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Introduction of Diphenylphosphinite Functional Groups onto Selected Positions on the Lower Rim of Calix[4]arenes and Calix[6]arenes

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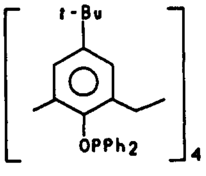
Calixarenes are a class of cyclic oligomers produced by the condensation of para-substituted phenols with formaldehyde.[1,2] The term "calixarene" was chosen for these compounds because it best describes the shape of these cyclic tetramers when they are present in the cone conformation. These compounds are receiving considerable interest because they can function as hosts for the clathrate encapsulation of small molecules within their cavities.[3] The two most frequently used calixarenes are the cyclic tetramers and hexamers, both of which can adopt different conformations other than that of the cone. Our interest in these compounds lies in their potential use as platforms for sequenced tricoordinate phosphorus groups on the lower rim. In this communication we show how, by using methoxy groups to block specific sites, we can introduce substituted phosphinite groups into chosen positions along the lower rim. Since compounds containing tricoordinate phosphorus are widely used as ligands for metal ions, this ability to control both the number and the geometric arrangement of the substituted phosphinite groups on this calixarene rim offers a potential new class of versatile ligands. Recently the fully hydroxylated *tert*-butylcalix[4]arene has been reacted with chlorodiphenylphosphine to give 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis((diphenylphosphino)oxy)calix[4]arene (**1**), and the compound was used as a phosphorus donor ligand for copper(I).[4] This compound **1** is the only example of a calixarene that has a tricoordinate phosphorus moiety attached to the *lower* rim.[5] This communication reports the use of selective methylation to block positions on the calixarene in order to bind the diphenylphosphinite moiety at specific hydroxylated sites on this lower rim.



1

tert-Butylcalix[4]arene can be converted into the symmetrical dimethoxy compound 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-dimethoxycalix[4]arene (**2**) by treatment with potassium carbonate and then with methyl-*p*-toluenesulfonate.[6] Using similar reaction conditions, we have now prepared 5,11,17,23,29,35-hexa-*tert*-butyl-37,39,41-trihydroxy-38,40,42-trimethoxycalix[6]arene (**3**) from *tert*-butylcalix[6]arene (eq 1).[7-9] When a similar reaction is carried out with the unsubstituted calix[6]arene, however, the product is 37,38,39-trihydroxy-40,41,42-trimethoxycalix[6]arene (**4**) (eq 2).[10] This compound **4** has methoxy groups in *adjacent* positions on the lower rim, rather than in *alternating* positions as found for compounds **2** and **3**. This difference in substitution patterns in the para-substituted and unsubstituted compounds results from the reduced steric interactions in the latter compound. In each case, methoxylation of the first hydroxyl group leads to increase steric hindrance at the lower rim, especially for attack at an adjacent hydroxy group. For the unsubstituted compound, however, steric relief can be gained by adoption of the partial cone conformation

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(1) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, England, 1989.

(2) Vicens, J.; Böhmer, V. *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Kluwer: Boston, MA, 1991.

(3) Bauer, L. J.; Gutsche, C. D. *J. Am. Chem. Soc.* **1985**, *107*, 6063–9. Shinkai, S. *Pure Appl. Chem.* **1986**, *58*, 1523–8. Shinkai, S.; Mori, S.; Koreishi, H.; Tsubaki, T.; Manabe, O. *J. Am. Chem. Soc.* **1986**, *108*, 2409–16. Chang, S. K.; Hwang, H. S.; Son, H.; Yauk, J.; Kang, Y. S. *J. Chem. Soc., Chem. Commun.* **1991**, 217–8.

(4) Floriani, C.; Jacoby, D.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1376–7.

(5) An example of a calix[4]arene with a diphenylphosphino group on the *upper* rim has recently been published; see: Hamada, F.; Fukugaki, T.; Murai, K.; Orr, G. W.; Atwood, J. L. *J. Incl. Phenom. Mol. Recog. Chem.* **1991**, *10*, 57–61.

