# Brief Communications

## Novel acetal-containing calix[4]resorcinolarene-based Mannich bases

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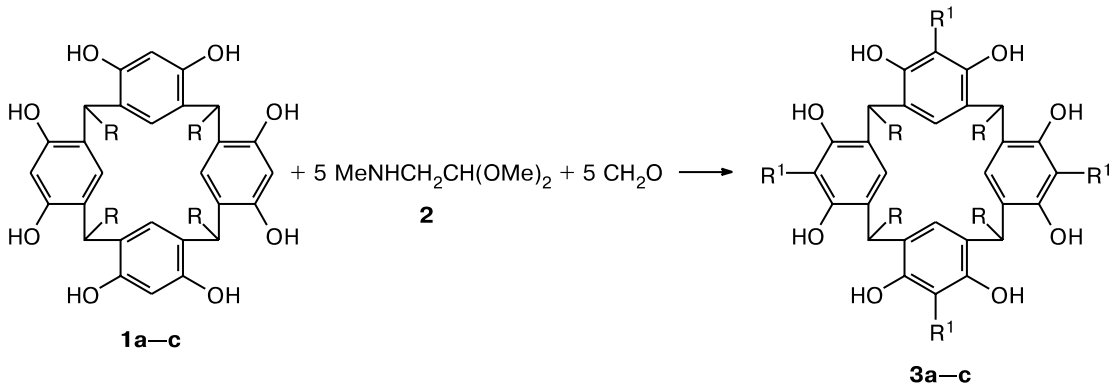
The reaction of calix[4]resorcinolarene with methylaminoacetaldehyde dimethyl acetal and formalin gave novel acetal-containing calix[4]resorcinolarene derivatives aminomethylated at the upper rim.

**Key words:** calix[4]resorcinolarenes, aminoalkylation, Mannich bases, acetals.

In the last decade, considerable interest arose in the chemistry of calixarenes. These cyclic condensation products from phenols and aldehydes contain reactive centers and thus can be further functionalized to give new types of spatially ordered structures for use as complexing and extracting agents, *etc*. Calix[4]resorcinolarenes containing *ortho*-aminomethyl fragments (relative to the hydroxy groups) in their aromatic rings are of undoubted interest as a starting spatially ordered matrix. The first representative of this class was obtained by the Mannich reaction of calix[4]resorcinolarene, formaldehyde, and a secondary amine.[1] Recently, we synthesized aminomethylated calix[4]resorcinolarenes containing NH groups and phosphonoylalkyl fragments at the upper rim of the molecule[2] and constructed a calixarene matrix by an acid-catalyzed reaction of resorcinol with a substituted acetal.[3] Now, it was interesting to obtain calix[4]resorcinolarenes bearing acetal fragments at the upper rim since their subsequent reactions with polyphenols can yield container-type and tubular structures. For this purpose, methylaminoacetaldehyde dimethyl acetal **2** was involved in the Mannich reaction with calixarenes **1a**—**c**; the calixarene : secondary amine : formaldehyde ratio was 1 : 5 : 5. The structures of compounds **3a**—**c** were proved by IR and $^1$H NMR spectroscopic data; their composition was confirmed by elemental analysis data.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2155—2156, October, 2003.

1066-5285/03/5210-2276 $25.00 




R = Me (**a**), Et (**b**), Pr (**c**); $R^1 = CH_2NMeCH_2CH(OMe)_2$

## Experimental

$^1$H NMR spectra were recorded on a Bruker MSL-400 instrument (400.13 MHz) in $CDCl_3$. The δ values were calculated with respect to the signals for residual protons of the solvent. IR spectra were recorded on a UR-20 instrument (Nujol) in the 400—3600 $cm^{-1}$ range.

Calix[4]resorcinolarenes **1a—c** were prepared according to a known procedure.[4] Compound **2** was purchased from Lancaster Co.

