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> LETTERS TO THE EDITOR

Synthesis of New Polyphenols Containing Aminoalkyl and Ammonium Fragments

N. I. Kharitonova, A. R. Burilov, A. S. Gazizov, and M. A. Pudovik

Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, ul. Akademika Arbuzova 8, Kazan, Tatarstan, 420088 Russia e-mail: pudovik@iopc.ru

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Recently we have shown that the condensation of resorcinol and methylresorcinol with dimethylacetal of methylaminoacetic α -aldehyde in aqueous hydrochloric acid leads to the formation of the hydrochlorides of the substituted polyphenols as the products of the reaction between two resorcinol molecules and one aminoacetal molecule [1]. In this work we studied the synthetic opportunities of the derived polyphenols. For modifications of these compounds we used the Mannich reaction [2]. The

initial 2,2-bis(2,4-dihydroxy-3-methylphenyl)-N,N-dimethylethylamine I was synthesized by the known method [1, 3] starting from 2-methylresorcinol and dimethylacetal of N,N-dimethylaminoacetaldehyde. The reaction of I with 2 equiv of formaldehyde in the presence of dimethylamine or morpholine results in compounds IIa and IIb in 98 and 84% yield respectively. In the presence of aromatic amines like aniline, diphenylamine, or benzidine the reaction affords a complex mixture of the unidentified products.



The obtained compounds containing three aminoalkyl groups along with two resorcinol fragments are of interest as new polydentate ligands [2].

The structure and composition of the products obtained were proved by spectroscopic methods and elemental analysis.

2,2-Bis[2,4-dihydroxy-3-methyl-5-(morpholinomethyl)phenyl]-*N,N*-dimethylethylamine hydrochloride (IIa). To a solution of 0.5 g of 2,2-bis-(2,4-dihydroxy-3-methylphenyl)-*N,N*-dimethylethylamine in a mixture of 5 ml of ethanol and 5 ml of benzene was added 0.25 g of morpholine and 0.19 g of 40% formaldehyde aqueous solution. The reaction mixture was stirred at room temperature for 24 h and concentrated. The formed precipitate was filtered off and dried in a vacuum (10 h, 15 mm Hg). Yield 0.65 g (98%), mp 134°C. IR spectrum, v, cm⁻¹: 1607 (Ar), 2723(NH⁺), 3320 (OH). ¹H NMR spectrum (CD₃OD), δ , ppm (*J*, Hz): 2.14 s (6H, ⁴CH), 2.57 s (12H, ¹²CH), 2.60 s (6H, ¹⁰CH), 3.38 d (2H, ⁹CH, *J* 9.60), 3.89 s and 3.90 s (4H, ¹¹CH), 4.78 t (1H, ⁸CH, *J* 9.54), 6.75 s (2H, ⁷CH). Found, %: C 61.15; H 9.01; Cl 7.60; N 8.79. C₂₄H₃₈ClN₃O₄. Calculated, %: C 61.59; H 8.18; Cl 7.57; N 8.98.

2,2-Bis[2,4-dihydroxy-3-methyl-5-(dimethylaminomethyl)phenyl]-*N,N***-dimethylethylamine hydrochloride (IIb)** was prepared similarly from 0.6 g of compound I, 0.25 g of 30% dimethylamine aqueous solution and 0.13 g of 40% formaldehyde aqueous solution. Yield 0.66 g (84%), mp 165°C. IR spectrum, v, cm⁻¹: 1610 (Ar), 2730 (NH⁺), 3180 (OH). ¹H NMR spectrum (CD₃OD), δ , ppm (*J*, Hz): 2.08 s (6H, ⁴CH), 2.50–2.75 m (8H, ¹²CH), 2.79 s (6H, ¹⁰CH), 3.16 s (4H, ¹¹CH), 3.17–3.68 m (8H, ¹³CH), 3.85 d (2H, ⁹CH, *J* 9.83), 4.92 t (1H, ⁸CH, *J* 7.45), 6.68 s (2H, ⁷CH). Found, %: C 60.72; H 7.85; Cl 6.51; N 7.78. C₂₈H₄₂ClN₃O₆. Calculated, %: C 60.91; H 7.6; Cl 6.42; N 7.67.

The ¹H NMR spectra were recorded on an Avance 600 instrument operating at 600.13 MHz the residual protons of CD₃OD serving as internal reference. The IR spectra were registered on a UR-20 spectrometer in the range of 400–3600 cm⁻¹ for the samples as mulls in mineral oil or in a thin layer. All the solvents were purified before use [4].

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