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LETTERS TO THE EDITOR

Acetylation of calix[4]resorcinols with Amino Acetal Fragments

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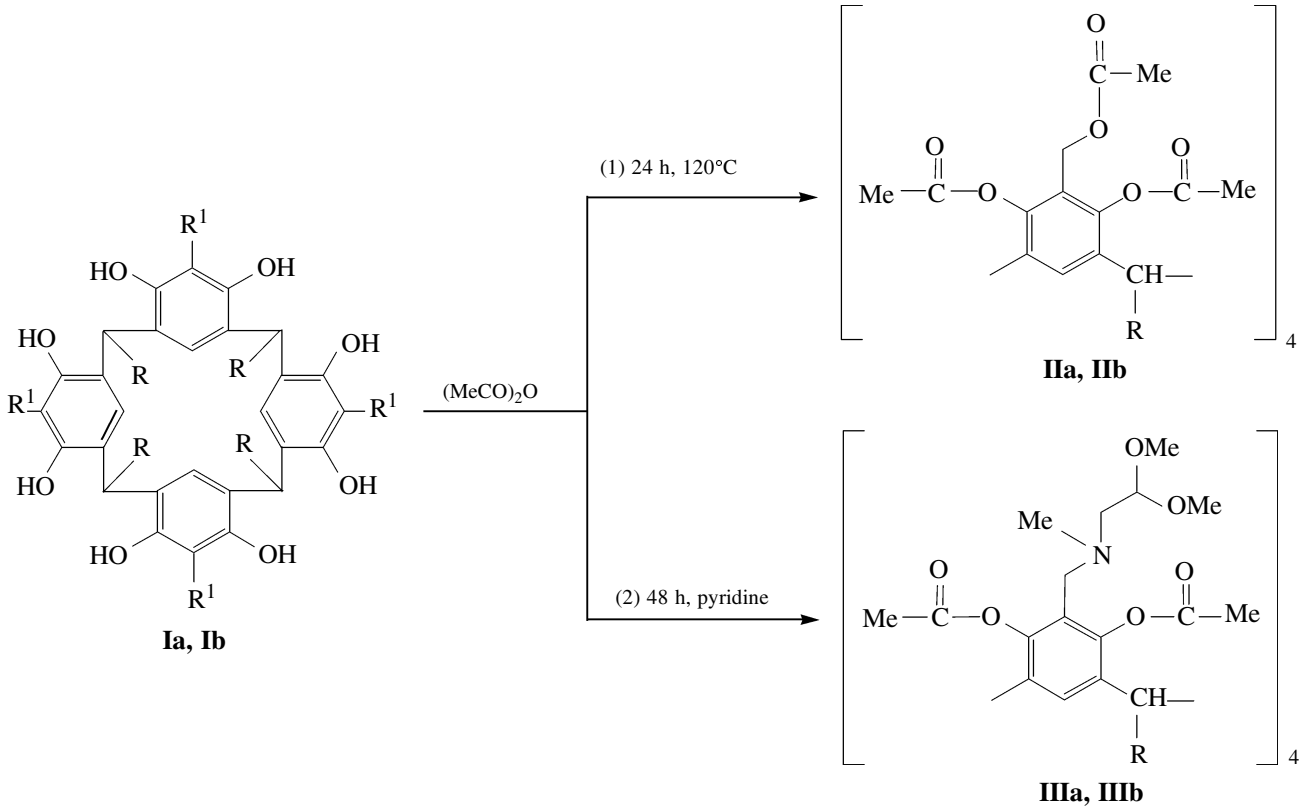
The chemistry of calixarenes attracts wide researchers' attention due to doubtless importance of such compounds as complexing agents, metal extractants, and polymer stabilizers [1–3]. A significant problem is the development of methods for functionalization of calixarenes aimed at creation on their basis of more complex structures with three-dimensional organization. Previously we prepared calix[4]arenes containing amino acetal fragments in the upper rim of the calixarene matrix (in *o*-position to hydroxy groups), **Ia** and **Ib** [4]. We found that, in the reaction of compounds **Ia** and **Ib** with excess acetic anhydride under rigorous conditions, they are completely acetylated, with simultaneous replacement of the amino acetal fragment by acetate to form calixarenes **IIa** and **IIb**. When carried out under mild conditions in the presence of pyridine, the reaction occurs as selective O-acetylation yielding calixarenes **IIIa** and **IIIb**. Thus, it becomes possible to protect hydroxy groups and perform reactions involving the acetal fragment.