(6) Dijkstra, P. J.; Bruniak, J. A.; Bugge, K. E.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1989**, *111*, 7567–75.

(7) Spectral data for **3** are as follows. FAB mass spectrum: *m/z* 1015. Anal. Calcd for $C_{69}H_{90}O_6{\cdot}CH_3OH$: C, 80.3; H, 9.04. Found: C, 80.0; H, 9.07. ^{1}H NMR ($CDCl_3$): δ 1.10 s (27H, $C\mathit{H}_3$), 1.19 s (27H, $C\mathit{H}_3$), 3.46 s (9H, $OC\mathit{H}_3$), 3.88 s (12H, $C\mathit{H}_2$), 6.77 s (3H, O*H*), 6.89 s (6H, C*H*), 7.01 s (6H, C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.8 s ($\mathit{C}H_2$), 31.2 s ($C(\mathit{C}H_3)_3$), 31.5 s ($C(\mathit{C}H_3)_3$), 33.9 s ($\mathit{C}(CH_3)_3$), 34.1 s ($\mathit{C}(CH_3)_3$), 61.0 s ($O\mathit{C}H_3$), 125.7, 126.6, 132.4, 142.4, 146.8, 149.8, 152.5 all s (*C*H and *C*). The ^{1}H NMR spectrum of **3** in $CDCl_3$ shows that the compound is conformationally labile. At 25 °C the methylene resonance at δ 3.88 is a sharp singlet, but at −50 °C it is beginning to broaden. By contrast, the unsubstituted calix[6]arene has been found to show a multiplet of 8 peaks at −50 °C, whereas the fully methoxylated calix[6]arene is reported to still show a sharp singlet even at −60 °C (see: Gutsche, C. D.; Bauer, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 6052–9. Gutsche, C. D.; Bauer, L. J. *J. Am. Chem. Soc.* **1985**, 6059–63). The mobility of **3**, therefore, appears to be intermediate between that of the fully hydroxylated and the fully methoxylated compounds.

(8) Since completion of this work, others have prepared this compound: Casnati, A.; Minari, P.; Pochini, A.; Ungaro, R. *J. Chem. Soc., Chem. Commun.* **1991**, 1413–4.

0020-1669/92/1331-4213\$03.00/0

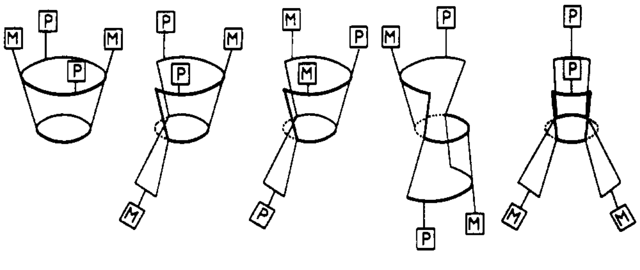
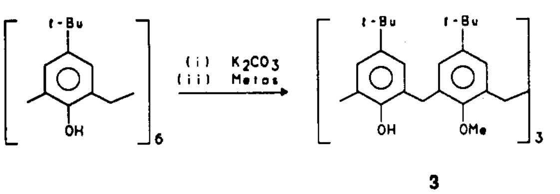
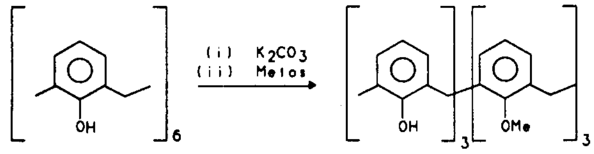


Figure 1. The five possible conformers of compound 4. The boxed-in "M" refers to OMe, and the boxed-in "P" refers to $OPPh_2$.



