ISSN 1070-4280, Russian Journal of Organic Chemistry, 2014, Vol. 50, No. 12, pp. 1757–1762. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © S.A. Konovalova, A.P. Avdeenko, A.A. Santalova, V.V. D'yakonenko, G.V. Palamarchuk, O.V. Shishkin, 2014, published in Zhurnal Organicheskoi Khimii, 2014, Vol. 50, No. 12, pp. 1776–1781.

Reaction of *N*-Aryl-1,4-Benzoquinone Imines with Sodium Arenesulfinates

S. A. Konovalova[a], A. P. Avdeenko[a], A. A. Santalova[a], V. V. D'yakonenko[b], G. V. Palamarchuk[b], and O. V. Shishkin[b, c]

[a] *Donbass State Engineering Academy, ul. Shkadinova 72, Kramatorsk, 84313 Ukraine*
e-mail: chimist@dgma.donetsk.ua

[b] *Institute for Single Crystals, National Academy of Sciences of Ukraine, pr. Lenina 60, Kharkiv, 61001 Ukraine*

[c] *Karazin Kharkiv National University, pl. Svobody 4, Kharkiv, 61022 Ukraine*

Received June 14, 2014

Abstract—*N*-Aryl-1,4-benzoquinone imines reacted with sodium arenesulfinates to give products of orbital-controlled nucleophilic 1,4- and 6,3-addition.

DOI: 10.1134/S1070428014120070

The regioselectivity of nucleophilic addition to *N*-aryl-1,4-benzoquinone imines is determined by electrophilicity of the substrate, nucleophilicity of the reagent, and hardness of the latter. Hard nucleophiles (Cl^-, Br^-) add to *N*-(4-methoxyphenyl)-1,4-benzoquinone imine in protic medium at the *ortho* position to the nitrogen atom according to the 6,3-addition scheme [1–3]. Introduction of electron-withdrawing substituents into the *N*-aryl fragment increases electrophilicity of quinone imine, and the addition pattern of hard nucleophiles changes from 6,3 to 1,4 [4].

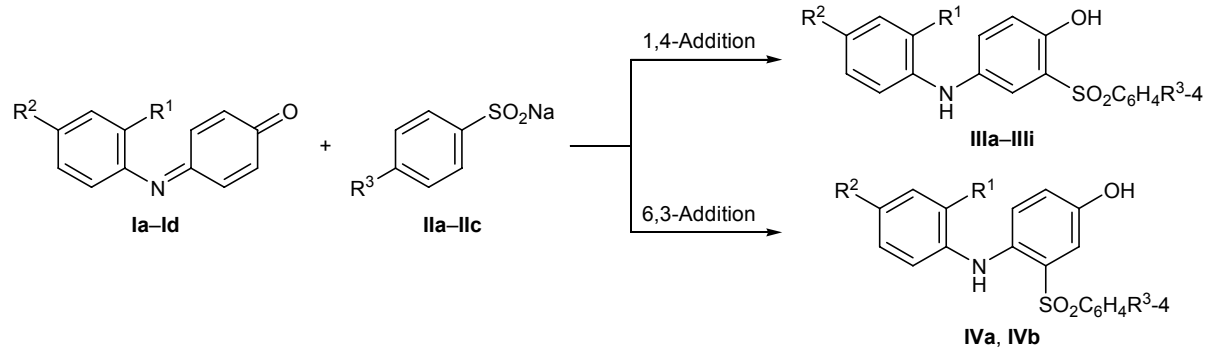
Soft nucleophiles [$ArNH_2$, ArS^-, $Ar(Alk)SO_2^-$] are capable of adding to *N*-aryl-1,4-benzoquinone imines in both aprotic and protic media. *N*-Phenyl- and *N*-(4-methylphenyl)-1,4-benzoquinone imines with free *ortho* position with respect to the carbonyl carbon atom were reported to react with sodium arenesulfinates in acetic acid to give only 1,4-addition products [5]. However, no ^{1}H NMR spectra of the products were given, and the reaction mixtures were not analyzed by ^{1}H NMR, so that other possible products could remain not detected. Reactions of sodium arenesulfinates with *N*-aryl-1,4-benzoquinone imines containing electron-withdrawing substituents in the *para* position of the aryl fragment were not studied previously. Taking the above state into account, in the present work we examined reactions of *N*-aryl-1,4-benzoquinone imines **Ia**–**Id** with sodium arenesulfinates **IIa**–**IIc**.

The reactions were carried out in acetic acid using 2 equiv of the nucleophile. Sodium arenesulfinates **IIa** and **IIb** contained methyl or methoxy group in the *para* position of the benzene ring to facilitate interpretation of the ^{1}H NMR spectra. In order to detect all possible products, a part of the crude product precipitated from the reaction mixture was recrystallized from acetic acid, the mother liquor was diluted with water, the precipitate was filtered off, and the three samples were analyzed by ^{1}H NMR. We thus succeeded in detecting compounds whose amount in the reaction mixture did not exceed a few percent.

