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Reactions of *N*-Arylsulfonyl-2-arenesulfonamido-1,4-benzo-quinone 4-Imines with Naphthols

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Abstract—Reactions of *N*-arylsulfonyl-2-arenesulfonamido-1,4-benzoquinone 4-imines unsubstituted in the ring or 6-chloro and 5,6-dichlorosubstituted with 1- or 2-naphthols and 2-methoxynaphthalene provided the corresponding *N*-arylsulfonyl-2-arenesulfonamido-6-[2-hydroxy(methoxy)-1-naphthyl]-4-aminophenols from the unsubstituted reagent and reduction products from the mono- and dichlorosubstituted quinone imines.

Unlike reaction of N-substituted para-benzoquinone imines with phenols and naphthols in alkali-water media (Burmistrov indophenol reaction [1]) that affords indophenols(naphthols), the reaction between N-substituted *para*-benzoquinone imines with phenols and naphthols in organic solvents in the presence of Lewis acids occurs as 1,4-addition yielding N-substituted 2-hydroxyaryl-4-aminophenols (naphthols).

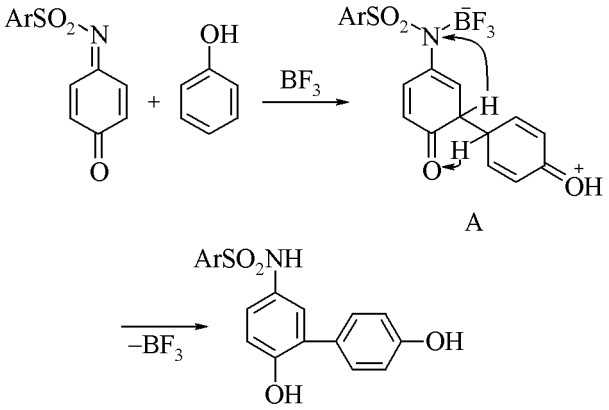
Both the phenolate ion in the Burmistrov indophenol reaction and the phenol molecule in the reaction with N-substituted *para*-benzoquinone imines in organic solvents in the presence of Lewis acids play the role of a CH-acid.

The reaction of phenols and naphthols in the presence of Lewis acid was in most detail investigated by an example of *N*-arylsulfonyl-2-chloro-1,4-benzo-(naphtho)quinone 4-imines [2–5]. It was demonstrated that phenols addition occurred in the 4-position, that of 1-naphthols in 2-position, and of 2-naphthols in 1-position [5]. The N-arylsulfonyl-2-chloro-1,4-benzoquinone imines react with phenols and naphthols similarly to quinone imines unsubstituted in the quinoid ring [4].

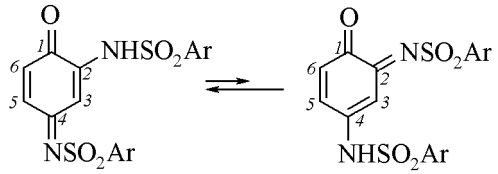
In reaction of *N*-arylsulfonyl-2,6-dichloro-1,4-benzoquinone 4-imines with 2-naphthol occurs nucleophilic substitution of one chlorine atom and reduction of the arising quinoid product into 4-amino-*N*-arylsulfonyl-6-(2-hydroxynaphthyl)-2-chlorophenols [4].

The methyl ethers of phenols and naphthols behave with *N*-arylsulfonyl-1,4-benzoquinone imines analogously to the corresponding phenols and naphthols [6].

The addition of phenols and naphthols in chloroform in the presence of BF_3 apparently occurs via intermediate formation of complex (A) [4].



2-Arenesulfonamido-*N*-arylsulfonyl-1,4-benzoquinone 4-imines can exist as two isomers (with *ortho*- and *para*-quinoid structure with the latter of lower redox potential prevailing). This fact affects the direction of their reactions with different nucleophiles. For instance, at HCl addition the Cl^- anion in the first stage enters into 6-position, and in the second stage into 5-position of the quinoid ring [7].



