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Letters to the Editor

Calix[4]resorcinolarene with (thiophosphoryl)thiomethyl fragments on the lower rim of the molecule

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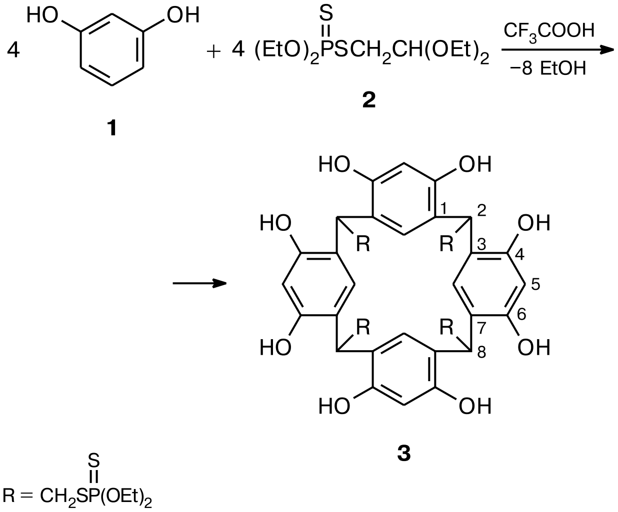
Functionalized calix[4]resorcinolarenes are recently being of great interest because can undoubtedly be used as complex-forming agents, metal extragents, and polymer stabilizers. In most cases, they were synthesized by tetramerization of aliphatic and aromatic aldehydes with resorcinol and other aromatic polyphenols.[1—3] We obtained the phosphorus-containing calixarene matrix by the one-step reaction of resorcinol (**1**) and phosphorus-containing acetal **2** under the acid catalysis conditions. As a result, the first representative of calix[4]resorcinolarenes (**3**) bearing the (thiophosphoryl)thiomethyl fragments on the lower rim of the molecule was obtained.



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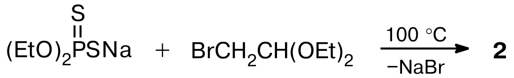
The starting acetal **2** was synthesized by the reaction of sodium diethyl dithiophosphate **4** with bromoacetal **5**.



$$\underset{\mathbf{4}}{(EtO)_2\overset{\overset{S}{\|}}{P}SNa} + \underset{\mathbf{5}}{BrCH_2CH(OEt)_2} \xrightarrow[-NaBr]{100\ ^{\circ}C} \mathbf{2}$$

^1H and ^{31}P NMR spectra were recorded on a Bruker MSL-400 instrument (400.13 MHz and 166.93 MHz, respectively) in DMSO-d_6. The δ values were calculated relatively to signals of residual protons of the deuterated solvent (^1H) and 85% H_3PO_4 served as the external standard (^{31}P). Mass spectra were recorded on a MALDI 2V5.2.0 instrument (1,8,9-trihydroxyanthracene matrix). IR spectra were obtained on a UR-20 spectrometer.

***O*,*O*-Diethyl-*S*-(2,2-diethoxyethyl) dithiophosphate (2).** A mixture of sodium diethyl dithiophosphate (**4**) (4.16 g, 20 mmol) and bromoacetal **5** (9.85 g, 50 mmol) was stirred for 1 h at 100 °C. After cooling to 20 °C, water (10 mL) and Et_2O (15 mL) were added to the reaction mixture. The ethereal layer was separated and dried over $MgSO_4$. The bromoacetal and Et_2O excess was removed in a vacuum of a water-aspirator pump. Compound **2** as a light yellow oil was obtained in 28% yield (1.7 g). Found (%): P, 9.98. $C_{10}H_{23}O_4PS_2$. Calculated (%): P, 10.26. ^1H NMR, δ: 1.12 (m, 12 H, Me); 2.71 (dd, 2 H, SCH_2, $^3J_{H,H} = 7.0$ Hz, $^3J_{P,H} = 10.2$ Hz); 3.48 (m, 4 H, $POCH_2$); 4.07 (q, 4 H, OCH_2, $J = 7.0$ Hz); 4.51 (t, 1 H, CH, $^3J = 7.0$ Hz). ^{31}P NMR, δ: 93.6.

4,6,10,12,16,18,22,24-Octahydroxy-2,8,14,20-tetrakis[(diethoxythiophosphoryl)thiomethyl]pentacyclo[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** (1.97 g, 6.5 mmol) in TFA (2 mL) was added dropwise to a solution of resorcinol (**1**) in TFA (7 mL). The oily layer formed was decanted and doubly precipitated with pentane from $CHCl_3$. Compound **3** as a white amorphous powder was isolated in 77% yield (1.61 g), m.p. 120 °C. Found (%): C, 44.77; H, 5.23; P, 10.17. $C_{48}H_{68}O_{16}P_4S_8$. Calculated (%): C, 45.00; H, 5.31; P, 9.69. IR, ν/cm^{-1}: 750—800 (P=S); 3100—3580 (OH). ^1H NMR, δ: 1.36 (m, 24 H, Me); 2.10 (m, 8 H, SCH_2); 4.16 (m, 16 H, OCH_2); 4.86 (m, 4 H, CH); 6.46 (br.s, 4 H, o-H_{arom}); 7.45 (br.s, 4 H, m-H_{arom}); 8.33 (br.s, 8 H, OH). ^{31}P NMR, δ: 92.8. MS: m/z 1305 [M + Na].

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