I, II, III, R = Et (**a**), Pr (**b**); **I**, R^1 = $CH_2N(Me)CH_2CH(OMe)_2$.

The structures of **IIa**, **IIb**, **IIIa**, and **IIIb** are confirmed by the IR, ^{1}H NMR, and ^{13}C NMR spectra, and their compositions, by elemental analysis.

4,6,10,12,16,18,22,24-Octaacetyl-5,11,17,23-tetra(acetyloxymethyl)-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 (IIa). A mixture of 5 g of calix[4]resorcinol **Ia** and 20 ml of acetic anhydride was heated for 24 h at 120°C, then the solvent was removed in a water-jet-pump vacuum of and residue was recrystallized from ethanol. The reaction product was dried in a vacuum (40°C, 0.06 mm Hg) to constant weight. 5.34 g (98%) of compound **IIa** was obtained, mp 236–238°C. IR spectrum, ν, cm^{-1}: 1615 (CH_{arom}), 1736 [C(O)Me], 1762 [$CH_2C(O)CH_3$]. ^{1}H NMR spectrum (chloroform-*d*), δ, ppm, (*J*, Hz): 0.92 t (12H, CH_2CH_3, $^3J_{HH}$ 7.14), 1.89 m (8H, $CHCH_2CH_3$), 1.97 s (12H, $CH_2OC(O)CH_3$), 2.26 m [24H, $OC(O)CH_3$], 3.91 m (4H, $CHCH_2$), 4.83 m (8H, CH_2O), 7.22 s (4H, *m*-CH_{arom}). ^{13}C NMR spectrum (chloroform-*d*), δ_C, ppm: 12.86 (CH_3), 20.43, 20.63 (CH_3), 27.16 (CH_2), 39.42 (CH), 56.70 (CH_2), 122.19, 122.67 ($C_{arom}CH_2$), 126.16, 126.91 ($C_{arom}H$), 133.93, 134.59 ($C_{arom}CH$), 146.56, 147.09 ($C_{arom}OH$), 168.40, 170.33 [$C(O)CH_3$]. Found, %: C 62.81; H 5.82. $C_{64}H_{72}O_{24}$. Calculated, %: C 62.74; H 5.92.

4,6,10,12,16,18,22,24-Octaacetyl-5,11,17,23-tetra(acetyloxymethyl)-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 (IIb) was prepared similarly from 1.0 g of calixarene **Ib** and 10 ml of acetic anhydride. Yield 0.4 g (74.0%), mp 238–240°C. IR spectrum, ν, cm^{-1}: 1615 (CH_{arom}), 1736 [$C(O)CH_3$], 1762 [$CH_2C(O)CH_3$]. ^{1}H NMR spectrum (chloroform-*d*), δ, ppm, (*J*, Hz): 0.83 t (12H, CH_2CH_3, $^3J_{HH}$ 7.14), 1.32 m (8H, CH_2CH_3), 1.96 m (8H, CH_2CH), 1.96 s [6H, $C(O)CH_3$], 1.98 s [6H, $C(O)CH_3$], 2.34 s [12H, $C(O)CH_3$], 2.36 s [12H, $C(O)CH_3$], 3.98 t (4H, $CHCH_2$), 4.86 m (8H, CH_2O), 7.29 s (4H, *m*-CH_{arom}). ^{13}C NMR spectrum (chloroform-*d*), δ_C, ppm: 13.73 (CH_3), 20.47, 20.62 (CH_3), 20.95 (CH_2), 35.97 (CH_2CH), 36.79 (CH), 56.61 (CH_2), 122.39 ($C_{arom}CH_2$), 126.06 ($C_{arom}H$), 135.64 ($C_{arom}CH$), 145.38, 147.69 ($C_{arom}OH$), 168.50, 170.36 [$C(O)CH_3$]. Found, %: C 63.57; H 6.69. $C_{68}H_{80}O_{24}$. Calculated, %: C 63.75; H 6.25.

