ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 3, pp. 487–488. © Pleiades Publishing, Ltd., 2007.
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## LETTERS TO THE EDITOR

# Reaction of Resorcinol with (2,2-Dimethoxyethyl)methylamine

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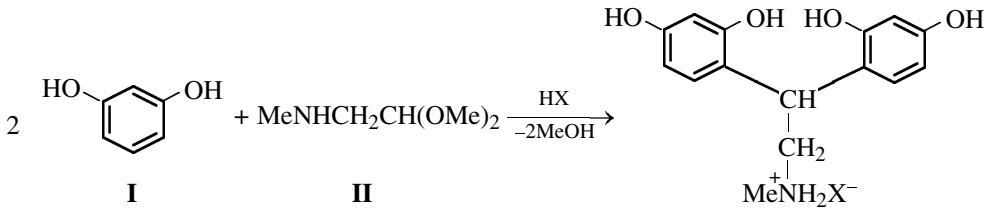
Received November 15, 2006

**DOI:** 10.1134/S1070363207030267

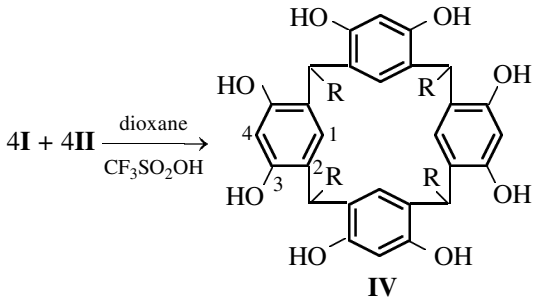
Recently we showed that phosphorylated acetals react with resorcinol to give calix[4]resocinols with phosphylated alkyl substituents on the lower rim [1]. To synthesize calixarenes containing amino groups and further involve them in functionalization, we have studied the reaction of resorcinol (**I**) with (2,2-dimethoxyethyl)methylamine (**II**) in aqueous solutions of hydrogen halides. Even though the reaction temperature and time were varied (from 25 to 80°C and from 4 h to 7 days, respectively), secondary amines hydrohalides **IIIa**, **IIIb** were obtained in all experiments, rather than calixarenes.




**I** **II** **IIIa, IIIb**

X = Cl (**a**), Br (**b**).

Similar dimeric products have only once been observed in the reactions of 2-nitroresorcinol with acetaldehyde and 4-methoxybenzaldehyde [2]. There is no doubt that the reaction result in that case is associated with the presence in the resorcinol molecule of the strongly acceptor nitro group. By studying the effect of the solvent and acid on the reaction pathway we found that the reaction produces calixarene **IV** when performed in dioxane in the presence of trifluoromethanesulfonic acid. Dioxane was chosen due to its high boiling point (the reaction occurs under rigid conditions) and ability to readily dissolve the starting compounds. The strong trifluoromethanesulfonic acid is soluble in dioxane.




**IV**

R = $CH_2{}^+NH_2Me \cdot CF_3SO_3^-$.

Thus, by varying conditions, one can make the reaction of resorcinol and its derivatives with (2,2-dimethoxyethyl)methylamine to form acyclic dimeric or cyclic tetrameric products.