The reactions of *N*-phenyl-, *N*-(4-methylphenyl)-, and *N*-(2-nitrophenyl)-1,4-benzoquinone imines **Ia**–**Ic** with sodium arenesulfinates **IIa**–**IIc** afforded exclusively 1,4-addition products **IIIa**–**IIIi**, in keeping with the data of [5, 6] (Scheme 1). However, introduction of two electron-withdrawing nitro groups into the *N*-aryl fragment (compound **Id**) changed the reaction direction, and *N*-(2,4-dinitrophenyl)-1,4-benzoquinone imine (**Id**) reacted with sodium arenesulfinates **IIa** and **IIb** to give mixtures of 1,4- and 6,3-addition products **IIIh**/**IVa** and **IIIi**/**IVb**, respectively, at ratios of 84 : 16 and 85 : 15.

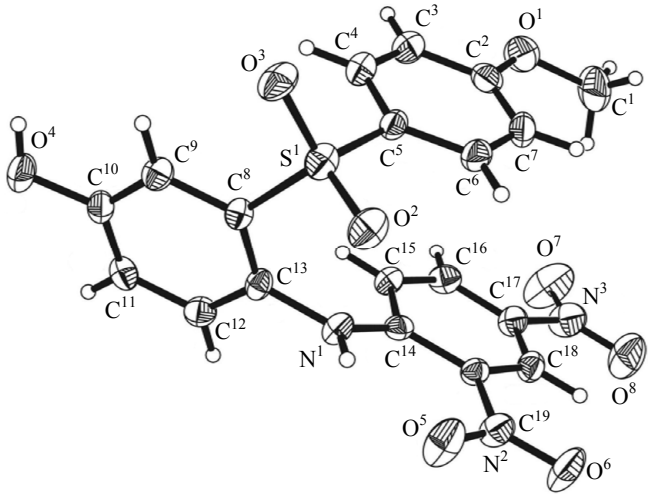
The ^{1}H NMR spectra of 1,4-addition products **IIIa**, **IIIb**, and **IIId**–**IIIi** contained a doublet signal from 3-H at δ 7.59–7.89 ppm with a *meta* coupling constant, the 5-H signal was a doublet of doublets at δ 7.15–

Scheme 1.



I, $R^1 = R^2 = H$ (**a**); $R^1 = H$, $R^2 = Me$ (**b**); $R^1 = O_2N$, $R^2 = H$ (**c**); $R^1 = R^2 = O_2N$ (**d**); **II**, $R^3 = Me$ (**a**), MeO (**b**), Cl (**c**); **III**, $R^1 = R^2 = H$, $R^3 = Me$ (**a**), MeO (**b**); $R^1 = H$, $R^2 = Me$, $R^3 = Me$ (**c**), MeO (**d**); $R^1 = O_2N$, $R^2 = H$, $R^3 = Me$ (**e**), MeO (**f**), Cl (**g**); $R^1 = R^2 = O_2N$, $R^3 = Me$ (**h**), MeO (**i**); **IV**, $R^1 = R^2 = O_2N$, $R^3 = Me$ (**a**), MeO (**b**).

7.50 ppm, and the 6-H proton resonated at δ 6.80–6.99 ppm. In the ^{1}H NMR spectra of 6,3-addition products **IVa** and **IVb**, the doublet signal (*meta* coupling) from 2-H was observed at δ 7.65–7.67 ppm, the 6-H signal appeared as a doublet of doublets at δ 7.16–7.21 ppm, and the 5-H doublet (*ortho* coupling) was located at δ 7.34 ppm. It is seen that signals from protons in the aminophenol fragment of 1,4-addition products **IIIa**, **IIIb**, and **IIId–IIIi** shift considerably downfield as the acceptor power of the substituent in the *N*-aryl ring increases. 6,3-Addition products **IVa** and **IVb** are characterized by downfield position of the 6-H signal and upfield position of the 5-H signal relative to the corresponding signals of regioisomers **IIIh** and **IIIi**, which is consistent with published data [6].



