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Phosphorylation of *p-tert*-butyl(thia)calixarenes by ethylene chlorophosphite

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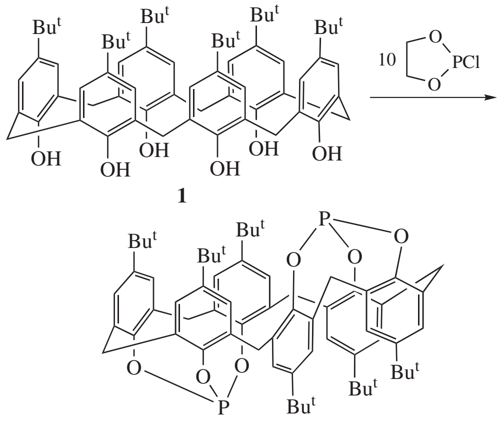
The one-step synthesis of a macrocyclic node was performed by the interaction of thiacalix[4]arene with ethylene chlorophosphite; new cyclic derivatives of calix[*n*]arenes containing phosphorus fragments at the lower rim in the 1,2- (*n* = 4) and 1,2,3-*alternate* (*n* = 6) configurations were obtained.

High interest in (thia)calix[*n*]arenes results from their applications in the extraction of metals, as membrane carriers, catalytic systems, *etc*.[1,2] Various derivatives of these macrocyclic compounds have been obtained,[3] in particular, the phosphorus derivatives of (thia)calix[*n*]arenes.[4–7]

Previously, it was determined that the interaction of calix[4]arene derivatives with ethylene chlorophosphite (ECP) unexpectedly leads to the formation of phosphonoyl derivatives in the 1,2-*alternate* configuration capable of selectively binding to the fluoride ion.[8] In this context, we studied the reaction of ECP with conformationally flexible *p-tert*-butylcalix[6]arene and *p-tert*-butylthiacalix[4]arene.

We found that a reaction of ECP with *p-tert*-butylcalix[6]arene **1** in *p*-bromotoluene at 150 °C, at reagent ratios of 1:3 and 1:6, does not occur. A ten-fold excess of a phosphorylating reagent in the reaction media leads to the formation of *p-tert*-butylcalix[6]arene bisphosphite **2** in the 1,2,3-*alternate* conformation (Scheme 1).[†] The preparation of phosphites on a calixarene platform by the treatment of a macrocyclic compound with PCl_3 has been described in the literature, though the obtained compounds were in the *cone* configuration.[9]



Scheme 1

The absorption bands of vibrations of the phosphoryl group and the P(O)H fragment are absent from the IR spectrum of compound **2**; however, there is an absorption band at 853 cm^{-1}, which corresponds to the $P(O–C)_3$ fragment. In the ^{31}P NMR spectrum of the macrocycle, a signal at 103.7 ppm is characteristic of phosphites. In the ^1H NMR spectrum of calix[6]arene **2**, aromatic protons are present as a singlet at 7.16 ppm and an AB spin system at 7.11 and 6.70 ppm with $^4J_{HH}$ 2.4 Hz. Methylene protons, which are characteristic of the macrocycle conformation, appear as a singlet at 3.74 ppm and an AB spin system at 4.55 and 3.56 ppm with $^2J_{HH}$ 13.4 Hz. This confirms the fact that macrocycle **2** is in the 1,2,3-*alternate* conformation. The signals of *tert*-butyl protons are observed as two singlets at 1.58 and 1.16 ppm with a 2:1 ratio of integral intensities, respectively. In the chemical ionization mass spectrum of compound **2**, an intense (100%) peak of the molecular ion with *m*/*z* 1028.5 was recorded.

The yield of product **2** was 48%. Apparently, the reaction time increased as compared with (*p-tert*-butyl)calix[4]arenes[8] as a result of the high conformational flexibility and low structure preorganization of **1** for interaction with ECP. Obviously, ECP is consumed in the polymerization reaction. Thus, an excess of the phosphorylating reagent in the reaction media is required for the formation of macrocycle **2**. The synthesis of *p-tert*-butylcalix[6]arene bisphosphite **2** may be performed in accordance with a published procedure[8] to afford a phosphonoyl compound. However, the presence of a large excess of ECP in the reaction mixture, which can also act as a chlorinating reagent on the phosphonoyl derivative, and the presence of a third neighboring OH group in the macrocyclic structure leads to etherification at the phosphorus atom and the formation of phosphite.