(1)

3

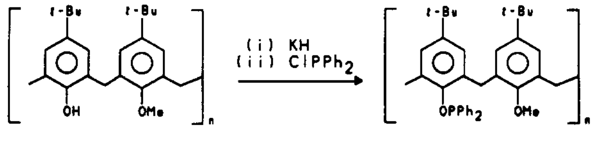


(2)

4

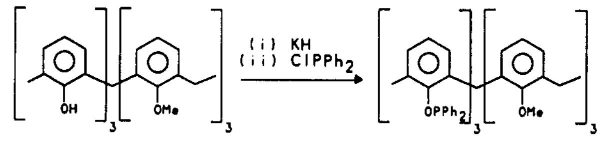
with the methoxy group pointing away from the lower rim. For the analogous compound with tertiary butyl substituents at the para positions of the upper rim, such an inversion will increase steric repulsions because the tertiary butyl group is more bulky than a methoxy group.

When the calix[4]arene **2** and the calix[6]arenes **3** and **4** are sequentially reacted with potassium hydride and then with chlorodiphenylphosphine, the compounds 5,11,17,23-tetra-*tert*-butyl-25,27-bis((diphenylphosphino)oxy)-26,28-dimethoxycalix[4]arene (**5**), 5,11,17,23,29,35-hexa-*tert*-butyl-37,39,41-tris((diphenylphosphino)oxy)-38,40,42-trimethoxycalix[6]arene (**6**), and 37,38,39-tris((diphenylphosphino)oxy)-40,41,42-trimethoxycalix[6]arene (**7**) are obtained in 30–40% yield (eqs 3 and 4).[11,12] These compounds have alternating (**5** or **6**) or sequential (**7**) diphenylphosphinite and methoxy groups on the lower rim of the calixarene.



(3)

$n = 2$ (**5**), 3 (**6**)



(4)

4 7

Calix[4]arenes can adopt four conformations. These four conformations are the cone, the 1,2-alternate, the 1,3-alternate, and the partial cone. For a symmetrically disubstituted compound such as **2** or **5**, however, two different partial cone conformers are now possible. One of these conformers (A) has the methoxy groups pointing away from the lower rim, and the other (B) has the diphenylphosphinite groups pointing away (Figure 1). Compound **5** is conformationally rigid in solution at 25 °C, and its conformation can be assigned as the partial cone A on the basis of its NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum of **5** shows a singlet at δ 114.2, thereby eliminating the partial cone conformation B. The ^1H NMR spectrum shows two singlet resonances for the methoxy groups at δ 2.38 and 3.07, along with four sets of doublet resonances due to the methylene groups at δ 3.13 ($^2J(HH) = 12.0$ Hz), 3.62 ($^2J(HH) = 15.4$ Hz), 4.05 ($^2J(HH) = 15.4$ Hz), and 4.29 ($^2J(HH) = 12.0$ Hz). The presence of the two methoxy resonances eliminates all structures except the partial cone conformation A in Figure 1. This assignment is further supported by the observation of the four sets of doublet methylene resonances arising from the presence of pairs of nonequivalent methylenic groups on opposite ends of the lower calixarene rim, along with a second pairwise inequivalence caused by each methylene group having an axial and an equatorial pair of hydrogens.

For the diphenylphosphinite-substituted calix[6]arene (**6**), the $^{31}P\{^1H\}$ NMR spectrum shows a single peak at δ 117.2, and the ^1H NMR spectrum shows a single resonance due to the methoxy hydrogens δ 2.34, in agreement with the alternating sequence of

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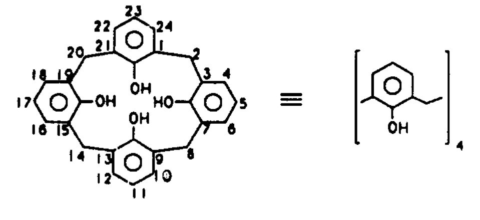
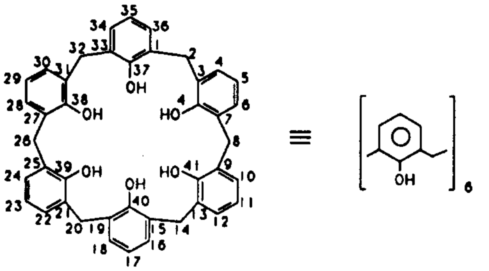
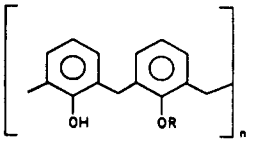
(9) The numbering and abbreviation systems used are taken from ref 1. These are as follows:

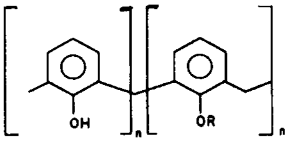




For compounds with *alternating* substituents R we use the abbreviation A, and for those with *adjacent* substituents R we use the abbreviation B.



A



B

(10) Spectral data for **4** are as follows. FAB mass spectrum: *m/z* 679. Anal. Calcd for $C_{45}H_{42}O_6 \cdot CH_3OH \cdot CHCl_3$: C, 68.0; H, 5.71. Found: C, 67.5; H, 5.80. ^1H NMR ($CDCl_3$): δ 3.29 s (3H, OCH_3), 3.77 s (4H, CH_2), 3.86 s (4H, CH_2), 3.98 d (6H, OCH_3), 4.05 s (4H, CH_2), 6.68–7.11 m (18H, CH(phenyl)), 7.58 s (1H, OH), 8.42 s (2H, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.6 (CH_2), 31.1 (CH_2), 31.5 (CH_2), 60.6 (OCH_3), 61.8 (OCH_3), 120.2–156.7 all s (20 CH and C peaks).

(11) Spectral data for **5** are as follows. FAB mass spectrum: *m/z* 1045. ^1H NMR (C_6D_6): δ 1.10 s (18H, CH_3), 1.48 s (18H, CH_3), 2.17 s (3H, OCH_3), 2.80 s (3H, OCH_3), 2.90 d (2H, CH_2, $^2J(HH) = 12.0$ Hz), 3.82 d (2H, CH_2, $^2J(HH) = 18.0$ Hz), 4.41 d (2H, CH_2, $^2J(HH) = 12.0$ Hz), 4.53 d (2H, CH_2, $^2J(HH) = 18.0$ Hz), 7.18–7.42 m (28H, CH(phenyl)). $^{13}P\{^1H\}$ NMR: δ 114.2.

(12) Spectral data for **6** are as follows. FAB mass spectrum: *m/z* 1568. ^1H NMR (CD_2Cl_2): δ 0.78 s (27H, CH_3), 1.32 s (27H, CH_3), 2.34 s (9H, OCH_3), 3.06 d (6H, CH_2, $J(HH) = 14.0$ Hz), 4.20 d (6H, CH_2, $J(HH) = 14.0$ Hz), 7.58 m (42H, CH(phenyl)). $^{13}P\{^1H\}$ NMR (C_6D_6): δ 117.2.

(13) Spectral data for **7** are as follows. FAB mass spectrum: *m/z* 1231. ^1H NMR (C_6D_6): δ 3.03 s (6H, OCH_3), 3.34 s (3H, OCH_3), 3.86 s (4H, CH_2), 3.85 s (4H, CH_2), 4.05 s (4H, CH_2), 6.80 m (48H, CH(phenyl)). $^{13}P\{^1H\}$ NMR: δ 117.6 s (1P), 118.1 s (2P).

methoxy and diphenylphosphinite groups. For the diphenylphosphinite-substituted calix[6]arene (**7**), the $^{31}P\{^1H\}$ NMR spectrum shows peaks at δ 117.6 and 118.1 in a ratio of 1:2, and the ^1H NMR spectrum shows peaks at δ 3.34 and 3.03 for the methoxy hydrogens, also in a 1:2 ratio. We presently have no information concerning the conformational preferences of compounds **6** and **7**.

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