**[2,2-Bis(2,4-dihydroxyphenyl)ethyl]methylammonium chloride (IIIa).** A mixture of 3.88 g of re-

sorcinol, 2.1 g of acetal **II**, 21 ml of water, 16 ml of ethanol, and 4.2 ml of conc. HCl was heated for 10 h at 70°C. The solvent was removed in a vacuum, the crystals that formed were filtered off, washed with ether, and dried in a vacuum (24 h, 20°C, 10 mm Hg). Yield 3.78 g (68.7%), mp 172–175°C. $^1$H NMR spectrum ($CD_3OD$), δ, ppm (*J*, Hz): 2.74 s (3H, $CH_3N$), 3.64 d (2H, $CH_2$, $^3J_{HH}$ 7.87), 4.89 t (1H, CH, $^3J_{HH}$ 7.87), 6.35 d (2H, $H^5_{arom}$, $^3J_{HH}$ 8.53), 6.45 s (2H, $H^3_{arom}$), 6.99 d (2H, $H^6_{arom}$, $^3J_{HH}$ 8.53). $^{13}$C NMR spectrum ($CD_3OD$), $\delta_C$, ppm (*J*, Hz): 34.11 ($CH_3N$), 37.04 (CH), 53.59 ($CH_2$), 103.82 ($C^6_{arom}$), 108.51 ($C^5_{arom}$), 118.45 ($C^1_{arom}$), 131.31 ($C^3_{arom}$), 156.22 ($C^2_{arom}$), 158.34 ($C^4_{arom}$). Mass spectrum: *m/z* 553 ($M^+$). Found, %: C 57.50; H 5.93; N 4.27. $C_{15}H_{18}ClNO_4$. Calculated, %: C 57.79; H 5.82; N 4.49.

**[2,2-Bis(2,4-dihydroxyphenyl)ethyl]methylammonium bromide (IIId)** was prepared in a similar way from 2.19 g of resorcinol, 1.05 g of acetal **II**, 10 ml of water, 10 ml of ethanol, 8.4 ml of 40% HBr. Yield 1.81 g (53.5%), mp 150–153°C. $^1$H NMR spectrum ($D_2O$), δ, ppm (*J*, Hz): 2.67 s (3H, $CH_3N$), 3.56 d (2H, $CH_2$, $^3J_{HH}$ 7.84), 4.87 t (1H, CH, $^3J_{HH}$ 7.84), 6.46 d (2H, $H^5_{arom}$, $^3J_{HH}$ 8.36), 6.87 d (2H, $H^6_{arom}$, $^3J_{HH}$ 8.36). Found, %: C 53.35; H 5.31; Br 21.22; N 3.71. $C_{17}H_{22}BrNO_4$. Calculated, %: C 53.12; H 5.73; ßr 20.83; N 3.64.

**2,8,14,20-Tetrakis(methylammoniomethyl)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-octaol tetratiflate (IV).** A mixture of 3 g of resorconol, 3.24 g of acetal **II**, 4.09 g of trifluoromethanesulfonic acid, and 25 ml of dioxane was heated for 6 h at 100°C. The precipitate that formed was filtered off, and the filtrate was heated for 3 h at 100°C. More crystals formed and were combined with the main portion of crystals, washed with dioxane, and dried in a vacuum (5 h, 20°C, 0.2 mm Hg). Yield 3.54 g (41.2%), mp 180–182°C. $^1$H NMR spectrum ($CD_3OD$), δ, ppm (*J*, Hz): 2.47 s (12H, $CH_3N$), 3.45 d (8H, $CH_2$, $^3J_{HH}$ 8.05), 4.68 t (4H, CH, $^3J_{HH}$ 8.05), 6.09 s (4H, $H^4_{arom}$), 6.72 s (4H, $H^1_{arom}$). $^{13}$C NMR spectrum ($D_2O$), $\delta_C$, ppm (*J*, Hz): 34.53 (CH), 36.07 ($CH_3N$), 53.65 ($CH_2$), 104.58 ($C^4_{arom}$), 119.06 ($C^2_{arom}$), 122.90 ($CF_3S$), 127.24 ($C^1_{arom}$), 154.73 ($C^3_{arom}$). IR spectrum, ν, cm$^{-1}$: 1600 (arom), 3100–3500 (OH). Mass spectrum, *m/z*: 663 ($M$ – $4CF_3SO_3H$). Found, %: C 37.79; H 3.36; N 4.08; S 9.67. $C_{40}H_{48}F_{12}N_4O_{20}S_4$. Calculated, %: C 38.10; H 3.81; N 4.44; S 10.17.

## ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 05-03-32 136).

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