Thus, increasing the conformational flexibility of calix[*n*]arene macrocycle would imply using a large excess of ECP in the reaction mixture to obtain the product. Furthermore, the occurrence of additional reaction centers in calix[6]arene **1** suggests that the reaction does not stop at the synthesis stage of the phosphonoyl compound but continues to result in the phosphite.

Next, we studied the interaction of ECP with *p-tert*-butylthiacalix[4]arene **3**. After 6 h, the initial thiacalixarene was quan-

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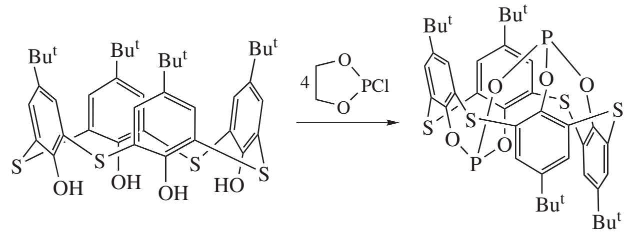
[†] *5,11,17,23,29,35-Hexa-*tert*-butyl-μ-37,38,39-phosphite-μ-40,41,42-phosphitecalix[6]arene* **2**. The mixture of 1.00 g (1.02 mmol) of 5,11,17,23,29,35-hexa-*tert*-butyl-37,38,39,40,41,42-hexahydroxycalix[6]arene and 0.91 ml (10.27 mmol) of ECP in 30 ml of *p*-bromotoluene in an argon atmosphere was heated with stirring for 6 h at 150 °C. Then the solvent was removed followed by chloroform extraction. The solvent was evaporated under reduced pressure. Yield of product **2**, 0.51 g (48%), mp 264 °C. IR (KBr, ν_{max}/cm^{-1}): 853 [$P–(O–C)_3$], 1198 (P–*O*–*Ph*). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.16 (s, 4H, H_{Ar}), 7.11 (d, 4H, H_{Ar}, $^4J_{HH}$ 2.4 Hz), 6.70 (d, 4H, H_{Ar}, $^4J_{HH}$ 2.4 Hz), 4.55 (d, 4H, Ar–CH_2–Ar, $^2J_{HH}$ 13.4 Hz), 3.74 (s, 4H, Ar–CH_2–Ar), 3.56 (d, 4H, Ar–CH_2–Ar, $^2J_{HH}$ 13.4 Hz), 1.58 (s, 36H, Ar–CMe_3), 1.16 (s, 18H, Ar–CMe_3). ^{31}P NMR (121 MHz, $CDCl_3$) δ: 103.7 (s). MS (CI) *m*/*z*: 1028.5 (M^+). Found (%): C, 76.94; H, 7.49; P, 6.17. Calc. for $C_{66}H_{78}O_6P_2$ (%): C, 77.02; H, 7.64; P, 6.02.



3

4

Scheme 2

titatively isolated using equimolar amounts of compound **3** and ECP (1:2). At molar ratios of 1:4 and 1:8 between the reagents, colorless crystalline compound **4** with high-melting point was formed (Scheme 2).[‡]

In the ^{31}P NMR spectrum without proton suppression, the phosphorus atoms of macrocycle **4** appear as a singlet at 121.9 ppm in the field characteristic of the trivalent three-coordinated phosphorus atom. The IR spectrum of product **4** shows bands at 821 and 932 cm^{-1} corresponding to the vibrations of the *O–P*O$_2$ and P–O–P fragments, respectively. At the same time, bands corresponding to the P(O)H fragment and the phosphoryl group are absent. In ^{1}H NMR spectrum of macrocycle **4**, *tert*-butyl protons are observed as a singlet at 1.24 ppm and aromatic protons manifest themselves as an AB spin system at 7.55 and 7.61 ppm with $^4J_{HH}$ 2.5 Hz.

