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LETTERS TO THE EDITOR

Reaction of α-Aminoacetals with 2-Methylresorcinol

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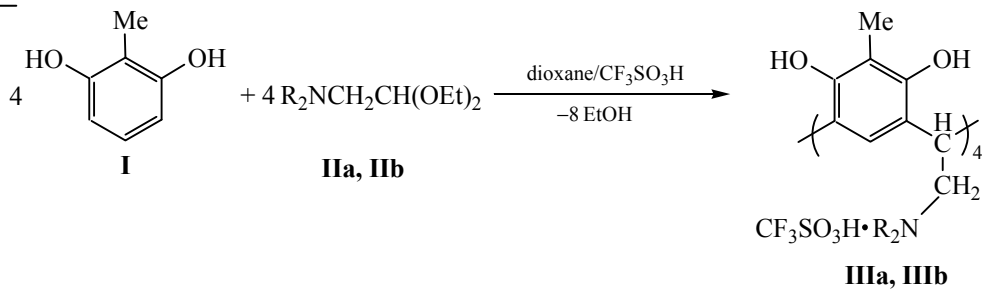
The main method of synthesis of calix[4-resorcinols is the condensation of resorcinol and its derivatives with aliphatic or aromatic aldehydes [1–3]. We have recently extended synthetic opportunities of this method by involvement into the reaction with resorcinol of phosphorylated acetals to obtain calix[4] resorcinols with phosphorylalkyl substituents at the lower rim of the molecule [4]. A special attention should be paid to their aminoalkyl analogs that can serve as primary compounds (due to involvement of amino groups) in the syntheses of new cavitands, container compounds, and nanotubes. For the synthesis of the calixarenes of this type we studied reaction of aminoacetaldehyde diethylacetal (**Ia**) and dimethylaminoacetaldehyde diethylacetal (**Ib**) with 2-methylresorcinol. We found that synthetic result of this reaction depends considerably on the reaction conditions. The process carried out in dioxane in the presence of trifluoromethanesulfonic acid leads to formation of calix[4]resorcinols **IIIa** and **IIIb** as the final products.

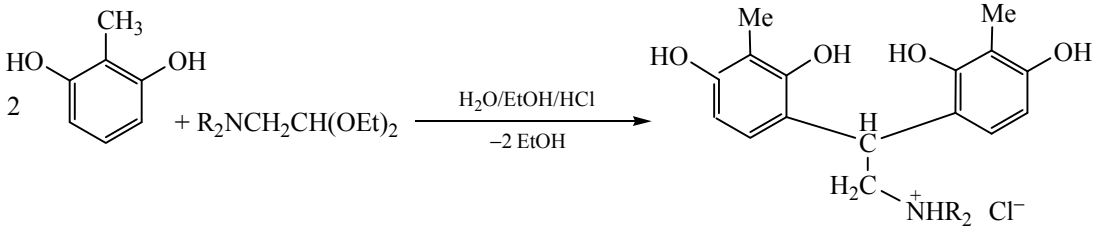


I **IIa, IIb** **IIIa, IIIb**

II, III: R = H (**a**), Me (**b**).

In water–alcohol medium containing some hydrochloric acid the same reaction affords diarylmethane derivatives **IVa, IVb**.

Structure of the synthesized compounds is confirmed by spectral methods, their composition, by the data of elemental analysis.



IVa, IVb

IV: R = H (**a**), Me (**b**).

2,8,14,20-Tetra(aminomethyl)pentacyclo[19.3.1.-$1^{3,7}$.$1^{9,13}$.$1^{15,19}$]octacosa-1(25),3,5,7(28),9,1,13-(27),15,17,-19(26),21,23-dodecaen-4,6,10,12,16,18,22,24-octol tetratriflate (IIIa). A solution of 2.29 g of methylresorcinol **I**, 1.94 g of acetal **IIa**, and 2.90 g of trifluoromethanesulfonic acid in 22 ml of anhydrous dioxane was heated for 5 h at 80°C. The solvent was removed and the residue was precipitated from ethanol into diethyl ether. 5.21 g (89.5 %) of compound **IIIa** was obtained, mp above 250°C. ^{1}H NMR spectrum (D_2O), δ, ppm (*J*, Hz): 2.11 s (12H, CH_3), 3.78 d (8H, CH_2, $^3J_{HH}$ 8.07), 4.85 t (4H, CH, $^3J_{HH}$ 7.88), 6.93 s (4H, CH_{arom}). IR spectrum, ν, cm^{-1}: 1603 (arom.), 3110–3490 (OH). Found, %: C 37.98; H 3.95; N 4.10; S 9.72. $C_{40}H_{48}F_{12}N_4O_{20}S_4$. Calculated, %: C 38.10; H 3.84; N 4.44; S 10.17.

