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SHORT COMMUNICATIONS

Synthesis of Salts of New Arylamides of 2-Hydroxy-5-nitroso-4,6-dimethylisophthalic Acid

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Completely substituted nitrosophenols containing methoxy-, ethoxy-, propoxy-, butoxycarbonyl substituents in the ortho-position with respect to the hydroxy group are obtained by the reactions of esters of acetonedicarboxylic acid with isonitrosacetylacetone [1–3]. Such nitrosophenols are readily reduced to persubstituted aminophenols [4] that at the modification of the amino group afford the derivatives exhibiting the antiarrhythmic action [5].

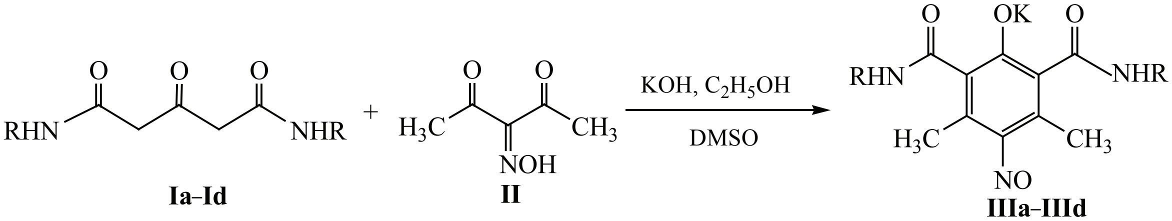
The aim of this study was the preparation of persubstituted nitrosophenols of analogous structure containing arylamide groups instead of ester groups that would give an opportunity to synthesize new biologically active substances.

The cyclization of arylamides of acetonedicarboxylic acid (**I**) dissolved in DMSO was carried out by the reaction with isonitrosoacetylacetone (**II**) in anhydrous ethanol containing potassium hydroxide. Nitrosophenols were isolated as potassium salts **III**.

The initial arylamides of acetonedicarboxylic acid (**I**) were obtained by heating diethyl acetonedicarboxylate with the corresponding anilines in a sealed ampule for 24 h by the procedure [6].

Compounds **IIIa–IIId** were obtained by cyclization using the procedure applied in the reaction of isonitrosoacetylacetone with dialkyl acetonedicarboxylate [2]. In 2 ml of anhydrous ethanol was dissolved 0.25 mmol of potassium hydroxide and to the solution was added 0.25 mmol of isonitrosoacetylacetone (**II**) and 0.5 mmol of arylamide of acetonedicarboxylic acid **Ia–Id** dissolved in 0.5 ml of DMSO. The mixture was maintained for some time at 18–20°C, therewith the color of the solution changed from orange to green. Potassium phenolate was isolated by adding anhydrous ethyl ether till the solution turned turbid. The brght green crystals of precipitated phenolate **III** were filtered off, recrystallized from ethanol, and dried in a vacuum over Na_2SO_4.

Potassium 2,6-bis(phenylcarbamoyl)-3,5-dimethyl-4-nitrosophenolate (IIIa). Reaction duration 6 h. Yield 0.105 g (88%), green crystals. IR spectrum: 1642 cm^{-1} [ν(C=O)]. UV spectrum, λ_{max}, nm (ε): 603 (73), 393 (16960). ^{1}H NMR spectrum, δ, ppm: 2.75 s (6H, $2CH_3$), 7.02 m ($2H_{arom}$), 7.30 m ($4H_{arom}$), 7.81 m ($4H_{arom}$), 11.16 br.s (2H, NH). ^{13}C NMR spectrum, δ, ppm: 17.2, 119.4,



Ia–Id **II** **IIIa–IIId**

R = C_6H_5 (**a**), C_6H_4Cl-*p*(**b**), C_6H_4Br-*p* (**c**), $C_6H_4CH_3$-*p* (**d**).

122.4, 125.0, 128.5, 131.6, 140.5, 160.3, 167.5, 177.0. Mass spectrum, m/z (I_{rel}, %): 93 (100), 66 (65), 39 (47), 32 (72).

Potassium 2,6-bis[(4-chloroppheny)carbamoyl]-3,5-dimethyl-4-nitrosophenolate (IIIb). Reaction duration 24 h. Yield 0.087 g (70%), green crystals. IR spectrum: 1634 cm^{-1} [ν(C=O)]. UV spectrum, λ_{max}, nm (ε): 612 (72), 392 (18390). ^{1}H NMR spectrum, δ, ppm: 2.75 s (6H, $2CH_3$), 7.32 d ($4H_{arom}$, ^3J 8.2 Hz), 7.84 d ($4H_{arom}$, ^3J 8.2 Hz), 11.48 br.s (2H, NH). ^{13}C NMR spectrum, δ, ppm: 17.0, 120.7, 120.8, 126.5, 128.4, 131.8, 139.4, 160.2, 167.5, 176.8. Mass spectrum, m/z (I_{rel}, %): 127 (85), 92 (26), 65 (54), 44 (45), 32 (100).