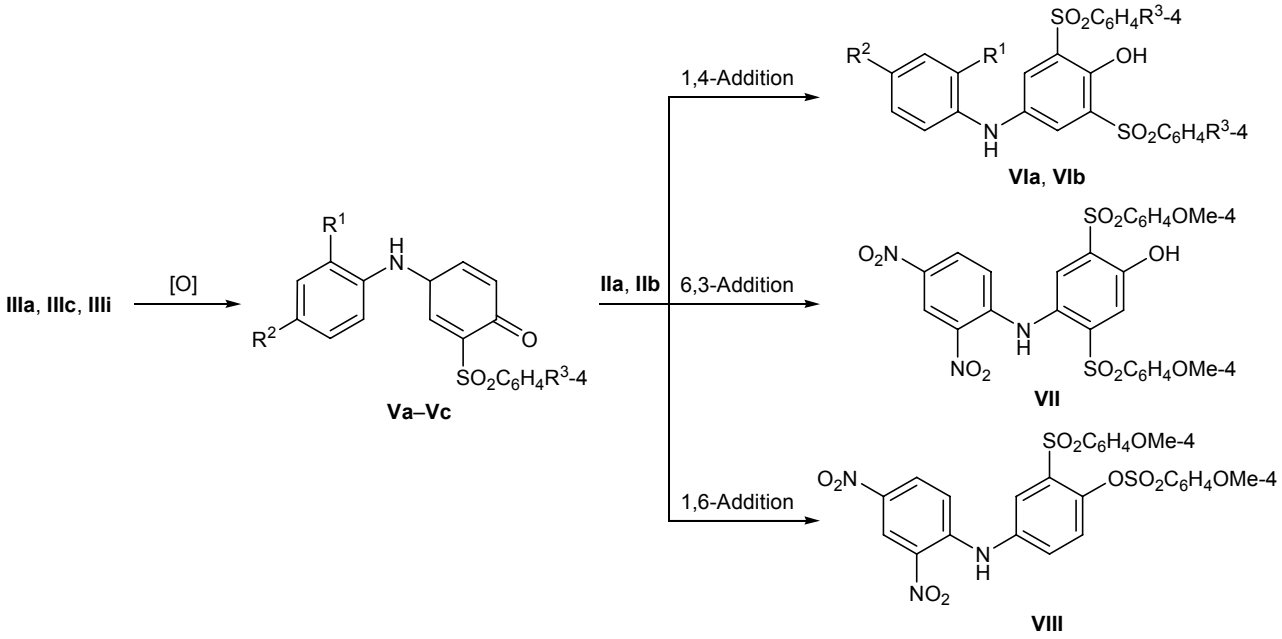
Structure of the molecule of 4-(2,4-dinitrophenylamino)-3-(4-methoxybenzenesulfonyl)phenol (**IVb**) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 30%.

The structure of the 6,3-addition products was unambiguously proved by X-ray analysis of 4-(2,4-dinitrophenylamino)-3-(4-methoxybenzenesulfonyl)-phenol (**IVb**) which was isolated in the pure state by several recrystallizations (see figure). According to the X-ray diffraction data, the substituents on C^8 and C^{13} in molecule **IVb** are oriented almost orthogonally to the C^8–C^{13} aromatic ring plane [the torsion angles $C^9C^8S^1C^5$ and $C^8C^{13}N^1C^{14}$ are −109.4(2) and −111.3(2)°, respectively]. The dinitrophenyl and methoxyphenyl fragments are almost coplanar to each other (the dihedral angle between the corresponding mean-square planes is 10.4°), and the shortest distance between carbon atoms is 3.43 Å. Such arrangement of the benzene rings and the presence of polar substituents therein suggest fairly strong stacking interaction which should stabilize the observed conformation.

Compounds **IIIa**, **IIIc**, and **IIIi** were oxidized with lead tetraacetate to the corresponding 1,4-benzoquinone imine derivatives **Va**–**Vc**, and the latter were brought into reaction with sodium arenesulfinates **IIa** and **IIb** (Scheme 2). Addition of the second sodium arenesulfinate molecule to quinone imines **Va** and **Vb** resulted in the formation of only 1,4-addition products **VIa** and **VIb**, which confirmed the data of [7]. However, from quinonimine **Vc** and sodium 4-methoxybenzenesulfinate **IIb** we obtained a mixture of 6,3- and 1,6-addition products **VII** and **VIII** at a ratio of 65:35.

Compound **VII** showed in the ^{1}H NMR spectrum singlets at δ 8.17 (3-H) and 7.80 ppm (6-H). The ^{1}H NMR spectrum of **VIII** contained a doublet at δ 7.86 ppm (3-H, *meta* coupling), a doublet of doublets at δ 7.41–7.44 ppm (5-H), and a doublet at δ 7.47 ppm (6-H, *ortho* coupling).

Scheme 2.



V, $R^1 = R^2 = H$, $R^3 = Me$ (**a**); $R^1 = H$, $R^2 = R^3 = Me$ (**b**); $R^1 = R^2 = O_2N$, $R^3 = MeO$ (**c**);
VI, $R^1 = R^2 = H$, $R^3 = Me$ (**a**); $R^1 = H$, $R^2 = R^3 = Me$ (**b**).