2,8,14,20-Tetra-(*N*,*N*-dimethylaminomethyl)pentacyclo[19.3.1.$1^{3,7}$.$1^{9,13}$.$1^{15,19}$]octacosa-1(25),3,5,7(28),9,-1,13(27),15,17,19(26),21,23-dodecaen-4,6,10,12,16,-18,22,24-octol tetratriflate (IIIb) was prepared similarly from 0.77 g of 2-methylresorcinol **I**, 1.0 g of acetal **IIb**, 0.97 g of trifluoromethanesulfonic acid in 8 ml of anhydrous dioxane. Yield 2.05 g (89 %), mp above 250°C. The ^{1}H NMR spectrum (D_2O), δ, ppm (*J*, Hz): 2.11 s (12H, CH_3), 3.06 s (24H, CH_3N), 4.20 d (8H, CH_2, $^3J_{HH}$ 8.43), 5.12 t (4H, CH, $^3J_{HH}$ 8.43), 7.17 s (4H, CH_{arom}). IR spectrum, ν, cm^{-1}: 1604 (arom.), 3100–3500 (OH). Found,` %: C 41.53; H 4.89; N 3.99; S 9.01. $C_{48}H_{64}F_{12}N_4O_{20}S_4$. Calculated, %: C 41.98; H 4.70; N 4.08; S 9.34.

1-Amino-2,2-bis(2,4-dihydroxy-3-methylphenyl)-ethane hydrochloride (IVa). A mixturte of 1.0 g of methylresorcinol **I**, 0.42 g of acetal **IIa**, 1.5 ml of concentrated solution of hydrochloric acid, 4 ml of distilled water, and 4 ml of ethanol was heated for 12 h at 90°C. The solvent was removed and the residue was reprecipitated from ethanol into diethyl ether. 0.53 g (40.4 %) of compound **IVa** was obtained, mp 125ºC. ^{1}H NMR spectrum (D_2O), δ, ppm (*J*, Hz): 1.92 s (6H, CH_3), 3.42 d (2H, CH_2, $^3J_{HH}$ 8.07), 4.74 t (1H, CH, $^3J_{HH}$ 8.07), 6.34 d (2H, *ortho*-CH_{arom}, $^3J_{HH}$ 8.68), 6.68 d (2H, *meta*-CH_{arom}, $^3J_{HH}$ 8.68). IR spectrum, ν, cm^{-1}: 1605 (arom.), 3100–3500 (OH). Found, %: C 58.43; H 6.29; Cl 10.95; N 4.12. $C_{16}H_{20}ClNO_4$. Calculated, %: C 58.99; H 6.19; Cl 10.88; N 4.30.

1-Amino-2,2-bis(2,4-dihydroxy-3-methylphenyl)-*N*,*N*-dimethylethane hydrochloride (IVb) is prepared similarly to compound **IVa** from 1.54 g of methylresorcinol **I**, 1.0 g of acetal **IIb**, 2.5 ml of concentrated solution of hydrochloric acid, 6 ml of water, and 6 ml of ethanol. 2.2 g (98.5 %) of compound **IVb** is obtained, mp 148ºC. ^{1}H NMR spectrum (D_2O), δ, ppm (*J*, Hz): 2.03 s (6H, CH_3), 2.81 s (6H, CH_3N), 3.58 d (2H, CH_2, $^3J_{HH}$ 7.70), 4.97 t (1H, CH, $^3J_{HH}$ 7.70), 6.46 d, (2H, *ortho*-CH_{arom}, $^3J_{HH}$ 8.80), 6.83 d(2H, *meta*-CH_{arom}, $^3J_{HH}$ 8.80). IR spectrum, ν, cm^{-1}: 1600 (arom.), 3100–3500 (OH). Found, %: C 60.89; H 6.95; Cl 10.53; N 3.55. $C_{18}H_{24}ClNO_4$. Calculated, %: C 61.10; H 6.84; Cl 10.02; N 3.96.

The ^{1}H NMR spectra were registered on an Avance 600 instrument at the operating frequency 600.13 MHz, the signals of residual protons of deuterated solvent (D_2O) serving as internal refernce. The IR spectra of the studied compounds were registered on an UR-20 spectrometer in the frequency range 400–3600 cm^{-1} from a paste with mineral oil or from thin layers.

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