4,6,10,12,16,18,22,24-Octaacetyl-5,11,17,23-tetra[(2,2-dimethoxyethyl)(methyl)aminomethyl]-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 (IIIa). A mixture of 1.0 g of calixarene **Ia**, 1 ml of acetic anhydride, and 0.1 ml of pyridine was kept for 48 h at 20°C; the solvent was removed in a water-jet-pump vacuum and the residue was recrystallized from ethanol. The product was dried in a vacuum (40°C, 0.06 mm Hg) to constant weight. Compound **IIIa** was obtained; yield 1.25 g (96.3%), mp 78–80°C. IR spectrum, ν, cm^{-1}: 1597 (CH_{arom}), 1759 [$CH_2C(O)CH_3$]. ^{1}H NMR spectrum (chloroform-*d*), δ, ppm, (*J*, Hz): 0.87 t (12H, CH_2CH_3, $^3J_{HH}$ 6.94), 1.90 m (8H, CH_2CH_3), 2.04 m (8H, CH_2CH), 2.27 s [24H, $C(O)CH_3$], 2.41 s (12H, NCH_3), 3.30 s (24H, OMe), 3.90 m (8H, CH_2N), 4.82 m [8H, $CH(OMe)_2$, $CHCH_2$], 6.96 s (4H, CH_{arom}). ^{13}C NMR spectrum (chloroform-*d*), δ_C, ppm: 12.80 (CH_3), 20.59 (CH_3), 27.73, 27.84 (CH_2CH), 36.16 (CH), 42.37 (NCH_3), 53.07, 53.36 (OCH_3), 58.89 ($ArCH_2$), 59.10 (NCH_2), 103.04 CH(OMe), 123.90 ($C_{arom}CH_2$), 125.11 ($C_{arom}H$), 133.08, 133.55 ($C_{arom}CH$), 146.38, 146.57 ($C_{arom}OH$), 168.47 [$C(O)CH_3$]. Found, %: C 61.97; H 7.65; N 3.82. $C_{76}H_{108}N_4O_{24}$. Calculated, %: C 62.45; H 7.45; N 3.83.

4,6,10,12,16,18,22,24-Octaacetyl-5,11,17,23-tetra[(2,2-dimethoxyethyl)(methyl)aminomethyl]-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 (IIIb) was prepared similarly from 1.0 g of calixarene **Ib**, 0.42 ml of pyridine, and 4.2 ml of acetic anhydride. Yield 1.19 g (93.3%), mp 64–66°C. IR spectrum, ν, cm^{-1}: 1597 (CH_{arom}), 1759 [$CH_2C(O)CH_3$]. ^{1}H NMR spectrum (chloroform-*d*), δ, ppm, (*J*, Hz): 0.85 t (12H, CH_2CH_3, $^3J_{HH}$ 6.94), 1.29 m (8H, CH_2CH_3), 1.85 m (8H, CH_2CH), 2.26 s [24H, $C(O)CH_3$], 2.32 s (12H, NCH_3), 3.27 s [24H, $CH(OMe)]_2$, 4.02 t (8H, CH_2N), 4.37 m [8H, $CH(OMe)_2$, $CHCH_2$], 6.92 s (4H, CH_{arom}). ^{13}C NMR spectrum (chloroform-*d*), δ_C, ppm: 13.69 (CH_3), 20.60 (CH_3), 20.89 (CH_2), 34.43 (CH_2CH), 36.42, 36.57 (CH), 42.31 (NCH_3), 53.01, 53.21 (OCH_3), 55.62 ($ArCH_2$), 58.47, 59.14 (NCH_2), 102.92 ($CHOCH_3$), 123.09, 123.85 ($C_{arom}CH_2$), 125.07, 125.50 ($C_{arom}H$); 135.41, 135.48 ($C_{arom}CH$), 147.77, 145.00 ($C_{arom}OH$), 168.38 [$C(O)CH_3$]. Found, %: C 62.97; H 7.81; N 3.70. $C_{80}H_{116}N_4O_{24}$. Calculated, %: C 63.30; H 7.70; N 3.69.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker MSL-400 instrument (operating frequencies 400.13 and 100.62 MHz, respectively), solvent chloroform-*d*. The IR spectra were recorded from mulls in Vaseline oil on a UR-20 spectrophotometer in the range 400–3600 cm^{-1}.

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