The results of this study led us to conclude that *N*-phenyl- and *N*-(4-methylphenyl)-1,4-benzoquinone imines **Ia** and **Ib** possessing relatively small redox potentials [2] react with sodium arenesulfinates to give only 1,4-addition products due to orbital control of the reaction, whereas single-electron transfer mechanism is hardly probable because of high LUMO energies, –331.42 and –324.12 kJ/mol for compounds **Ia** and **Ib**, respectively.

The formation of mixtures of 1,4- and 6,3-addition products in the reactions of *N*-(2,4-dinitrophenyl)-1,4-benzoquinone imine with sodium arenesulfinates is also consistent with the orbital control of nucleophilic addition. Introduction of two strong electron-withdrawing substituents into the *N*-aryl fragment changes contributions of carbon atoms of the quinoid ring to the LUMO toward increased contribution of C^3. According to the results of quantum chemical calculations, the orbital coefficients of C^2, C^3, C^5 and C^6 in the LUMO are, respectively, 0.0785, 0.0808, 0.1271, and 0.1885 for quinone imine **Ib** and 0.3667, 0.6288, 0.1222, and 0.2500 for **Id**.

The reaction of even more electron-deficient *N*-(2,4-dinitrophenyl)-2-(4-methoxybenzenesulfonyl)-1,4-benzoquinone imine (**Vc**) with sodium 4-methoxybenzenesulfinate resulted in the formation of 6,3- and 1,6-addition products. The latter is most likely to be formed via radical ion mechanism [8] since introduction of electron-withdrawing $ArSO_2$ group into the quinoid ring increases the redox potential [7] and reduces the LUMO energy.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 MHz relative to tetramethylsilane as internal reference. The purity of quinone imines **Ia**–**Id** and **Va**–**Vc** was checked by TLC on Silufol UV-254 plates; samples were applied from solutions in chloroform, benzene–hexane (10:1) was used as eluent; and spots were visualized under UV light.

The X-ray diffraction data for compound **IVb** were obtained on an Xcalibur-3 diffractometer (MoK_α radiation, CCD detector, graphite monochromator, ω-scanning, $2\theta_{max} = 60°$). Monoclinic crystals; unit cell parameters (21°C): $a = 7.947(3)$, $b = 36.290(3)$, $c = 7.371(2)$ Å; $\beta = 117.59(2)$; $V = 1884.0(2)$ Å^3; M 445.40; $Z = 4$; space group $P2_1/c$; $d_{calc} = 1.570$ g× cm^{-3}; $\mu(MoK_\alpha) = 0.229$ mm^{-1}; $F(000) = 920$. Total of 22421 reflection intensities were measured, including 5454 independent reflections ($R_{int} = 0.07$). The structure was solved by the direct method using SHELXTL [9]. The positions of hydrogen atoms were determined from the difference electron density maps and were refined according to the riding model ($U_{iso} = n U_{eq}$,

where n = 1.5 for methyl groups, and n = 1.2 for other hydrogen atoms). The structure was refined against F^2 by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms; final divergence factors wR_2 = 0.032 for 5454 reflections and R_1 = 0.035 for 1646 reflections with $F > 4\sigma(F)$; goodness of fit S = 0.718. The coordinates of atoms and complete tables of bond lengths and bond angles were deposited to the Cambridge Crystallographic Data Centre (entry no. CCDC 995309).

Quantum chemical calculations were performed using Firefly QC suite [10] based in part on the GAMESS (US) code [11]. All geometric parameters of 1,4-benzoquinone imine molecules were optimized at the DFT B3LYP/6-31+G(*d*) level of theory.

Quinone imines **Ia**–**Ic** were synthesized by oxidation of the corresponding 4-aminophenols with lead dioxide in benzene, quinone imine **Id** was prepared by oxidation of 4-(2,4-dinitrophenylamino)phenol with lead tetraacetate in acetic acid as described in [12], and quinone imines **Va**–**Vc** were obtained according to the procedure reported in [5]. Compounds **Ia**, **Ib**, and **IIIc** were described previously [12, 13]. Sodium arenesulfinates **IIa**–**IIc** were synthesized according to [14].

4-(2-Nitrophenylimino)cyclohexa-2,5-dien-1-one (Ic). Yield 80%, mp 110–111°C; published data [12]: mp 112–113°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.55 d (1H, 6-H, J = 9.9 Hz), 6.74 d (1H, 2-H, J = 10.2 Hz), 6.79 d (1H, 3′-H, J = 8.1 Hz), 6.87 d (1H, 4′-H), 7.36 d (2H, 3-H, 5-H, J = 7.8 Hz), 7.63 t (1H, 5′-H), 8.15 d (1H, 6′-H, J = 7.8 Hz). Found, %: N 12.04, 12.39. $C_{12}H_8N_2O_3$. Calculated, %: N 12.28.

