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LETTERS TO THE EDITOR

New Type of Calix[4]resorcinolarenes with Phosphorus-containing Alkyl Fragments in the Lower Rim

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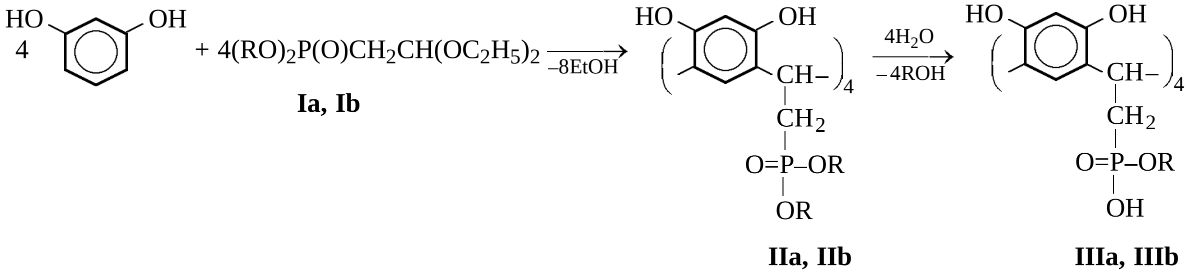
Calix[4]resorcinolarenes are commonly synthesized by tetramerization of aliphatic and aromatic aldehydes with resorcinol [1–3]. We have for the first time studied reaction of phosphorus-containing acetals with resorcinol under conditions of acid catalysis. This procedure allowed us to prepare first representatives of calix[4]resorcinolarenes **IIIa, IIIb** bearing phosphorus-containing fragments on the lower rim. Note that, instead of expected full phosphonates **IIa**, their hydrolysis products **IIIa, IIIb** are formed. This is evidently connected with hydrolysis of initially formed phosphorylated calix[4]resorcinolarenes **IIa** under the experimental conditions.



I–III, R = C_2H_5 (**a**), C_4H_9 (**b**).

4,6,10,12,16,18,22,24-Octahydroxy-2,8,14,20-tetra[(ethoxy)(hydroxy)phosphorylmethyl]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 (IIIa). A solution of 3.55 g of acetal **Ia** in 5 ml of ethanol was added to a mixture of 1.6 g of resorcinol, 10 ml of water, 5 ml of ethanol and 3.6 ml of concentrated sulfuric acid with stirring and cooling. The reaction mixture was stirred for 1 h at 20°C and then heated for 1 h at 50°C. The oilish layer was decanted, triturated with acetonitrile, filtered, and evaporated in a vacuum (10 mm). The residue was dried in a vacuum (0.04 mm) to isolate 2.0 g (59%) of compound **IIa**, mp 250°C (decomp.). ^{1}H NMR spectrum (methanol-d_4), δ, ppm (*J*, Hz): 1.40 t (12H, CH_3, $^3J_{HH}$ 7.0), 1.63 m (8H, CH_2P), 3.95 m (8H, OCH_2), 5.07 br.m (4H, CH), 6.50 s (4H, *o*-CH_{arom}), 7.25 s (4H, *m*-CH_{arom}). ^{13}C NMR spectrum (acetone-d_6, DMSO), δ_C, ppm (J, Hz): 17.35 q (CH_3, $^1J_{CH}$ 124.4), 63.45 t (CH_2O, $^1J_{CH}$ 142.6), 79.64 d.d (CH, $^1J_{CH}$ 149.0, $^2J_{CP}$ 7.0), 102.55 d (*m*-C_{arom}, $^1J_{CH}$ 155.9), 123.4 s (C_{arom}), 139.25 d (*o*-C_{arom}, $^1J_{CH}$ 153.55), 154.37 s ($C_{arom}OH$). ^{31}P NMR spectrum (acetone): δ_P 31.2 ppm. *M* 975. Found, %: C 48.75; H 5.77; P 12.86. $C_{40}H_{52}O_{20}P_4$. Calculated, %: C 49.18, H 5.33, P 12.70.

4,6,10,12,16,18,22,24-Octahydroxy-2,8,14,20-tetra[(butoxy)(hydroxy)phosphorylmethyl]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 (IIIb) was obtained analogously by addition of a solution of 1.75 g of acetal **Ib** in 4 ml of ethanol to a mixture of

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0.62 g of resorcinol, 8 ml of water, 8 ml of ethanol, and 1.4 ml of hydrochloric acid. Yield 1.2 g (78%), mp 165–166°C. ^{1}H NMR spectrum (methanol-d_4), δ, ppm (J, Hz): 1.10 t (12H, CH_3, $^3J_{HH}$ 7.0), 1.41–1.70 br.m (16H, CH_2), 1.89 m (8H, CH_2P), 4.20 m (8H, OCH_2), 5.17 br.m, (4H, CH), 6.48 s (4H, *o*-CH_{arom}), 7.32 s (4H, *m*-CH_{arom}). ^{13}C NMR spectrum (methanol-d_4), δ_C, ppm (J, Hz): 13.99 q (CH_3, $^1J_{CH}$ 124.4), 19.64 t [$(CH_2)_2$, $^1J_{CH}$ 122.06], 33.48 t (CH_2P, $^1J_{CH}$ 125.60), 66.71 t (CH_2O, $^1J_{CH}$ 142.60), 69.65 d.d (CH, $^1J_{CH}$ 150.90, $^2J_{CP}$ 7.04), 104.05 d (C_{meta}, $^1J_{CH}$ 155.90), 122.53 s (CH_{arom} CH), 129.96 d (*o*-C_{arom}, $^1J_{CH}$ 154.60), 154.26 s (C_{arom} OH). ^{31}P NMR spectrum: δ_P 31.14 ppm. *M* 1114. Found, %: C 52.55; H 6.43; P 11.85. $C_{48}H_{68}O_{20}P_4$. Calculated, %: C 52.94; H 6.25; P 11.40.

The ^{1}H NMR spectra were recorded on a Bruker WM-250 (250.13 MHz) spectrometer. The ^{31}P and ^{13}C NMR spectra were measured on a Bruker MSL-400 spectrometer (166.93 and 100.6 MHz) against residual proton signals of deuterated solvents (methanol-d_4, acetone-d_6) and external 85% phosphoric acid. The mass spectra were obtained on an MALDI-2 V5.2.0 spectrometer.

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