ISSN 1070-4280, Russian Journal of Organic Chemistry, 2014, Vol. 50, No. 2, pp. 200–204. © Pleiades Publishing, Ltd., 2014.
Original English Text © S.A. Konovalova, A.P. Avdeenko, A.A. Santalova, 2014, published in Zhurnal Organicheskoi Khimii, 2014, Vol. 50, No. 2, pp. 209–213.

Reaction of *N*-Arylsulfonyl-2(3)-arylsulfonylamino-Substituted 1,4-Benzoquinonimines with Sodium Arylsulfinates

S. A. Konovalova, A. P. Avdeenko, and A. A. Santalova

Donbass State Engineering Academy, Kramatorsk, 84313 Ukraine
e-mail: chimist@dgma.donetsk.ua

Received October 25, 2013

Abstract—*N*-Arylsulfonyl-3-arylsulfonylamino-substituted 1,4-benzoquinonimine reacts with sodium arylsulfinates regiospecifically along 1,4-addition scheme; *N*-tosyl-2-(tosylamino)-substituted 1,4-benzoquinonimine regioselectively affords products of 1,4- and 6,3-addition with the latter prevailing. Arylsulfinate anion enters predominantly in the *para*-position with respect to the $ArSO_2NH$ group.

DOI: 10.1134/S1070428014020109

This study is a continuation of the research on the reactions of *N*-substituted 1,4-benzoquinonimines with nucleophilic reagents. It was formerly established that *N*-arylsulfonyl-2(3)-arylsulfonylamino-substituted 1,4-benzoquinonimines reacted regiospecifically with hydrazoic acid and aromatic amines. Nucleophiles N_3^- and $ArNH^-$ enter exclusively in the *para*-position with respect to the $ArSO_2NH$ group forming the products of 6,3- and 1,4-addition respectively [1–3]. The addition of hydrogen chloride to *N*-aryl-sulfonyl-2(3)-arylsulfonylamino-substituted 1,4-benzoquinonimine also proceeds regiospecifically, but in both cases the chlorine atom of the HCl molecule adds only in the position *6* of the quinoid ring giving a single isomer, the product of 1,4-addition [2, 4]. These differences may be ascribed to different hardness of the nucleophiles.

The target of this study was investigation of the reaction between *N*-arylsulfonyl-2(3)-aryl-sulfonylamino-substitute 1,4-benzoquinonimines **Ia, Ib, II** and soft nucleophiles, sodium arylsulfinates.

The reaction of benzoquinonimines **Ia, Ib, II** with sodium arylsulfinates **IIIa, IIIb** was carried out in acetic acid at the reagents ratio 1 : 2. Me and MeO groups were mainly utilized as substituents in the *para*-position of the arylsulfonyl fragments of quinonimines and sodium arylsulfinates in order to simplify the assignment of the proton signals in the ^1H NMR spectra.