4-(2,4-Dinitrophenylimino)cyclohexa-2,5-dien-1-one (Id). Yield 80%, mp 160–161°C; published data [15]: mp 161.5–162°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.68 br.s (2H, 2-H, 6-H), 6.72 s (2H, 3-H, 5-H), 7.02 d (1H, 6′-H, J = 8.7 Hz), 8.46–8.50 d.d (1H, 5′-H, J = 2.1, 9.0 Hz), 9.02 d (1H, 3′-H, J = 2.4 Hz). Found, %: N 15.21, 15.52. $C_{12}H_7N_3O_5$. Calculated, %: N 15.38.

2-(4-Methylbenzenesulfonyl)-4-(phenylimino)-cyclohexa-2,5-dien-1-one (Va). Yield 90%, mp 124–126°C; published data [5]: mp 126–127°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *Z* isomer (55%): 2.44 s (3H, Me), 6.49 d (1H, 6-H, J = 10.5 Hz), 6.94 d (1H, 3-H, J = 2.4 Hz), 7.31–7.53 m (5H, Ph), 7.43 d (2H, 2″-H, 6″-H, J = 8.4 Hz), 8.02 d (2H, 3″-H, 5″-H, J = 8.4 Hz), 8.06–8.26 d.d (1H, 5-H, J = 2.4, 10.5 Hz); *E* isomer (45%): 2.43 s (3H, Me), 6.63 d (1H, 6-H, J = 9.9 Hz), 7.14–7.18 d.d (1H, 5-H, J = 2.4, 9.9 Hz), 7.31–7.53 m (5H, Ph), 7.34 d (1H, 3-H, J = 2.4 Hz), 7.50 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.92 d (2H, 3″-H, 5″-H, J = 8.1 Hz). Found, %: N 3.96, 4.21; S 9.33, 9.62. $C_{19}H_{15}NO_3S$. Calculated, %: N 4.15; S 9.50.

2-(4-Methylbenzenesulfonyl)-4-(4-methylphenylimino)cyclohexa-2,5-dien-1-one (Vb). Yield 65%, mp 147–148°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *Z* isomer (45%): 2.41 s (3H, Me), 6.58 d (1H, 6-H, J = 9.9 Hz), 7.01 d (1H, 3-H, J = 2.1 Hz), 7.42 d (2H, 2″-H, 6″-H, J = 8.4 Hz), 7.48 d (2H, 2′-H, 6′-H, J = 8.7 Hz), 7.84 d (2H, 3″-H, 5″-H, J = 8.4 Hz), 7.87 d (2H, 3′-H, 5′-H, J = 8.7 Hz), 8.04–8.16 d.d (1H, 5-H, J = 2.4 Hz); *E* isomer (55%): 2.39 s (3H, Me), 6.70 d (1H, 6-H, J = 10.2 Hz), 6.98–7.12 d.d (1H, 5-H, J = 2.4 Hz), 7.35 d (1H, 3-H, J = 2.1 Hz), 7.46 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.48 d (2H, 2′-H, 6′-H, J = 8.7 Hz), 7.94 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 7.96 d (2H, 3′-H, 5′-H, J = 8.7 Hz). Found, %: N 3.78, 4.08; S 8.95, 9.23. $C_{20}H_{17}NO_3S$. Calculated, %: N 3.99; S 9.12.

4-(2,4-Dinitrophenylamino)-2-(4-methoxybenzenesulfonyl)cyclohexa-2,5-dien-1-one (Vc). Yield 79%, mp 135–136°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.89 s (3H, MeO), 6.63 br.s (1H, 6-H), 7.01 d (2H, 2″-H, 6″-H, J = 8.4 Hz), 7.02 d (1H, 6′-H, J = 8.4 Hz), 7.34 d (1H, 3-H, J = 2.4 Hz), 8.03 br.s (1H, 5-H), 8.05 d (2H, 3″-H, 5″-H, J = 8.4 Hz), 8.51–8.54 d.d (1H, 5′-H, J = 2.4, 9.0 Hz), 9.06 d (1H, 3′-H, J = 2.1 Hz). Found, %: N 9.56, 9.66; S 7.28, 7.36. $C_{19}H_{13}N_3O_8S$. Calculated, %: N 9.48; S 7.23.

Reaction of quinone imines Ia–Id and Va–Vc with sodium arenesulfinates IIa–IIc (*general procedure*). Sodium arenesulfinate **IIa**–**IIc**, 4 mmol, was added in one portion to a solution of 2 mmol of quinone imine **Ia**–**Id** or **Va**–**Vc** in 20 mL of glacial acetic acid heated to 70°C. When the mixture turned colorless, it was cooled, and water was added until complete precipitation. The colorless solid was filtered off and washed first with cold and then with warm water. A part of the crude product was recrystallized from acetic acid. The mother liquor was diluted with water, and the precipitate was filtered off. The three crystalline samples were analyzed by ^{1}H NMR.