Potassium 2,6-bis[(4-bromophenyl)carbamoyl]-3,5-dimethyl-4-nitrosophenolate (IIIc). Reaction duration 48 h. Yield 0.1 g (37%), green crystals. IR spectrum: 1665 cm^{-1} [ν(C=O)]. UV spectrum, λ_{max}, nm (ε): 613 (73), 393 (20210). ^{1}H NMR spectrum, δ, ppm: 2.76 s (6H, $2CH_3$), 7.45 d ($4H_{arom}$, ^3J 8.7 Hz), 7.80 d ($4H_{arom}$, ^3J 8.7 Hz), 11.58 br.s (2H, NH). ^{13}C NMR spectrum, δ, ppm: 17.0, 113.9, 121.0, 121.2, 123.8, 131.3, 139.9, 160.8, 167.5, 176.7. Mass spectrum, m/z (I_{rel}, %): 173 (13), 63 (31), 45 (19), 32 (100).

Potassium 2,6-bis[(4-methylphenyl)carbamoyl]-3,5-dimethyl-4-nitrosophenolate (IIId). Reaction duration 24 ч. Yield 0.11 g (90%), green crystals. IR spectrum: 1638 cm^{-1} [ν(C=O)]. UV spectrum, λ_{max}, nm (ε): 607 (66), 394 (13630). ^{1}H NMR spectrum, δ, ppm: 2.30 s (6H, $2CH_3$), 2.75 s (6H, $2CH_3$), 7.12 d ($4H_{arom}$, ^3J 8.4 Hz), 7.71 d ($4H_{arom}$, ^3J 8.4 Hz), 11.10 br.s (2H, NH). ^{13}C NMR spectrum, δ, ppm: 17.0, 19.9, 119.3, 119.4, 124.6, 128.9, 131.5, 138.1, 160.7, 167.4, 176.8. Mass spectrum, m/z (I_{rel}, %): 106 (65), 77 (23), 44 (36), 32 (100).

^{1}H (600.13 MHz) and ^{13}C (151.91 MHz) NMR spectra were registered in acetone-d_6 on a spectrometer Bruker Avance III 600 at the Krasnoyarsk regional ceneter for joint use of the Siberian Division of the Russian Academy of Sciences, mass spectra, on an instrument Finnigan MAT 8200, UV spectra, on a spectrophotometer Helios Omega in the measurement range 190–1100 nm in quartz celle of 1 cm. Salt concn. in 0.1 N aqueous potassium hydroxide $0.1 \cdot 10^{-4}$ mol l^{-1} in the UV region, and in the region of n-π* transition of the nitroso group (600–700 nm) concn. $0.1 \cdot 10^{-2}$ mol l^{-1}. IR spectra were recorded on an IR microscope SpecTRA TECH InspectIR based on an IR Fourier spectrophotometer Impact 400. The sample of the substance was placed on a gold plate, adjusted with a roller blade, placed on the microscope, and the spectrum of partial internal reflection was recorded. Detector MCT/A, lens Si Caplugs, range of wave numbers 4000–650 cm^{-1}, resolution 1.928 cm^{-1}, number of scans 64, software OMNIC 5.1 E.S.P. the reaction progress was monitored and the homogeneity of the compounds obtained was checked by TLC on Sorbfil PTSKh-AF-V plates (Russia) with UV indicator, eluent toluene, spots visualized under UV irradiation.

REFERENCES

1. Belyaev, E.Yu., Tovbis, M.S., and El'tsov, A.V., *Zh. Org. Khim.,* 1978, vol. 14, p. 2375.
2. Semin, I.V., Sokolenko, V.A., and Tovbis, M.S., *Zh. Org. Khim.,* 2007, vol. 43, p. 545.
3. Slaschinin, D.G., Alemasov, Yu.A., Tovbis, M.S., and Kirik, S.D., *J. Mol. Struct*. 2011, vol. 985, p. 184.
4. Slaschinin, D.G., Tovbis, M.S., Root, E.V., Zadov, V.E., and Sokolenko, V.A., *Zh. Org. Khim.,* 2010, vol. 46, p. 527.
5. Eiden, F., Leister, H.P., and Mayer, D., *Arz. Forsch.* 1983, vol. 33,p. 101.
6. Besthorm, E. and Garden, E. *Ber*. 1903, vol. 33, p. 3435.