The reaction with aromatic amines occurs as addition of arylamino group to 5-position of the quinoid ring with simultaneous nucleophilic substitution of the $ArSO_2$ group adjacent to the imine nitrogen followed by oxidation of the intermediate compound with air oxygen to afford *N*-aryl-5-arylamino-2-arenesulfonamido-1,4-benzoquinone-4-imines (B) as final products [8].

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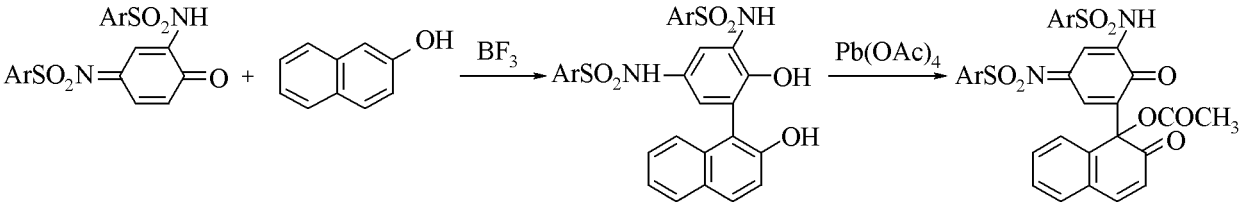
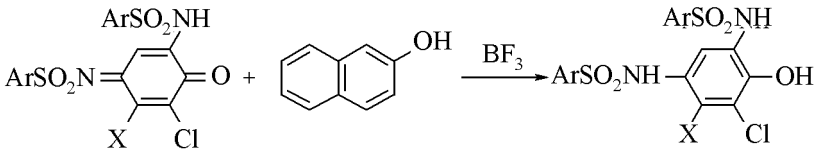
Scheme 1.



Ia–c **IVa–c** **Va–c**

Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**).

Scheme 2.



IIa–c, IIIa–c **VIa–c, VIIa–c**

Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**); X = H (**II, VI**), Cl (**III, VII**).

The other direction of reaction between *N*-arylsulfonyl-2-arenesulfonamido-1,4-benzoquinone 4-imines with naphthols also was not excluded.

The reaction with naphthols was studied on unsubstituted in the quinoid ring **Ia–c** and also on 6-chloro **IIa–b**, and 2,6-dichloro **IIIa–c** derivatives of N-arylsulfonyl-2-arenesulfonamido-1,4-benzoquinone imines.

Quinone imines **Ia–c** react with 2-naphthol similarly to unsubstituted in the ring *N*-arylsulfonyl-1,4-benzoquinone imines, i.e. 2-naphthol adds by 1,4 scheme to quinone imine with its active 1-position yielding 2,4-diarenesulfonamido-6-(2-hydroxy-1-naphthyl)phenols **IVa–c** (Scheme 1). The reaction was carried out in chloroform in the presence of catalytic amounts of boron trifluoride etherate.

We showed formerly [9] by an example of reaction between *N*-arylsulfonyl-1,4-benzoquinone 4-imines with phenols that on their oxidation with lead tetraacetate formed quinoneiminequinol acetates, and by measuring the redox potentials of 4-arenesulfonamido-2-(2-hydroxy-1-naphthyl)phenols it was demonstrated that the first stage consisted in formation of quinone imine and only in the second stage arose quinoneiminequinol acetate [10]. The oxidation of compounds **IVa–c** with lead tetraacetate also gave rise to *N*-arylsulfonyl-2-arenesulfonamido-6-(1-acetoxy-1,2-dihydro-2-oxo-1-naphthyl)-1,4-benzoquinone 4-imines **Va–c** (Scheme 1).

In reaction with 2-naphthol *N*-arylsulfonyl-2-arenesulfonamido-6-chloro-1,4-benzoquinone 4-imines **IIa–c** undergo reduction to the corresponding *N*-arylsulfonyl-2-arenesulfonamido-6-chloro-4-arenesulfonamidophenols **VIa–c**. Similarly reacted *N*-arylsulfonyl-2-arenesulfonamido-5,6-dichloro-1,4-benzoquinone imines **IIIa–c** (Scheme 2).

