

A Facile Method to Synthesize Spiro-calix[4]arenes

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Abstract: The spiro-calix[4]arenes **3a-b** can be synthesized conveniently by the reaction of *p*-tert-butylcalix[4]arene (**1a**) or calix[4]arene (**1b**) with pentaerythritol tetrakis(2-chloroacetate) (**2**).

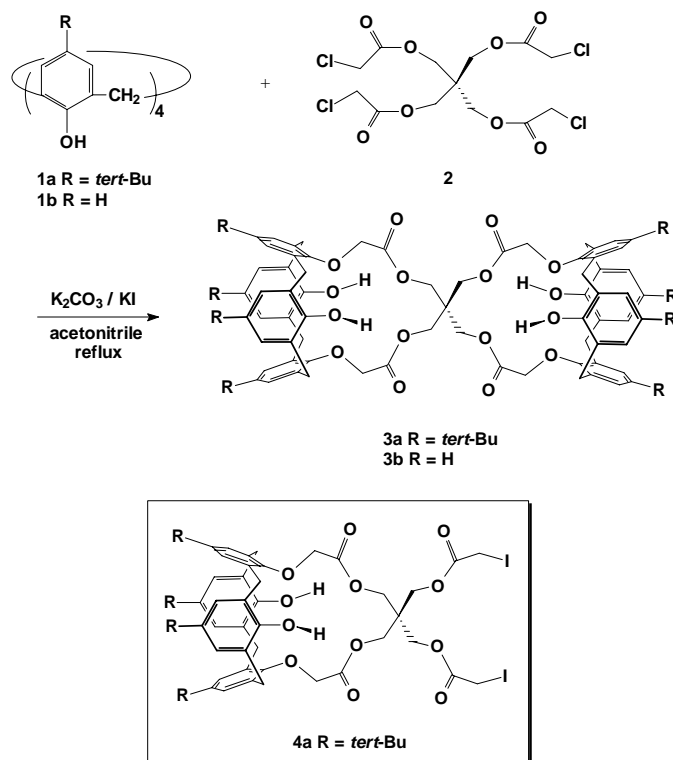
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Calixarenes have absorbed considerable interests for their outstanding abilities of recognition for cations, anions and organic molecules¹. In order to include larger and more complex molecules, polytopic receptors were designed from two or more host macrocycles linked by one or several links. Therefore, double-calixarenes and oligocalixarenes have been synthesized and reviewed². Among these polytopic receptors, double-calixarenes can be used as the mimic of ion channel or to self-organize koilands including ditopic substrates³. Spiro-crown ethers⁴ and spiro-calixarenes⁵ have been reported and their properties of recognition for cations have been also investigated. In order to improve the approach of synthesis and to research the properties of different type of spiro-calixarenes, we synthesized conveniently the spiro-calix[4]arenes containing ester group.

p-tert-Butylcalix[4]arene (**1a**) or calix[4]arene (**1b**) reacts with 1/2 equivalent pentaerythritol tetrakis(2-chloroacetate) (**2**) in acetonitrile. In the presence of equivalent K₂CO₃ and KI, the mixture was refluxed for about 12~16 h. After work-up, spiro-calix[4]arene **3a** or **3b** is obtained in the yield of 60 or 65 %, respectively⁶. (**Scheme 1**) And if equivalent amount of pentaerythritol tetrakis(2-chloroacetate) (**2**) is added, the compound **4a** containing two 2-idoacetate groups could be separated, which was a very useful starting material for synthesis of functional calixarene derivatives⁷.

The structures of spiro-calixarenes **3a** and **3b** have been determined by the ¹H-NMR, ¹³C-NMR, MS, IR spectra and elemental analysis. In their IR spectra, the absorption at about 1750 cm⁻¹ suggested that these two compounds contain ester groups. In their ¹H-NMR spectra, the signals of protons of methylene group between two phenol rings appear in AB system, which suggest that these compounds are all in cone conformations.

Scheme 1



References and notes

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- 3a**: yield: 60 %; m.p. > 300 °C. MS (maldi-TOF): m/z 1615.9 (M^+Na). 1H -NMR ($CDCl_3$) δ 1.08 (s, 36H, $C(CH_3)_3$), 1.24 (s, 36H, $C(CH_3)_3$), 3.32 and 4.21 (AB, $J = 12.8$ Hz, 16H, $ArCH_2Ar$), 4.66 (s, 8H, CO_2CH_2), 4.67 (s, 8H, $ArOCH_2$), 6.95 (s, 8H, ArH), 7.00 (s, 8H, ArH), 7.65 (s, 4H, OH). ^{13}C -NMR ($CDCl_3$) δ 31.06, 31.60 ($C(CH_3)_3$), 32.13 ($ArCH_2Ar$), 33.76, 34.08 ($C(CH_3)_3$), 43.11 ($C(CH_2)_4$), 63.90 (CO_2CH_2), 72.83 ($ArOCH_2$), 125.23, 125.95, 127.19, 132.94, 141.61, 147.67, 149.30, 150.32 (ArC), 168.63 (CO_2); IR (KBr) ν 3480, 1751 (CO), 1485 cm^{-1} . Anal. Calcd. for $C_{101}H_{124}O_{16}$: C, 76.10; H, 7.84. Found: C, 75.75; H, 7.85.
3b: yield: 65 %; m.p. > 300 °C. MS (maldi-TOF): m/z 1167.2 (M^+Na). 1H -NMR ($CDCl_3$) δ 3.35 and 4.18 (AB, $J = 13.1$ Hz, 16H, $ArCH_2Ar$), 4.65 (s, 8H, CO_2CH_2), 4.77 (s, 8H, $ArOCH_2$), 6.64 (t, $J = 7.4$ Hz, 4H, ArH), 6.80 (t, $J = 7.3$ Hz, 4H, ArH), 6.95 (d, $J = 7.5$ Hz, 8H, ArH), 7.03 (d, $J = 7.5$ Hz, 8H, ArH), 7.99 (s, 4H, OH). ^{13}C -NMR ($CDCl_3$) δ 31.79 ($ArCH_2Ar$), 43.72 ($C(CH_2)_4$), 64.77 (CO_2CH_2), 73.39 ($ArOCH_2$), 119.67, 126.67, 128.06, 128.99, 129.74, 133.63, 151.02, 153.43 (ArC), 168.75 (CO_2); IR (KBr) ν 3392, 1749 (CO), 1467 cm^{-1} . Anal. Calcd. for $C_{69}H_{60}O_{16} \cdot H_2O$: C, 71.24; H, 5.37. Found: C, 71.11; H, 5.88.
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