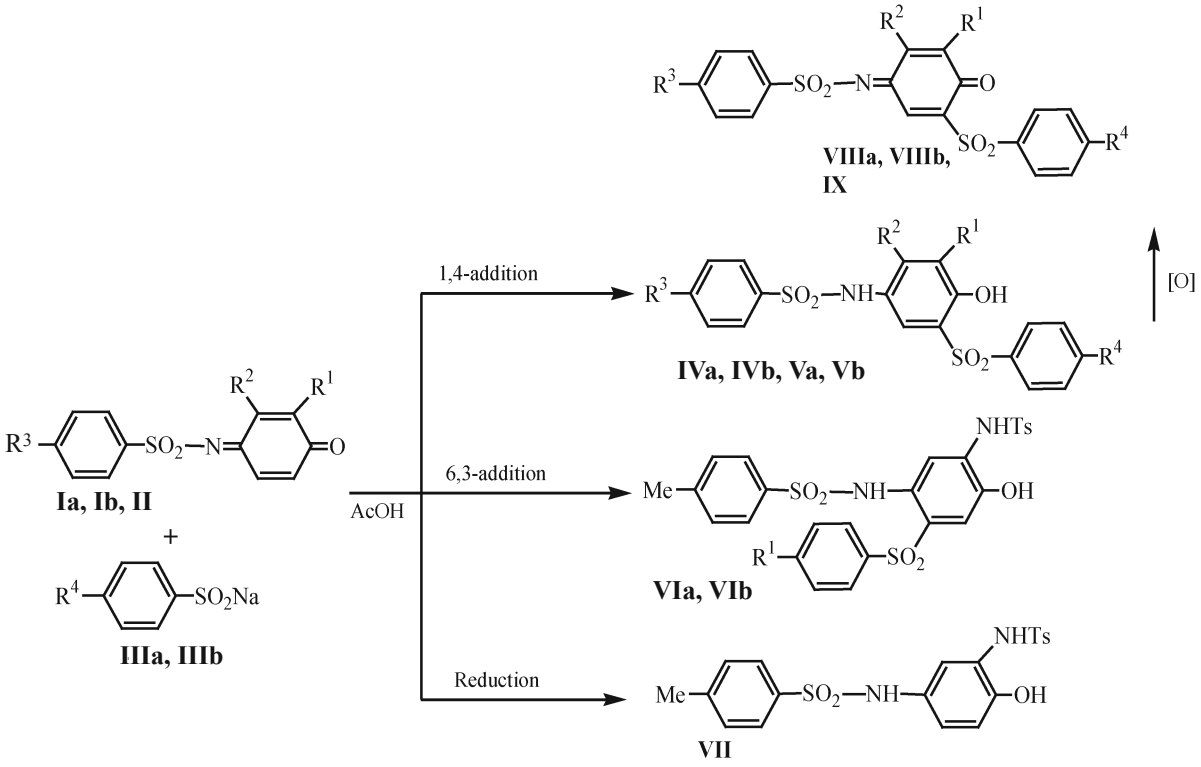
To discover all probable reaction products we analyzed by ^1H NMR spectroscopy the noncrystallized precipitate isolated from the reaction mixture, the product obtained by crystallization, and the precipitate obtained from the filtrate after crystallization.

As showed the experiments, *N*-arylsulfonyl-3-arylsulfonylamino-substituted 1,4-benzoquinonimines **Ia, Ib** added the arylsulfinate ion exclusively to the *para*-position with respect to the $ArSO_2NH$ group with the formation of products of 1,4-addition **IVa, IVb** (see the scheme), similarly to the reaction with sodium azide [1], aromatic amines [2, 3], and hydrogen chloride [2, 4]. The ^1H NMR spectra of compounds **IVa, IVb** contain two singlets of protons H^3 and H^6 in the regions δ 7.04–7.10 and 6.87–6.88 ppm.

N-(Tosyl)-2-(tosylamino)-substituted 1,4-benzo-quinonimine (**II**) reacting with sodium arylsulfinates **IIIa**, **IIIb** gives simultaneously two reaction products by 1,4-addition (**Va, Vb**) and by 6,3-addition (**VIa, VIb**) into the *para*-position with respect to TsNH group with the prevalence of the latter compound. The reaction mixture contained also an insignificant quantity of compound **VII**, the reduced form of the initial quinonimine (see the scheme). According to ^1H NMR data the percent ratio in the reaction mixture of isomers **Va, VIa** was 42 : 58, and isomers **Vb, VIb**, 41 : 59. By several consecutive crystallizations we succeeded to isolate compounds **Va, VIa, VIb** in an individual state.

The structure of compounds **VIa, VIb** is confirmed by ^1H NMR spectra where the signals of protons H^2 and H^5 from the phenol fragment appear as singlets at δ 7.22 and 7.40 (**VIa**) and at δ 7.22 and 7.39 ppm (**VIb**). In

Scheme.



I, $R^1 = R^3 = H$, $R^2 = NHSO_2C_6H_5$ (**a**); $R^1 = H$, $R^2 = TsNH$, $R^3 = Me$ (**b**); **II**, $R^1 = TsNH$, $R^2 = H$, $R^3 = Me$; **III**, $R^4 = Me$ (**a**), MeO (**b**); **IV**, $R^1 = R^3 = H$, $R^2 = NHSO_2C_6H_5$, $R^4 = MeO$ (**a**); $R^1 = H$, $R^2 = TsNH$, $R^3 = Me$, $R^4 = MeO$ (**b**); **V**, $R^1 = TsNH$, $R^2 = H$; $R^3 = R^4 = Me$ (**a**); $R^3 = Me$, $R^4 = MeO$ (**b**); **VI**, $R^1 = Me$ (**a**), MeO (**b**); **VIII**, $R^1 = R^3 = H$, $R^2 = NHSO_2C_6H_5$, $R^4 =$ MeO (**a**); $R^1 = H$, $R^2 = TsNH$, $R^3 = Me$, $R^4 = MeO$ (**b**); **IX**, $R^1 = TsNH$, $R^2 = H$, $R^3 = R^4 = Me$.

the ^1H NMR spectra of products of 1,4-addition **Va, Vb** the protons H^3 and H^5 of the phenol fragment appear as doublets due to the spin-spin coupling with *meta*-protons at δ 7.39, 7.19 (**Va**) and 7.37, 7.20 ppm (**Vb**) respectively.