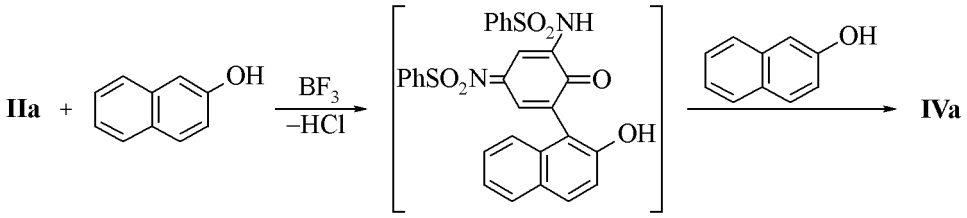
In the study of the reaction between 2-naphthols and substituted benzoquinone imines **IIa–c** in one case alongside the reduction was observed a nucleophilic substitution of a chlorine with 2-hydroxynaphthyl moiety with simultaneous reduction of the intermediate quinone imine into compound **IVa** identical to that obtained in reaction of quinone imine **Ia** with 2 naphthol (Scheme 3).

2-Methoxynaphthalene reacts with quinone imines **Ia–c**–**IIIa–c** similarly to 2-naphthol. With unsubstituted quinone imines **Ia–c** occurs addition of 2-methoxynaphthalene to substrate along 1,4-scheme at the active 1-position (Scheme 4) to yield compounds **VIIIa–c**.

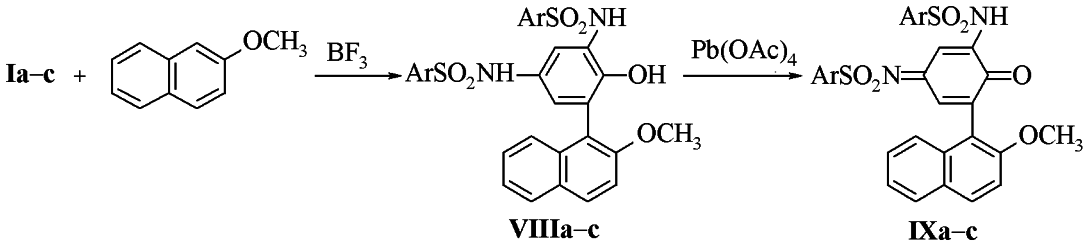
With mono- and dichloroquinone imines **IIa–c, IIIa–c** we did not observe nucleophilic substitution of chlorine, and in all cases, as with 2-naphthol, were separated the corresponding reduced forms of quinone imines **VIa–c, VIIa–c**.

Compounds **VIIIa–c** on oxidation with lead tetraacetate afford *N*-arylsulfonyl-2-arenesulfonamido-6-(2-methoxy-1-naphthyl)-1,4-benzoquinone

Scheme 3.



Sceheme 4.



Ar = Ph (**a**), 4-μeC$_6$H$_4$ (**b**), 4-ClC$_6$H$_4$ (**c**).

4-imines **IXa–c**. In the case 2-methoxy-1-naphthyl fragment unlike 2-hydroxy-1-naphthyl moiety did not suffer oxidation to quinol acetate.

In contrast to *N*-arylsulfonyl-1,4-benzoquinone imines [5] quinone imines **Ia–c, IIa–c, IIIa–c** are reduced by 1-naphthol into the corresponding *N*-arylsulfonyl-2-arenesulfonamido-4-amino-phenols **Xa–c**, **VIa–c, VIIa–c**. No hydroxyarylation was observed.

The composition and structure of the newly synthesized compounds are confirmed by elemental analyses (Table 1) and ^{1}H NMR spectra (Table 2).

The structure of previously known compounds arising in the course of reactions (**VIa–c, VIIa–c** and 2,4-diarenesulfonamidophenols **Xa–c**) was confirmed by comparison with authentic samples. In the IR spectra of compounds **Va–c** appear absorption band in the range 3260–3250, 1755–1750, 1670–1660, 1645–1630, 1600–1590, 1340–1320 and 1180–1170 cm^{-1} characteristic of groups NH, C=O, C=N, and SO_2 respectively.

