bridged calixarene phosphites: dramatic influence of a *tert*-butyl group at the upper rim of the macrocycle upon anion binding

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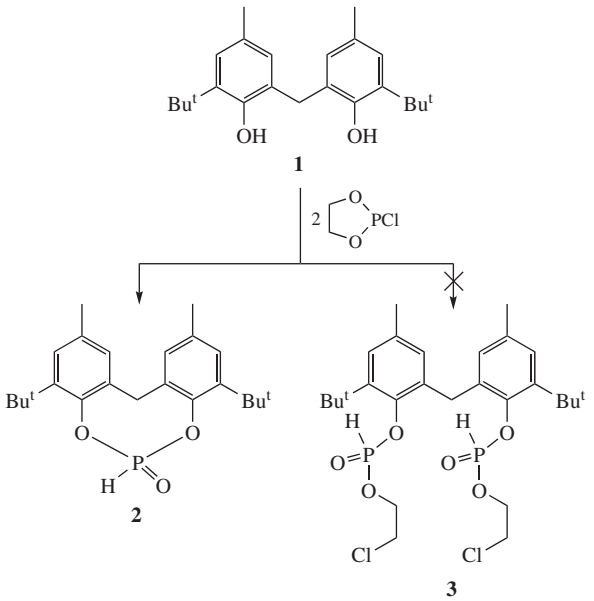
New cyclic phosphite derivatives of calix[4]arenes in 1,2-*alternate* configuration were obtained by the interaction of calix[4]arenes with ethylene chlorophosphite; the influence of a *tert*-butyl group at the upper rim of the macrocycle upon anion binding was shown.

Calix[4]arenes are plenty favorable molecular platforms for the creation of three-dimensional structures with different sizes of intramolecular cavities, number, type and spatial orientation of binding sites, abilities to formation of asymmetric cavities and equilibrium change between receptor rigidity and flexibility.[1,2] Therefore, calix[4]arene derivatives are used for binding various small molecules and ions.[3–5]

Functionalization of phenol groups, aromatic and bridged fragments in calixarenes by corresponding organophosphorus reagents dramatically changes the effectiveness and selectivity of binding ions and neutral organic molecules.[6,7] The introduction of two α-aminophosphonate fragments in 1,3-positions at the upper and lower rims of a calix[4]arene platform was shown[8] to lead to a change in their complexing properties toward aromatic α-amino acids in comparison with their acyclic analogues.

The proton-donating ability of phosphonoyl groups and their reduced self-association ability make organophosphorus compounds the promising effective receptors and anion carriers.[7] Thus, it was interesting to prepare new substituted at the lower rim calix[4]arenes, containing phosphonoyl groups, and to study their complexing ability toward anions.



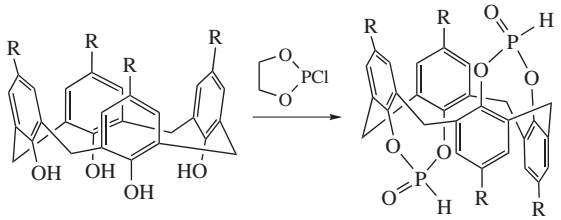
Scheme 1

We used the reaction of bis- and tetrakis-phenols with ethylene chlorophosphite (ECP). It is known that the reaction of this compound with phenol affords the phenyl ester of 2-chloroethylphosphorous acid.[9] We carried out the reaction of bisphenol with ECP in a 1:2 molar ratio. However, cyclic phosphite **2** was obtained instead of expected bis(hydrogenphosphite) **3** (Scheme 1). According to reported data,[10] a part of the phosphorylation reagent can be spent for secondary reaction – polymerization, so we employed a fourfold excess of ECP in reaction with bisphenol **1**. However, in this case, phosphite **2** was isolated in 96% yield.†

Apparently, formation of compound **2** results from intramolecular transesterification of the vicinal hydroxyl group in originally formed monophosphorylated derivative. Note that using ECP as phosphorylating reagent has advantages in comparison with the known synthesis of similar compounds by interaction with PCl_3.[11]

Treatment of *p-tert*-butylcalix[4]arene **4** with ECP (a 1:4 ratio) under similar conditions gave a high-melting crystalline compound after 6 h in 82% yield. To confirm the formation of compound **5** (Scheme 2), NMR and IR spectroscopy and mass spectrometry were used. ^{31}P NMR spectrum of **5** in $CDCl_3$ shows only one signal at –0.4 ppm ($^1J_{PH}$ 779.3 Hz).

The presence of two doublets (3.59 and 4.47 ppm, AB spin system, $^2J_{HH}$ 14.9 Hz) and a singlet at 4.12 ppm, which correspond to the methylene bridge protons of calix[4]arene in ^{1}H NMR spectrum, clearly indicate the 1,2-*alternate* conformation of calix[4]arene **5**. That was also confirmed by the appearance of two signals at 31.4 ppm in its ^{13}C NMR spectrum.[12]



4 R = Bu^t
6 R = H

5 R = Bu^t
7 R = H

Scheme 2

† For preparation procedure and characteristics of 2-*H*-5,15-di(*tert*-butyl)-7,13-dimethyl-2-oxodibenzo[*d*,*g*]-1,3,2-dioxaphosphocin **2**, see Online Supplementary Materials.