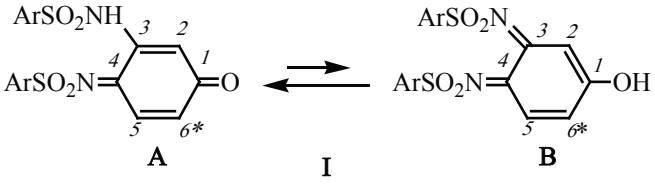
It should be mentioned that the structure determination of the products of addition to quinonimine **II** provided certain difficulties, since in the precipitates obtained from the reaction mixture always three compounds were present (considering the presence of the reduced form of the initial quinonimine), therefore the ^1H NMR spectra in the region 6.00–8.00 ppm were very intricate. When we failed to isolate individual compounds from the mixture the ratio of the reaction products was estimated from the integral intensity of the protons from the MeO and Me groups since the signals of the MeO protons belonging to the added arylsulfinate ion possessed characteristic chemical shifts for the products of 1,4- (δ 3.81−3.82 ppm) and 6,3- (δ 3.84 ppm) addition.

In order to confirm once more the structure of the obtained compounds the products of 1,4-addition **IVa, IVb, Va** were oxidized with lead tetraacetate in glacial acetic acid into the corresponding quinonimines **VIIIa**, **VIIIb, IX**, for the ^1H NMR spectra of quinonemonoimines were more informative. In the ^1H NMR spectrum of quinonimine **IX** the doublets of protons H^3 and H^5 of the quinoid fragment appear with the coupling constant 8.1 Hz at 7.96 and 7.78 (*Z*-isomer) and with the coupling constant 2.4 Hz at 9.05 and 6.79 ppm (*E*-isomer). In the ^1H NMR spectra of quinonimines **VIIIa, VIIIb** the singlets of protons H^3 and H^6 of the quinoid ring are observed at 8.88, 6.41 (**VIIIa**) and 8.88, 6.37 ppm (**VIIIb**) unambiguously proving the assumed structure of compounds **VIIIa**, **VIIIb, IX** as products of 1,4-addition.

Thus the performed research resulted in establishing that *N*-arylsulfonyl-3-(arylsulfonylamino)-substituted 1,4-benzoquinonimines reacted with sodium arylsulfinates regiospecifically along the 1,4-addition scheme, whereas *N*-(4-tosyl)-2-(4-tosyl)amino-substituted 1,4-benzoquinonimine reacted regioselectively adding the arylsulfinate ion in 1,4- and 6,3-positions with the latter

direction prevailing. Basing on the above it is possible to conclude that the main factor governing the site of the attack of arylsulfinate ion on the quinonimine is the position of $ArSO_2NH$ group in the quinoid fragment: The arylsulfinate ion adds exclusively to the *para*-position with respect to $ArSO_2NH$ group in 3-(arylsulfonylamino)-substituted 1,4-benzoquinonimines and predominantly to the *para*-position with respect to $ArSO_2NH$ group in 2-(arylsulfonylamino) derivatives.

The *N*-arylsulfonyl-2(3)-(arylsulfonylamino)-substituted 1,4-benzoquinonimines are characterized by *ortho*-*para*-quinoid tautomerism [2, 5]. In the nucleophilic addition reactions in most cases the *N*-arylsulfonyl-1,4-benzoquinonemonoimines direct the nucleophile (in particular, the sulfinate ion) in positions *2* and *6* of the quinoid ring [6–8], and *o*-quinonimines, in positions *1* and *6* [5]. In the *N*-arylsulfonyl-3-(arylsulfonylamino) derivatives of 1,4-benzoquinonimine **I** both *ortho*- and *para*-quinoid forms have concerted orientation. In quinonimines **I** in their *p*-quinoid form **A** the position *2* is shielded with $ArSO_2NH$ group, and in the *o*-quinoid form **B** the position *1* is occupied by the OH group. Therefore the arylsulfinate ion attacks only the position *6*, and the regiospecific 1,4-addition is observed.