The spectral data indicate that product **4** has a highly symmetrical structure. The results of the mass-spectrometric study of thiacalix[4]arene **4** finally confirmed that the reaction of *p-tert*-butylthiacalix[4]arene with ECP leads to pyrophosphite. NMR data indicate that macrocycle **4** has the 1,2-*alternate* conformation, which is consistent with published data.[10] Thus, the presence of two doublets due to aromatic protons in the NMR spectrum as an AB spin system is characteristic of this conformation, which was established earlier by 1D and 2D NMR spectroscopy and X-ray analysis.[10] Note that the two phosphorus atoms are connected by an oxygen bridge through the macrocyclic ring. Earlier, macrocycles with the pyrophosphate group at the lower rim were obtained by the pyrolysis of corresponding diethylphosphate esters of classical calix[*n*]arenes in a vacuum.[11]

For the refinement of the molecular structure of synthesized node **4**, molecular modeling at the semiempirical level using the quantum-mechanical method PM3 was carried out[§] (Figure 1). The length of the P–O–P bond in molecular node **4** is 3.30 Å, which is consistent with the literature data[12,13] for pyrophosphites and pyrophosphates. It is known that the P–O–P angles of the latter ones are in the range of 120–180°.[12,13] According to the molecular modeling the P–O–P angle in compound **4** is 169°.

The formation of product **4** by the interaction of thiacalix[4]arene **3** with ECP can occur *via* the highly reactive intermediate – phosphonoyl derivative similar to *p-tert*-butylcalix[4]arene bis(hydrogen phosphite) in the 1,2-*alternate* conformation.[8] Note that the reaction of bisphenol containing a bridging sulfur atom with ECP[¶] indirectly confirms the formation of a similar structure. The presence of only four neighboring phenolic groups in macrocycle **3**, in contrast to *p-tert*-butylcalix[6]arene, leads to the formation of pyrophosphite rather than phosphite. However, as a result of increasing the size of a molecular cavity in compound **3**, as compared with *p-tert*-butylcalix[4]arenes, the generation of the bridge structure (–O–) within the macrocycle becomes possible. It can be assumed that the intramolecular etherification of the phosphorus atom occurs to afford pyrophosphite **4**.

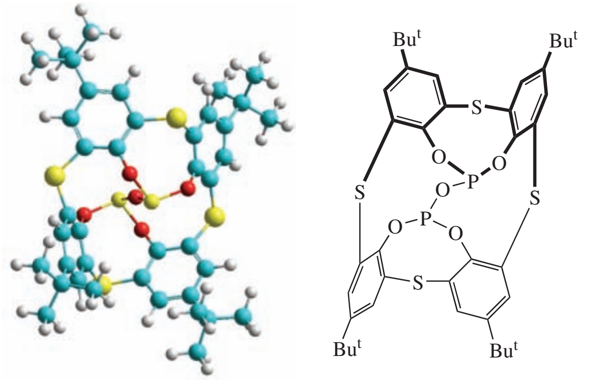


Figure 1 The geometry of molecular node **4** calculated by the PM3 method.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2012.01.007.

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[‡] *5,11,17,23-Tetra-*tert*-butyl-μ-25,26,27,28-pyrophosphitethiacalix[4]arene* **4**. The mixture of 1.00 g (1.39 mmol) of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxythiacalix[4]arene and 0.49 ml (5.56 mmol) of ECP in 20 ml of *p*-bromotoluene in an argon atmosphere was heated with stirring for 6 h at 150 °C. Then, the solvent was removed and the residue was extracted by a small amount of CCl$_4$. The solvent was removed. A pure sample of **4** was obtained by recrystallization of the resulting solid from CCl$_4$–*n*-hexane. Yield of product **4**, 0.59 g (56%), mp 338 °C. IR (KBr, ν_{max}/cm^{-1}): 821 (*O–P*O$_2$), 932 (P–O–P), 1266 (P–*O–Ph*). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 7.61 (d, 4H, H$_{Ar}$, $^4J_{HH}$ 2.5 Hz), 7.55 (d, 4H, H$_{Ar}$, $^4J_{HH}$ 2.5 Hz), 1.24 (s, 36H, Ar–C*Me*$_3$). ^{31}P NMR (121 MHz, CDCl$_3$) δ: 121.9 (s). MS (CI), *m/z*: 794.0 (M$^{+\cdot}$). Found (%): C, 60.41; H, 5.68; P, 7.69. Calc. for $C_{40}H_{44}S_4O_5P_2$ (%): C, 60.43; H, 5.58; P, 7.79.

[§] Molecular mechanics MM+ and semiempirical method PM3 included in the MOPAC 2009 package were used.

[¶] For the reaction of bisphenol with ECP, see Online Supplementary Materials.