Russian Journal of General Chemistry, Vol. 71, No. 3, 2001, pp. 480–481. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 3, 2001, pp. 517–518.
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LETTERS TO THE EDITOR

Aminomethylated Calix[4]resorcinolarenes Having NH Groups

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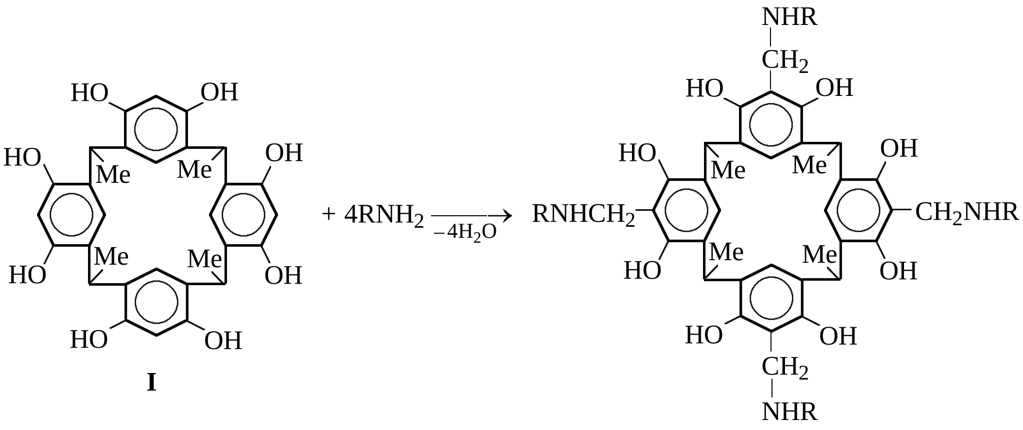
Received August 16, 2000

An important problem in the chemistry of calixarenes [1–3] is elaboration of procedures for their functionalization with the goal of obtaining efficient complexing agents, extractants, etc. Undoubtedly, calix[4]resorcinolarenes having aminomethyl fragments in the *ortho*-position with respect to the aromatic hydroxy groups attract interest as initial spatially ordered matrix. The first representative of this class of compounds was prepared by the Mannich reaction of calix[4]resorcinolarene **I**, formaldehyde, and secondary amine [4]. It was also shown that analogous reactions with primary amines result in formation of intractable mixtures of products. We were the first to obtain aminomethyl derivatives **IIIa** and **IIIb** having NH groups by the Mannich reaction with promary amines **IIa** and **IIb**. The use of enantiomerically pure (–)-(*S*)-α-methylbenzylamine allowed us to synthesize the first calixarene possessing optically active aminomethyl moieties on the upper rim.



I

IIIa, IIIb

RNH_2 = $H_2NCH_2CH_2NMe_2$ (**a**), (–)-(*S*)-$H_2NCH(Me)Ph$ (**b**).

4,6,10,12,16,18,22,24-Octahydroxy-5,11,17,19-tetrakis(2-dimethylaminoethylaminomethyl)-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 (IIIa). To a solution of 2 g of calixarene **I** in 30 ml of 1:1 benzene–ethanol we added 1.62 g of amine **IIa** and 1.37 g of a 40% formaldehyde solution. The mixture was kept for 24 h at 20°C, the solvent was removed under reduced pressure (water-jet pump), and the residue was washed with acetonitrile and diethyl ether and dried in a vacuum (80–100°C, 0.04 mm, oil pump) until constant weight. Yield 3 g (86%). mp >270°C (decomp.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.70 d (12H, CH_3CH, $^3J_{HH}$ = 7.0 Hz), 2.12 s (24H, CH_3N), 2.35 m [8H, $CH_2N(CH_3)_2$], 2.62–2.82 m [8H, $CH_2CH_2N(CH_3)_2$],

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4.01 s (8H, $C_{arom}CH_2N$), 4.50 q (4H, CH_3CH, $^3J_{HH}$ = 7.0 Hz), 6.4 br.s (8H, OH), 7.35 s (4H, H_{arom}). Found, %: C 65.46; H 8.97; N 12.09. $C_{52}H_{80}N_8O_8$. Calculated, %: C 66.10; H 8.47; N 11.86.

4,6,10,12,16,18,22,24-Octahydroxy-5,11,17,19-tetrakis[(α-methylbenzyl)aminomethyl]-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 (IIIb) was synthesized in a similar way from 0.81 g of calixarene **I**, 0.92 g of amine **IIb**, and 0.56 g of a 40% formaldehyde solution. Yield 1.55 g (97%). mp >290°C (decomp.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.37 d (12H, $PhCHCH_3$, $^3J_{HH}$ = 7.0 Hz), 1.68 d (12H, CH_3CH, $^3J_{HH}$ = 7.0 Hz), 3.67 q (4H, PhC*H*, $^3J_{HH}$ = 7.0 Hz), 3.89 m (8H, CH_2N), 4.52 q (4H, CH_3CHC_{arom}, $^3J_{HH}$ = 7.0 Hz), 7.10–7.83 m (32H, H_{arom}, OH).

The ^{1}H NMR spectra were recorded on a Bruker WM-250 spectrometer (250.13 MHz); the chemical shifts were measured relative to the solvent signal (residual protons).

ACKNOWLEDGMENTS

This study was financially supported by the Russian Foundation for Basic Research (project no. 99-03-32999).

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