A **I** **B**

In *N*-arylsulfonyl-2-(arylsulfonylamino) derivative **II** the orientation of *para*- and *ortho*-quinoid forms is not concerted. In the *para*-quinoid form **C** of quinonemonoimines **II** the active position is the position *6* of quinoid ring, and in the *ortho*-quinoid form **D**, the position *5* of quinoid ring (position *4* is occupied with $ArSO_2NH$ group). As mentioned above, for compound **II** both 1,4- and 6,3-additions occur with the prevalence of the latter due to the stronger orienting effect of $ArSO_2NH$ group into the *para*-position *5*, regardless of the presence of a bulky group in the position *4*.

Hence the performed experiments made it possible to establish that in reactions of *N*-arylsulfonyl-2(3)-(arylsulfonylamino)-substituted 1,4-benzoquinonimines with sodium arylsulfinates the orientation of the addition of arylsulfinate ion in the quinonimine ring is mainly governed by $ArSO_2NH$ group.

EXPERIMENTAL

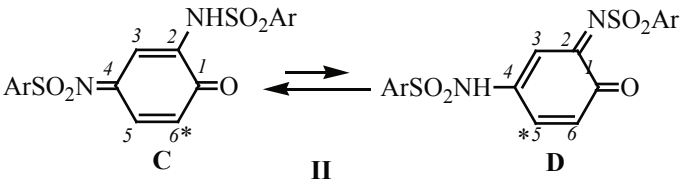
^1H NMR spectra were registered on a spectrometer Varian VXR-300 (300 MHz), internal reference TMS. The purity of quinonimines **VIIIa**, **VIIIb**, **IX** was checked by TLC on Silufol UV-254 plates, solvent chloroform, eluent benzene–hexane, 10 : 1, and development under UV irradiation.

Quinonimine **II** was synthesized by procedure [9] by the oxidation of 2,4-bis(*p*-toluenesulfonylamino)phenol with lead tetraacetate in acetic acid. Quinonimines **Ia**, **Ib** were prepared by method [2] by the oxidation of the appropriate *o*-phenylenedi(arylsulfonylamides) with iodozobenzene diacetate in the presence of boron trifluoride etherate in acetic acid medium. Sodium arylsulfinates **IIIa**, **IIIb** were prepared as described in [10].

Characteristics of quinonimines **Ia**, **Ib** [2], **II** [9] are in agreement with published data.

Reactions of quinonimines Ia, Ib, II with sodium arylsulfinates IIIa, IIIb. To a boiling solution of 2 mmol of quinonimine in 20 mL of glacial acetic acid was added in one portion 4 mmol of an appropriate sodium arylsulfinate **IIIa**, **IIIb**, and the mixture was stirred. After discoloration of the solution within several minutes the solution was cooled, and water was added till complete precipitation of reaction products. The colorless precipitate was filtered off and washed with water. A part of the precipitate was recrystallized from acetic acid. The filtrate obtained at the recrystallization was diluted with water, the separated precipitate was filtered off. The obtained precipitates were studied by ^1H NMR spectroscopy.

2-(4-Methoxyphenylsulfonyl)-4,5-bis(phenylsulfonylamino)phenol (IVa). Yield 83%, mp 177−178°C.



C **II** **D**

^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.82 s (3H, MeO), 6.88 s (1H, H^6), 7.04 s (1H, H^3), 7.07 d (2H, 4-MeOC$_6$H$_4$, H^{6,2}, *J* 9.0 Hz), 7.50 d (2H, 4-MeOC$_6$H$_4$, H^{5,3}, *J* 9.0 Hz), 7.57–7.88 m (10H, 2Ph), 9.42 s (1H, NH), 9.58 br.s (1H, NH), 10.96 s (1H, OH). Found, %: N 4.81, 5.06; S 17.04, 16.65. $C_{25}H_{22}N_2O_8S_3$. Calculated, %: N 4.87; S 16.74.

