Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2012, **22**, 21–22
Mendeleev Communications

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

Ivan I. Stoikov,* Olga A. Mostovaya, Alena A. Yantemirova, Igor S. Antipin and Alexander I. Konovalov

A. M. Butlerov Chemical Institute, Kazan (Volga Region) Federal University, 420008 Kazan, Russian Federation. Fax: +7 843 233 7416; e-mail: Ivan.Stoikov@mail.ru

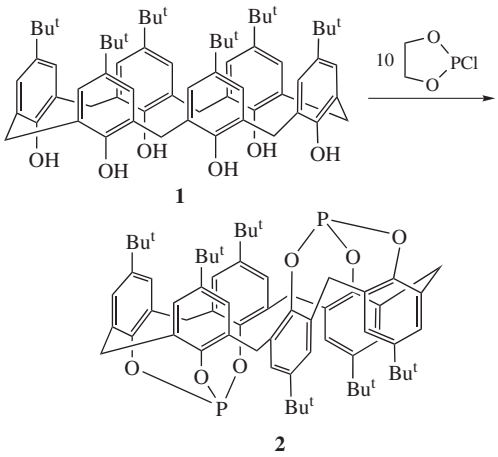
DOI: 10.1016/j.mencom.2012.01.007

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-

† *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–C*H*$_2$–Ar, $^2J_{HH}$ 13.4 Hz), 3.74 (s, 4H, Ar–C*H*$_2$–Ar), 3.56 (d, 4H, Ar–C*H*$_2$–Ar, $^2J_{HH}$ 13.4 Hz), 1.58 (s, 36H, Ar–C*Me*$_3$), 1.16 (s, 18H, Ar–C*Me*$_3$). ^{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.