**4,6,10,12,16,18,22,24-Octahydroxy-5,11,17,23-tetrakis[(2,2-dimethoxyethyl)methylaminomethyl]-2,8,14,20-tetramethylpentacyclo[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 (3a).** Acetal **2** (1.43 g, 12 mmol) and aqueous 30% $CH_2O$ (1.20 g, 12 mmol) were successively added to a stirred solution of calixarene **1a** (1.31 g, 2.4 mmol) in 30 mL of 95% EtOH and 30 mL of benzene; the reaction mixture was kept at 20 °C for one day; then the solvent was removed *in vacuo* (water aspirator pump). The residue was reprecipitated from chloroform with hexane, and the product was filtered off and kept *in vacuo* (40 °C, 0.06 Torr) to a constant weight to give compound **3a** (2.19 g, 85%), m.p. 106—108 °C. Found (%): C, 62.67; H, 8.55; N, 4.71. $C_{56}H_{84}N_4O_{16}$. Calculated (%): C, 62.92; H, 7.87; N, 5.24. IR, ν/$cm^{-1}$: 1610 (CH arom.), 3300 (OH). $^1$H NMR, δ: 1.74 (d, 12 H, $CHC\underline{H}_3$, $J$ = 6.9 Hz); 2.31 (s, 12 H, NMe); 2.64 (br.m, 8 H, $NC\underline{H}_2CH$); 3.34 (s, 24 H, OMe); 3.77 (m, 8 H, $C_{arom}C\underline{H}_2N$); 4.51 (br.m, 8 H, $C\underline{H}Me$, $C\underline{H}(OMe)_2$); 7.05 (s, 4 H, $m$-$H_{arom}$); 8.33 (br.s, 8 H, HO).

**4,6,10,12,16,18,22,24-Octahydroxy-5,11,17,23-tetrakis(2,2-dimethoxyethyl)methylaminomethyl-2,8,14,20-tetraethylpentacyclo[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 (3b)** was obtained from calixarene **1b** (1.44 g, 2.4 mmol), acetal **2** (1.43 g, 12 mmol), and aqueous 30% $CH_2O$ (1.20 g, 12 mmol) as described for compound **3a**. The yield of compound **3b** was 2.43 g (90%), m.p. 116—118 °C. Found (%): C, 63.67; H, 7.55; N, 4.68. $C_{60}H_{92}N_4O_{16}$. Calculated (%): C, 64.06; H, 8.19; N, 4.98. IR, ν/$cm^{-1}$: 1610 (CH arom.), 3300 (OH). $^1$H NMR, δ: 0.89 (br.m, 12 H, $CH_2C\underline{H}_3$); 2.11 (m, 8 H, $MeC\underline{H}_2CH$); 2.35 (s, 12 H, NMe); 2.64 (br.m, 8 H, $NC\underline{H}_2CH$); 3.33 (s, 24 H, OMe); 3.85 (br.s, 8 H, $C_{arom}C\underline{H}_2N$); 4.18 (br.m, 4 H, $CH_2C\underline{H}(OMe)_2$); 4.53 (br.m, 4 H, $C_{arom}C\underline{H}CH_2$); 7.12 (s, 4 H, $m$-$H_{arom}$).

**4,6,10,12,16,18,22,24-Octahydroxy-5,11,17,23-tetrakis(2,2-dimethoxyethyl)methylaminomethyl-2,8,14,20-tetrapropylpentacyclo[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 (3c)** was obtained from calixarene **1c** (1.57 g, 2.4 mmol), acetal **2** (1.43 g, 12 mmol), and aqueous 30% $CH_2O$ (1.20 g, 12 mmol) as described for compound **3a**. The yield of compound **3c** was 2.06 g (73%), m.p. 102—104 °C. Found (%): C, 64.60; H, 8.67; N, 4.20. $C_{64}H_{100}N_4O_{16}$. Calculated (%): C, 65.08; H, 8.47; N, 4.75. IR, ν/$cm^{-1}$: 1610 (CH arom.), 3300 (OH). $^1$H NMR, δ: 0.95 (t, 12 H, $CHC\underline{H}_3$, $J$ = 7.0 Hz); 1.26 (m, 8 H, $CH_2C\underline{H}_2CH$); 2.17 (m, 8 H, $MeCH_2C\underline{H}_2$); 2.31 (s, 12 H, NMe); 2.60 (br.m, 8 H, $NC\underline{H}_2CH$); 3.33 (s, 24 H, OMe); 3.85 (br.s, 8 H, $C_{arom}C\underline{H}_2N$); 4.31 (br.m, 4 H, $CH_2C\underline{H}(OMe)_2$); 4.51 (br.m, 4 H, $C_{arom}C\underline{H}CH_2$); 7.13 (s, 4 H, $m$-$H_{arom}$); 8.25 (br.s, 8 H, HO).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 02-03-33037) and the International Bureau of the Federal Ministry of Education and Research (BMBF, RUS 02/034) (Germany).

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*Received July 17, 2003*