2-(4-Methoxyphenylsulfonyl)-4,5-bis(tosylamino)phenol (IVb). Yield 87%, mp 240–241°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.35 s (3H, 4-MeC$_6$H$_4$SO$_2$NH), 2.42 s (3H, 4-MeC$_6$H$_4$SO$_2$NH), 3.82 s (3H, MeO), 6.87 s (1H, H^6), 7.07 d (2H, 4-MeOC$_6$H$_4$, H^{6,2}, *J* 8.7 Hz), 7.08 s (1H, H^3), 7.38 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H$^{6',2'}$, *J* 7.8 Hz), 7.41 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H$^{6'',2''}$, *J* 7.8 Hz), 7.53 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H$^{5',3'}$, *J* 7.8 Hz), 7.53 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H$^{5'',3''}$, *J* 7.8 Hz), 7.75 d (2H, 4-MeOC$_6$H$_4$, H^{5,3}, *J* 8.7 Hz), 9.36 s (1H, NH), 9.43 br.s (1H, NH), 10.94 s (1H, OH). Found, %: N 4.74, 4.47; S 15.58, 15.96. $C_{27}H_{26}N_2O_8S_3$. Calculated, %: N 4.65; S 15.96.

2-Tosyl-4,6-bis(tosylamino)phenol (Va). Yield 26%, mp 207–208°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.36 s (6H, 2×4-MeC$_6$H$_4$SO$_2$NH), 2.39 s (3H, 4-MeC$_6$H$_4$SO$_2$), 7.19 d (1H, H^5, *J* 2.7 Hz), 7.27 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H^{6,2}, *J* 8.1 Hz), 7.34 d (2H, 4-MeC$_6$H$_4$SO$_2$, H$^{6',2'}$, *J* 7.8 Hz), 7.37 d (2H, 4-MeC$_6$H$_4$SO$_2$, H$^{6'',2''}$, *J* 8.4 Hz), 7.39 d (1H, H^3, *J* 2.7 Hz), 7.48 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H^{5,3}, *J* 8.1 Hz), 7.49 d (2H, 4-MeC$_6$H$_4$SO$_2$, H$^{5'',3''}$, *J* 8.4 Hz), 7.55 d (2H, 4-MeC$_6$H$_4$SO$_2$, H$^{5',3'}$, *J* 7.8 Hz), 9.33 br.s (1H, NH), 9.68 br.s (1H, NH), 10.16 br.s (1H, OH). Found, %: N 7.14, 6.88; S 15.69, 15.99. $C_{18}H_{14}N_2O_5S_2$. Calculated, %: N 6.96; S 15.93.

2-(4-Methoxyphenylsulfonyl)-4,6-bis(tosylamino)-phenol (Vb). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.35 s (6H, 2×4-MeC$_6$H$_4$SO$_2$), 3.81 s (3H, MeO), 7.08 d (2H, 4-MeOC$_6$H$_4$, H^{6,2}, *J* 8.7 Hz), 7.20 d (1H, H^5, *J* 2.7 Hz), 7.27 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H$^{6',2'}$, *J* 8.1 Hz), 7.37 d (1H, H^3, *J* 3.0 Hz), 7.39 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H$^{6'',2''}$, *J* 8.4 Hz), 7.47 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H$^{5',3'}$, *J* 8.1 Hz), 7.50 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H$^{5'',3''}$, *J* 8.4 Hz), 7.76 d (2H, 4-MeOC$_6$H$_4$, H^{5,3}, *J* 8.7 Hz), 9.06 s (1H, NH), 9.75 s (1H, NH), 10.16 s (1H, OH).

3-Tosyl-4,6-bis(tosylamino)phenol (VIa). Yield 30%, mp 224–226°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.35 s (3H, 4-MeC$_6$H$_4$SO$_2$NH), 2.37 s (3H, 4-MeC$_6$H$_4$SO$_2$NH), 2.38 s (3H, 4-MeC$_6$H$_4$SO$_2$), 7.22 s (1H, H^2), 7.29 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H^{6,2}, *J* 8.1 Hz), 7.34 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H$^{6',2'}$, *J* 8.4 Hz), 7.36 d (2H, 4-MeC$_6$H$_4$SO$_2$, H$^{6'',2''}$, *J* 7.8 Hz), 7.40 s (1H, H^5), 7.53 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H^{5,3}, *J* 8.1 Hz), 7.56 d (2H, 4-MeC$_6$H$_4$SO$_2$, H$^{5'',3''}$, *J* 7.8 Hz), 7.63 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H$^{5',3'}$, *J* 8.4 Hz), 9.09 s (1H, NH), 9.91 br.s (1H, NH), 10.56 br.s (1H, OH). Found, %: N 4.60, 4.86; S 16.73, 16.55. $C_{27}H_{26}N_2O_7S_3$. Calculated, %: N 4.77; S 16.40.