2-(4-Methylbenzenesulfonyl)-4-(phenylamino)-phenol (IIIa). Yield 92%, mp 82–84°C; published data [5]: mp 83–84°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.37 s (3H, Me), 6.76–7.21 m (5H, Ph), 6.95 d (1H, 6-H, J = 8.4 Hz), 7.24–7.26 d.d (1H, 5-H, J = 3, 7.8 Hz), 7.34 d (2H, 2″-H, 6″-H, J = 8.7 Hz), 7.65 d (1H, 3-H, J = 3 Hz), 7.79 d (2H, 3″-H, 5″-H, J = 8.7 Hz), 8.10 s (1H, NH), 10.20 br.s (1H, OH). Found,

%: N 3.85, 3.98; S 8.89, 9.14. $C_{19}H_{17}NO_3S$. Calculated, %: N 4.12; S 9.42.

2-(4-Methoxybenzenesulfonyl)-4-(phenylamino)-phenol (IIIb). Yield 86%, mp 82–84°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.83 s (3H, MeO), 6.76–7.22 m (5H, Ph), 6.96 d (1H, 6-H, J = 7.8 Hz), 7.11 d (2H, 2″-H, 6″-H, J = 9.0 Hz), 7.23–7.26 d.d (1H, 5-H, J = 2.7, 7.8 Hz), 7.65 d (1H, 3-H, J = 2.7 Hz), 7.87 d (2H, 3″-H, 5″-H, J = 9.0 Hz), 8.10 s (1H, NH), 10.28 br.s (1H, OH). Found, %: N 3.85, 3.98; S 8.89, 9.14. $C_{19}H_{17}NO_4S$. Calculated, %: N 3.94; S 9.02.

2-(4-Methoxybenzenesulfonyl)-4-(4-methylphenylamino)phenol (IIId). Yield 81%, mp 144–146°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.22 s (3H, 4′-Me), 3.83 s (3H, MeO), 6.80 d (1H, 6-H, J = 8.7 Hz), 6.88 d (2H, 2′-H, 6′-H, J = 7.8 Hz), 7.04 d (2H, 3′-H, 5′-H, J = 7.8 Hz), 7.10 d (2H, 2″-H, 6″-H, J = 9.0 Hz), 7.15–7.18 d.d (1H, 5-H, J = 2.7, 8.7 Hz), 7.59 d (1H, 3-H, J = 2.7 Hz), 7.85 d (2H, 3″-H, 5″-H, J = 9.0 Hz), 7.96 br.s (1H, NH), 10.09 s (1H, OH). Found, %: N 3.86, 3.77; S 8.84, 8.46. $C_{20}H_{19}NO_4S$. Calculated, %: N 3.79; S 8.68.

2-(4-Methylbenzenesulfonyl)-4-(2-nitrophenylamino)phenol (IIIe). Yield 79%, mp 163–164°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.39 s (3H, 4″-Me), 6.85 t (1H, 4′-H), 6.94 d (1H, 6-H, J = 7.8 Hz), 6.97 d (1H, 3′-H, J = 9.0 Hz), 7.40 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.43–7.46 d.d (1H, 5-H, J = 1.8, 8.4 Hz), 7.81 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 7.50 t (1H, 5′-H), 7.82 d (1H, 3-H, J = 1.8 Hz), 8.12 d (1H, 6′-H, J = 8.4 Hz), 9.39 s (1H, NH), 10.83 s (1H, OH). Found, %: N 7.35, 7.17; S 8.06, 8.38. $C_{19}H_{16}N_2O_5S$. Calculated, %: N 7.29; S 8.34.

2-(4-Methoxybenzenesulfonyl)-4-(2-nitrophenylamino)phenol (IIIf). Yield 89%, mp 150–151°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.84 s (3H, MeO), 6.85 t (1H, 4′-H), 6.95 d (1H, 6-H, J = 8.7 Hz), 6.97 d (1H, 3′-H, J = 8.4 Hz), 7.12 d (2H, 2″-H, 6″-H, J = 7.8 Hz), 7.42–7.45 d.d (1H, 5-H, J = 1.8, 8.4 Hz), 7.50 t (1H, 5′-H), 7.81 d (1H, 3-H, J = 1.8 Hz), 7.88 d (2H, 3″-H, 5″-H, J = 7.8 Hz), 8.12 d (1H, 6′-H, J = 8.7 Hz), 9.38 s (1H, NH), 10.82 s (1H, OH). Found, %: N 7.12, 6.94; S 8.14, 8.29. $C_{19}H_{16}N_2O_6S$. Calculated, %: N 7.00; S 8.01.

