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LETTERS TO THE EDITOR

Reaction of B-Aminosubstituted Acetals and Aldehydes with 2-Methylresorcinol

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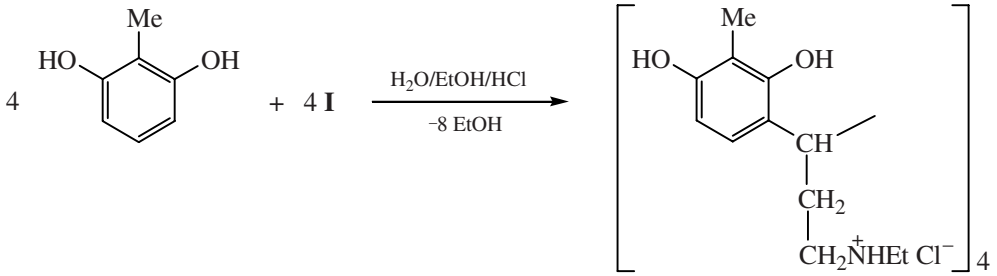
Resorcinol and 2-methylresorcinol condensation with a-methylaminoacetic aldehyde dimethylacetal in aqueous solutions of hydrogen halides leads to the formation of substituted diarylethylmethylamine hydrohalides, the products of reaction of two resorcinol molecules with one molecule of aminoacetal [1–4]. Meanwhile, the same reactions carried out in dioxane as a solvent in the presence of trifluoromethanesulfonic acid afford the respective calixarenes [5]. For revealing the effect of the length of carbon bridge binding the amino group with the aldehyde or acetal fragment on the synthetic result of this reaction we carried out the reaction of 2-methylresorcinol with 3,3-diethoxy-1-(diethylamino)propane (**I**). The acetal **I** was prepared by the reaction of 3,3-diethoxy-1-cloropropane with diethylamine in the presence of potassium carbonate.

$$ClCH_2CH_2CH(OEt)_2 + Et_2NH \xrightarrow{K_2CO_3} Et_2NCH_2CH_2CH(OEt)_2$$

I

The reaction of acetal **I** with 2-methylresorcinol in water–alcohol medium in the presence of hydrochloric acid leads to the formation of calixarene (**II**).



II

A significant effect on the final result of this reaction produces the steric factor. When in the reaction with 2-methylresorcinol in aqueous solution of hydrochloric acid the β-aminoaldehyde **III** is used with its a-carbon atom bound to two methyl groups the final product of reaction is substituted diarylpropyldiethylamine hydrochloride (**IV**).

Structure and composition of the obtained products are confirmed by the spectral data and elemental analysis.

3,3-Diethoxy-1-(diethylamino)propane (I). A mixture of 2.0 g of 3,3-diethoxy-1-chloropropane [6], 0.87 g of diethylamine, 4.97 g of potassium carbonate, and 10 ml of acetone was heated with stirring for 12 h at 60°C. Precipitate formed was filtered off, the filtrate was distilled in a vacuum, 1.54 g (63.2%) of compound **I** was thus obtained, bp 85–88°C (15 mm Hg), n_D^{20} 1.4102. ^{1}H NMR spectrum (CD_3OD), δ, ppm, (*J*, Hz): 1.17–1.22 m (12H, CH_3), 1.82–1.87 m (2H, CH_2CH), 3.45–3.56 m (8H, CH_2N, CH_2O), 3.62–3.71 m (2H, CH_2N), 4.66 t (1H, CH, $^3J_{HH}$ 5.86).

2,8,14,20-Tetra-(2-*N*,*N*-diethylamino)ethylpentacyclo[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-dodecaene-4,6,10,12,16,18,22,24-octol hydrochloride (II). A mixture of 0.58 g of 2-methylresorcinol, 0.95 g of acetal **I**, 5 ml of ethanol, 5 ml of distilled water, and 2.1 ml of concentrated hydrochloric acid was heated for 0.5 h at 50°C and then kept for 3 days at 20°C. The precipitate formed was separated from the reaction mixture and reprecipitated from chloroform into pentane, and the light powder obtained was dried in a vacuum (5 h, 0.01 mm Hg) to constant weight. 0.74 g (58.2%) of compound **II** was obtained, mp above 250°C. The ^{1}H NMR spectrum (CD_3OD), δ, ppm: 1.09–1.67 m (12H, CH_3), 2.01–2.23 m (20H, CH_3C_{arom}, CH_2CH), 3.12–3.42 m (8H, CH_2N), 4.41–4.62 m (4H, CH), 6.71–7.10 m (4H, CH_{arom}). IR spectrum, ν, cm^{-1} : 1600 (arom.), 3100–3500 (OH). Found, %: C 61.53; H, 8.68; Cl 12.98; N 5.01. $C_{56}H_{88}C_{l4}N_4O_8$. Calculated, %: C 61.87; H 8.16; Cl 13.04; N 5.15.

1-(*N*,*N*-Diethylamino)-2,2-dimethyl-3,3-bis(2,4-dihydroxy-3-methylphenyl)propane hydrochloride (IV). A mixture of 1.73 g of 2-methylresorcinol, 0.9 g of dimethylaminodimethylpropanal (**III**) [7], 3 ml of concentrated hydrochloric acid, and 9 ml of distilled water was heated for 2 h at 60°C. The solvent was then removed and the residue was reprecipitated from ethanol into diethyl ether. The precipitate formed was dried in a vacuum (5 h, 0.01 mm Hg). 2.6 g (94.2 %) of compound **IV** was obtained, mp 120°C. ^{1}H NMR spectrum (D_2O), δ, ppm (*J*, Hz): 1.03 s (6H, CMe_2), 2.03 s (6H, CCH_3), 2.70 s (6H, NMe_2), 2.92 s (2H, CCH_2N), 5.04 s (1H, CH), 6.47 d (2H, *ortho*-CH_{arom}, $^3J_{HH}$ 8.6), 7.18 d (2H, *meta*-CH_{arom}, $^3J_{HH}$ 8.6). ^{13}C NMR spectrum (D_2O) δ, ppm (*J*, Hz): 9.10 (C^1, $^1J_{CH}$ 127.8), 23.78 (C^{10}, $^1J_{CH}$ 127.5), 38.90 (C^9), 39.24 (C^8, $^1J_{CH}$ 126.6), 46.99 (C^{12}, $^1J_{CH}$ 144.2), 69.67 (C^{11}, $^1J_{CH}$ 144.5), 108.39 (C^6, $^1J_{CH}$ 159.7), 112.89 (C^2), 121.89 (C^4), 128.15 (C^5, $^1J_{CH}$ 159.7), 152.95 (C^7), 153.16 (C^3). IR spectrum, ν, cm^{-1}: 1603 (arom.), 2723 (NH^+), 3172 (OH). Found, %: C 63.38; H 7.30; N 3.42; Cl 8.90. $C_{21}H_{30}ClNO_4$. Calculated, %: C 63.71; H 7.58; N 3.53; Cl 8.97.

^{1}H and ^{13}C NMR spectra were registered on an Avance 600 instrument with operating frequencies 600.13 and 150.90 MHz, respectively, relative to the signals of residual protons of a deuterated solvent (D_2O, CD_3OD). The IR spectra were registered on a UR-20 spectrometer in the range of 400–3600 cm^{-1} from the paste in mineral oil or from thin layer.

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