3-(4-Methoxyphenylsulfonyl)-4,6-bis(tosylamino)phenol (VIb). Yield 28%, mp 185–187°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.35 s (6H, 2×4-MeC$_6$H$_4$SO$_2$NH), 3.84 s (3H, MeO), 7.06 d (2H, 4-MeOC$_6$H$_4$, H^{6,2}, *J* 8.1 Hz), 7.22 s (1H, H^2), 7.30 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H$^{6',2'}$, *J* 7.5 Hz), 7.34 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H$^{6'',2''}$, *J* 7.5 Hz), 7.39 s (1H, H^5), 7.54 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H$^{5',3'}$, *J* 7.5 Hz), 7.62 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H$^{5'',3''}$, *J* 7.5 Hz), 7.63 d (2H, 4-MeOC$_6$H$_4$, H^{5,3}, *J* 8.1 Hz), 9.13 br.s (1H, OH), 10.23 br.s (2H, NH). Found, %: N 4.41, 4.59; S 16.26, 16.38. $C_{27}H_{26}N_2O_8S_3$. Calculated, %: N 4.65; S 15.96.

2,4-Bis(tosylamino)phenol (VII). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.32 s (3H, 4-MeC$_6$H$_4$SO$_2$), 2.34 s (3H, 4-MeC$_6$H$_4$SO$_2$NH), 6.51 d (1H, H^6, *J* 8.7 Hz), 6.57 d.d (1H, H^5, *J* 8.4 Hz), 7.12 d (1H, H^3, *J* 2.4 Hz), 7.27 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H^{6,2}, *J* 7.8 Hz), 7.30 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H^{5,3}, *J* 7.8 Hz), 7.51 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H$^{6',2'}$, *J* 8.4 Hz), 7.53 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H$^{5',3'}$, *J* 8.4 Hz), 9.34 br.s (1H, NH), 9.48 br.s (1H, NH), 9.70 br.s (1H, OH).

4-Imino-2-(4-methoxyphenylsulfonyl)-5-(phenylsulfonylamino)-*N*-(phenylsulfonyl)-cyclohexa-2,5-dien-1-one (VIIIa). Yield 73%, mp 163–165°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.88 s (3H, MeO), 6.41 s (1H, H^6), 7.00 d (2H, 4-MeOC$_6$H$_4$, H^{6,2}, *J* 8.7 Hz), 7.51–8.04 m (10H, 2Ph), 7.65 s (1H, NH), 7.99 d (2H, 4-MeOC$_6$H$_4$, H^{5,3}, *J* 8.7 Hz), 8.88 s (1H, H^3). Found, %: N 5.05, 5.16; S 16.63, 17.11. $C_{25}H_{20}N_2O_8S_3$. Calculated, %: N 4.89; S 16.80.

4-Imino-2-(4-methoxyphenylsulfonyl)-*N*-tosyl-5-(tosylamino)cyclohexa-2,5-dien-1-one (VIIIb). Yield 82%, mp 185–187°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.43 (3H, 4-MeC$_6$H$_4$SO$_2$NH), 2.53 s (3H, 4-MeC$_6$H$_4$SO$_2$N), 3.88 s (3H, MeO), 6.37 s (1H, H^6), 7.00 d (2H, 4-MeOC$_6$H$_4$, H^{6,2}, *J* 9.0 Hz), 7.32 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H$^{6',2'}$, *J* 8.1 Hz), 7.46 d (2H, 4-MeC$_6$H$_4$SO$_2$N, H$^{6'',2''}$, *J* 8.1 Hz), 7.69 s (1H, NH), 7.90 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H$^{5',3'}$, *J* 8.1 Hz), 7.90 d

(2H, 4-MeC$_6$H$_4$SO$_2$N, H$^{5'',3''}$, *J* 8.1 Hz), 7.99 d (2H, 4-MeOC$_6$H$_4$, H^{5,3}, *J* 9.0 Hz), 8.88 s (1H, H^3). Found, %: N 4.39, 4.62; S 16.30, 16.56. $C_{27}H_{24}N_2O_8S_3$. Calculated, %: N 4.66; S 16.01.