2-(4-Chlorobenzenesulfonyl)-4-(2-nitrophenylamino)phenol (IIIg). Yield 90%, mp 178–179°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.86 t (1H, 4′-H), 6.97 d (1H, 6-H, J = 8.4 Hz), 6.99 d (1H, 3′-H, J = 8.4 Hz), 7.47–7.50 d.d (1H, 5-H, J = 1.8, 8.4 Hz), 7.50 t (1H, 5′-H), 7.69 d (2H, 2″-H, 6″-H, J = 8.4 Hz), 7.84 d (1H, 3-H, J = 1.8 Hz), 7.94 d (2H, 3″-H, 5″-H, J = 8.4 Hz), 8.12 d (1H, 6′-H, J = 8.1 Hz), 9.39 s (1H, NH), 10.98 s (1H, OH). Found, %: N 7.15, 7.18; S 7.85, 7.99. $C_{18}H_{13}ClN_2O_5S$. Calculated, %: N 6.92; S 7.92.

4-(2,4-Dinitrophenylamino)-2-(4-methylbenzenesulfonyl)phenol (IIIh). Yield 65%, mp 193–193.5°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.39 s (3H, 4″-Me), 6.99 d (1H, 6-H, J = 8.4 Hz), 7.02 d (1H, 6′-H, J = 8.4 Hz), 7.41 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.47–7.50 d.d (1H, 5-H, J = 2.1, 8.4 Hz), 7.83 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 7.89 d (1H, 3-H, J = 2.1 Hz), 8.21–8.24 d.d (1H, 5′-H, J = 2.7, 8.4 Hz), 8.90 d (1H, 3′-H, J = 2.1 Hz), 10.14 s (1H, NH), 11.59 s (1H, OH). Found, %: N 9.62, 9.90; S 7.50, 7.16. $C_{19}H_{15}N_3O_7S$. Calculated, %: N 9.79; S 7.47.

4-(2,4-Dinitrophenylamino)-2-(4-methoxybenzenesulfonyl)phenol (IIIi). Yield 69%, mp 205–206°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.84 s (3H, MeO), 6.99 d (1H, 6-H, J = 9.0 Hz), 7.01 d (1H, 6′-H, J = 8.7 Hz), 7.13 d (2H, 2″-H, 6″-H, J = 9.0 Hz), 7.46–7.49 d.d (1H, 5-H, J = 2.1, 8.7 Hz), 7.87 d (1H, 3-H, J = 2.1 Hz), 7.88 d (2H, 3″-H, 5″-H, J = 9.0 Hz), 8.20–8.23 d.d (1H, 5′-H, J = 2.1, 8.4 Hz), 8.89 d (1H, 3′-H, J = 2.1 Hz), 10.14 s (1H, NH), 11.07 s (1H, OH). Found, %: N 9.48, 9.69; S 7.21, 7.48. $C_{19}H_{15}N_3O_8S$. Calculated, %: N 9.43; S 7.20.

4-(2,4-Dinitrophenylamino)-3-(4-methylbenzenesulfonyl)phenol (IVa). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.13 s (3H, 4″-Me), 6.20 d (1H, 6′-H, J = 9.0 Hz), 7.11 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.18–7.21 d.d (1H, 6-H, J = 2.1, 9.0 Hz), 7.34 d (1H, 5-H, J = 8.4 Hz), 7.51 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 7.67 d (1H, 2-H, J = 2.7 Hz), 7.84–7.87 d.d (1H, 5′-H, J = 3, 8.4 Hz), 8.82 d (1H, 3′-H, J = 3.0 Hz), 9.83 s (1H, NH), 10.67 br.s (1H, OH).

4-(2,4-Dinitrophenylamino)-3-(4-methoxybenzenesulfonyl)phenol (IVb). Yield 8%, mp 254–255°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.61 s (3H, MeO), 6.21 d (1H, 6′-H, J = 9.0 Hz), 6.82 d (2H, 2″-H, 6″-H, J = 8.7 Hz), 7.16–7.19 d.d (1H, 6-H, J = 2.4, 9.0 Hz), 7.34 d (1H, 5-H, J = 8.7 Hz), 7.55 d (2H, 3″-H, 5″-H, J = 8.7 Hz), 7.65 d (1H, 2-H, J = 2.1 Hz), 7.85–7.88 d.d (1H, 5′-H, J = 2.7, 8.7 Hz), 8.84 d (1H, 3′-H, J = 2.7 Hz), 9.82 s (1H, NH), 10.60 br.s (1H, OH). Found, %: N 9.55, 9.73; S 7.41, 7.32. $C_{19}H_{15}N_3O_8S$. Calculated, %: N 9.43; S 7.20.

