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Letters to the Editor

Calix[4]resorcinolarenes with phosphinoylalkyl substituents on the lower rim of the molecule

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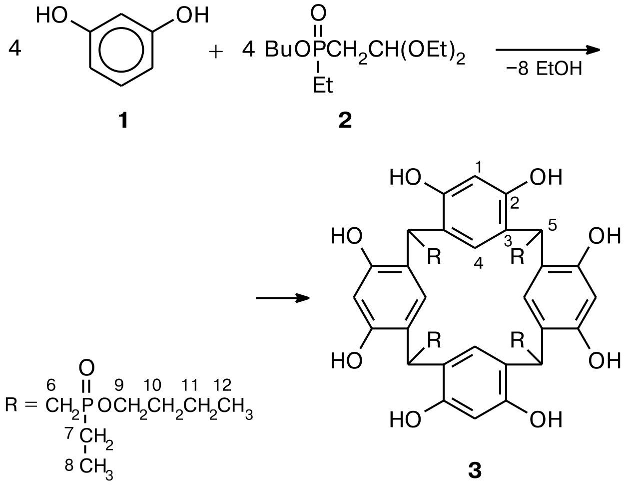
The method of synthesis of calix[4]resorcinolarenes is based on tetramerization of aliphatic and aromatic aldehydes with resorcinol.[1—3] The stability of calixarene macrocycles, which are bowl-shaped in the majority of cases, and the possibility of modifying their hydrophilic and hydrophobic fragments by organic and organometallic reagents make the chemistry of these compounds rather attractive and promising. Compounds of this type are of obvious interest as complexing agents, metal extractants, and polymer stabilizers. We were the first to attain one-step formation of a phosphorus-containing calixarene matrix *via* acid-catalyzed reaction of resorcinol (**1**) with a phosphorus-containing acetal (**2**). This gave the first representative of calix[4]resorcinolarene (**3**) bearing phosphinoylalkyl fragments on the lower rim of the molecule.

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in DMSO-d_6 on a Bruker MSL-400 instrument (400.13 MHz, 100.62 MHz, 166.93 MHz, respectively). The δ values were referred to the solvent signals (^{1}H, ^{13}C) or to an external standard (^{31}P), 85% H_3PO_4. Mass spectra were recorded on a MALDI 2 V5.2.0 instrument (1,8,9-tetrahydroxyanthracene as the matrix).



Phosphorus-containing acetal **2** was prepared by a known procedure.[4]

4,6,10,12,16,18,22,24-Octahydroxy-2,8,14,20-tetrakis{[butoxy(ethyl)phosphoryl]methyl}penta-

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cyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27), 15,17,19(26),21,23-dodecaene (3). A solution of acetal **2** (5.2 g, 4.8 mmol) in 5 mL of EtOH was added with cooling and stirring over a period of 0.5 h to a mixture of resorcinol **1** (2.15 g, 4.8 mmol), 20 mL of water, 15 mL of EtOH, and 5.2 mL of concentrated hydrochloric acid. The reaction mixture was heated with stirring (1 h, 50 °C) and kept for 5 days at 20 °C. The resulting oily layer was decanted, triturated with MeCN, washed with EtOH, and dried *in vacuo* (5 h, 90 °C, 10 Torr and 4 h, 90 °C, 0.02 Torr) to give 4.3 g (77%) of compound **3** as a white amorphous powder that gets dark on heating above 250 °C (deomp.). ^{1}H NMR, δ: 0.83 (m, 24 H, Me); 1.24 (m, 32 H, CH_2); 3.72 (m, 8 H, CH_2); 4.59 (m, 4 H, CH); 6.26 (br.s, 4 H, *o*-H arom.); 7.17 (br.s, 4 H, *m*-H arom.); 9.00 (br.s, 8 H, OH). ^{13}C NMR, δ: 4.27 (q, C(8), $^1J_{C,H}$ = 124.7 Hz, $^2J_{C,C}$ = 6.3 Hz); 12.49 (q, C(12), $^1J_{C,H}$ = 124.7 Hz); 17.28 (t, C(11), $^1J_{C,H}$ = 123.7 Hz); 19.52 (dt, C(7), $^1J_{P,C}$ = 90.6 Hz; $^1J_{C,H}$ = 119.8 Hz); 31.21 (t, C(10), $^1J_{C,H}$ = 120.3 Hz); 61.82 (t, C(9), $^1J_{C,H}$ = 125.6 Hz, $^2J_{P,C}$ = 9.0 Hz); 101.81 (d, C(4), $^1J_{C,H}$ = 121.7 Hz); 120.64 (s, C(3)); 128.22 (d, C(1), $^1J_{C,H}$ = 145.4 Hz); 152.65 (s, C(2)). ^{31}P NMR (DMSO), δ: 59.7. MS: *m/z* 1159 [M + Na]. IR, ν/cm^{-1}: 1150—1170 (P=O); 3100—3580 (OH). Found (%): C, 58.64; H, 8.22. $C_{56}H_{84}O_{16}P_4$. Calculated (%): C, 59.15; H, 7.39.

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