4-Imino-2-tosyl-6-(tosylamino)-*N*-(tosyl)-cyclohexa-2,5-dien-1-one (IX). Yield 76%, mp 209–210°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *E*-isomer: 2.44 s (3H, 4-MeC$_6$H$_4$SO$_2$NH), 2.45 s (3H, 4-MeC$_6$H$_4$SO$_2$N), 2.48 s (3H, 4-MeC$_6$H$_4$SO$_2$), 6.79 d (1H, H^5, *J* 2.4 Hz), 7.34 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H^{6,2}, *J* 8.1 Hz), 7.40 d (2H, 4-MeC$_6$H$_4$SO$_2$, H$^{6',2'}$, *J* 8.1 Hz), 7.40 d (2H, 4-MeC$_6$H$_4$SO$_2$N, H$^{6'',2''}$, *J* 8.1 Hz), 7.75 br.s (1H, NH), 7.86 d (2H, 4-MeC$_6$H$_4$SO$_2$, H$^{5',3'}$, *J* 8.1 Hz), 7.91 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H^{5,3}, *J* 8.1 Hz), 7.92 d (2H, 4-MeC$_6$H$_4$SO$_2$N, H$^{5'',3''}$, *J* 8.1 Hz), 9.05 d (1H, H^3, *J* 2.4 Hz); *Z*-isomer: 2.44 s (3H, 4-MeC$_6$H$_4$SO$_2$NH), 2.45 s (3H, 4-MeC$_6$H$_4$SO$_2$N), 2.48 s (3H, 4-MeC$_6$H$_4$SO$_2$), 7.34 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H^{6,2}, *J* 8.1 Hz), 7.40 d (2H, 4-MeC$_6$H$_4$SO$_2$, H$^{6',2'}$, *J* 8.1 Hz), 7.40 d (2H, 4-MeC$_6$H$_4$SO$_2$N, H$^{6'',2''}$, *J* 8.1 Hz), 7.72 br.s (1H, NH), 7.78 d (1H, H^5, *J* 2.4 Hz), 7.86 d (2H, 4-MeC$_6$H$_4$SO$_2$, H$^{5',3'}$, *J* 8.1 Hz), 7.91 d (2H, 4-MeC$_6$H$_4$SO$_2$NH, H^{5,3}, *J* 8.1 Hz), 7.92 d (2H, 4-MeC$_6$H$_4$SO$_2$N, H$^{5'',3''}$, *J* 8.1 Hz), 7.96 d (1H, H^3, *J* 2.4 Hz). Found, %: N 4.75, 4.97; S 16.60, 16.71. $C_{27}H_{24}N_2O_7S_3$. Calculated, %: N 4.79; S 16.45.

REFERENCES

1. Avdeenko, A.P., Menafova, Yu.V., Evgrafova, N.I., Zhukova, S.A., Dementii, L.V., Marchenko, I.L., *Russ. J. Org. Chem.,* 1997, vol. 33, p. 221.
2. Avdeenko, A.P., *Russ. J. Org. Chem.,* 1998, vol. 34, p. 515.
3. Avdeenko, A.P., Evgrafova, N.I., Tolmachev, A.A., and Polyakov, A.E., *Zh. Org. Khim.,* 1990, vol. 26, p. 1751.
4. Avdeenko, A.P., Evgrafova, N.I., Mishchenko, A.I., and Belambri Nur Urida., *Zh. Org. Khim.,* 1987, vol. 23, p. 97.
5. Adams, R. and Stewart, G.M., *J. Am. Chem. Soc*., 1952, vol. 72, p. 5876.
6. Adams, R., Reifschneider, W., *Bull. Soc. Chim*., 1958, p. 23.
7. Toropin, N.V., Burmistrov, K.S., Burmistrov, S.I., Zaichenko, N.L., *Zh. Org. Khim.,* 1986, vol. 22, p. 999.
8. 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.
9. Titov, E.A., Avdeenko, A.P., and Rudchenko, V.F., *Zh. Org. Khim.,* 1972, vol. 8, p. 2546.
10. *Sint. Org. Prep*., 1949, vol. 1, p. 394.