4-(2,4-Dinitrophenylamino)-2,5-bis(4-methoxybenzenesulfonyl)phenol (VII). Yield 51%, mp 174–

176°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.63 s (3H, MeO), 3.84 s (3H, MeO), 6.79 d (1H, 6′-H, J = 8.4 Hz), 6.94 d (2H, 2″-H, 6″-H, J = 8.4 Hz), 7.09 d (2H, 2‴-H, 6‴-H, J = 8.7 Hz), 7.65 d (2H, 3″-H, 5″-H, J = 8.4 Hz), 7.80 s (1H, 6-H), 7.82–7.85 d.d (1H, 5′-H, J = 2.7, 8.7 Hz), 7.83 d (2H, 3‴-H, 5‴-H, J = 8.7 Hz), 8.17 s (1H, 3-H), 8.85 d (1H, 3′-H, J = 2.4 Hz), 10.28 s (1H, NH), 10.94 s (1H, OH). Found, %: N 7.00, 6.87; S 10.14, 10.40. $C_{26}H_{21}N_3O_{11}S_2$. Calculated, %: N 6.83; S 10.42.

4-(2,4-Dinitrophenylamino)-2-(4-methoxybenzenesulfonyl)phenyl 4-methoxybenzenesulfonate (VIII). Yield 40%, mp 152–153°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.65 s (3H, MeO), 3.85 s (3H, MeO), 6.89 s (1H, 6′-H), 6.75 d (2H, 2″-H, 6″-H, J = 8.4 Hz), 7.14 d (2H, 2‴-H, 6‴-H, J = 8.7 Hz), 7.41–7.44 d.d (1H, 5-H, J = 3, 9.0 Hz), 7.47 d (1H, 6-H, J = 8.4 Hz), 7.53 d (2H, 3″-H, 5″-H, J = 8.4 Hz), 7.86 d (1H, 3-H, J = 2.1 Hz), 7.89–7.92 d.d (1H, 5′-H, J = 2.3, 9.0 Hz), 7.91 d (2H, 3‴-H, 5‴-H, J = 8.7 Hz), 8.89 d (1H, 3′-H, J = 2.4 Hz), 10.18 s (1H, NH). Found, %: N 6.67, 6.95; S 10.31, 10.58. $C_{26}H_{21}N_3O_{11}S_2$. Calculated, %: N 6.83; S 10.42.

REFERENCES

1. Burmistrov, K.S. and Yurchenko, A.G., *Zh. Org. Khim*., 1994, vol. 30, p. 744.
2. Burmistrov, K.S., Toropin, N.V., Vakulenko, A.V., Yurchenko, A.G., and Markov, V.I., *Vopr. Khim. Khim. Tekhnol*., 2000, no. 2, p. 30.
3. Toropin, N.V. and Burmistrov, K.S., *Zh. Org. Khim*., 1983, vol. 19, p. 1546.
4. Burmistrov, K.S. and Yurchenko, A.G., *Zh. Org. Khim*., 1985, vol. 21, p. 575.
5. Burmistrov, S.I., Toropin, N.V., and Burmistrov, K.S., *Vopr. Khim. Khim. Tekhnol*., 1980, no. 61, p. 36.
6. Burmistrov, S.I. and Toropin, N.V., *Zh. Org. Khim*., 1985, vol. 21, p. 1544.
7. Burmistrov, K.S., *Doctoral (Chem.) Dissertation*, Dnepropetrovsk, 1990.
8. Konovalova, S.A., Avdeenko, A.P., Vasil'eva, V.M., and Yusina, A.L., *Russ. J. Org. Chem*., 2014, vol. 50, p. 1422.
9. Sheldrick, G.M., *SHELXTL PLUS. PC Version. A system of Computer Programs for the Determination of Crystal Structure from X-Ray Diffraction Data. Rev.5.1*, 1998.
10. Granovsky, A.A., *Firefly version 7.1.G*. http://classic.chem. msu.su/gran/firefly/index.html
11. Schmidt, M.W., Baldridge, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.J., Koseki, S., Matsunaga, N., Nguyen, K.A., Su, S., Windus, T.L., Dupuis, M., and Montgomery, J.A., Jr., *J. Comput. Chem*., 1993, vol. 14, p. 1347.
12. Burmistrov, K.S. and Burmistrov, S.I., *Ukr. Khim. Zh*., 1978, vol. 44, p. 832.
13. Pirozhenko, V.V., Burmistrov, K.S., Belov, V.V., and Nichvoloda, V.N., *Ukr. Khim. Zh*., 1992, vol. 58, p. 68.
14. Whitmore, F.C. and Hamilton, F.H., *Org. Synth*., 1922, vol. 2, p. 89.
15. Titov, E.A. and Avdeenko, A.P., *Zh. Org. Khim*., 1972, vol. 8, p. 616.