The ^{1}H NMR spectra of compounds **IVb, c, Va, c, VIIIa–c** are in total agreement with their assumed structures.

Table 1. Yields, melting points, and elemental analyses of aminophenols **IVa–c, VIIIa–c** and of their oxidation products **Va–c, IXa–c**

Compd. no.	Yield, %	mp, °C (solvent for crystallization)	Found S, %	Formula	Calculated S, %
IVa	72	278 ($C_6H_5NO_2$)	11.43, 11.72	$C_{28}H_{23}N_2O_6S_2$	11.70
IVb	80	261 (CH_3CO_2H)	10.78, 10.96	$C_{30}H_{27}N_2O_6S_2$	11.13
IVc	77	252 (CH_3CO_2H)	10.04, 10.23	$C_{28}H_{21}Cl_2N_2O_6S_2$	10.39
Va	96	177 (decomp.) (toluene)	10.72, 10.78	$C_{30}H_{23}N_2O_7S_2$	10.90
Vb	81	181 (decomp.) (CH_3CO_2H)	9.88, 10.02	$C_{34}H_{26}N_2O_7S_2$	10.03
Vc	81	204 (decomp.) (toluene)	9.61, 9.67	$C_{30}H_{20}Cl_2N_2O_7S_2$	9.77
VIIIa	53	235 (CH_3CO_2H)	11.32, 11.67	$C_{29}H_{24}N_2O_6S_2$	11.43
VIIIb	70	243 (CH_3CO_2H)	11.74, 11.85	$C_{31}H_{28}N_2O_6S_2$	10.88
VIIIc	72	215 (CH_3CO_2H)	10.07, 10.21	$C_{29}H_{22}Cl_2N_2O_6S_2$	10.17
IXa	97	136 (decomp.) (CH_3CO_2H)	11.45, 11.54	$C_{29}H_{22}N_2O_6S_2$	11.47
IXb	73	141 (decomp.) (CH_3CO_2H)	10.95, 10.98	$C_{31}H_{26}N_2O_6S_2$	10.92
IXc	76	163 (decomp.) (CH_3CO_2H)	10.10, 10.22	$C_{29}H_{20}Cl_2N_2O_6S_2$	10.21

Table 2. Spectra ^{1}H NMR (**IVb, c, VIIIa–c**) and (**Va, c**)

Compd.	Solvent	Chemical shift, δ, ppm						
		H^3	H^5	H (naftalin)	$ArSO_2$	NH, OH	CH_3CO	CH_3O
IVb	DMSO-d_6	6.42 d	7.22 d	6.47-7.76 m (6H)	7.31-7.53 d.d (8H), 2.34 c (3H, CH_3), 2.35 c (3H, CH_3) 8.00 br.s (1H)	9.72 br.s (1H), 9.35 br.s (1H), 9.03 br.s (1H),	–	–
IVc	DMSO-d_6	6.48 br.s	7.19 br.s	6.50-7.71 m (6H)	7.55-7.74 A-A (8H)	9.84 br.s (2H), 8.95 br.s (2H)	–	–
Va	$CDCl_3$	7.88 d	7.36 d	6.33-8.08 m (6H)	6.33-8.08 m (10H)	8.88 br.s (1H)	2.02 c (3H)	–
Vc	Aceton-*d*6	7.76 d	7.32 d	6.22-8.12 m (6H)	7.47-7.79 d.d (4H), 7.64-7.79 d.d (4H)	9.30 m.c (1H)	2.04 c (3H)	–
VIIIa	DMSO-d_6	6.40 d	7.25 d	6.47-7.92 m (6H)	7.20-7.65 m (10H)	9.83 br.s (1H), 9.17 br.s (1H), 8.13 br.s (1H)	–	3.65 c (3H)
VIIIb	DMSO-d_6	6.39 d	7.24 d	6.50-7.94 m (6H)	7.32-7.54 d.d (8H), 2.35 c (6H, CH_3)	9.79 br.s (1H), 9.12 br.s (1H), 8.14 br.s (1H)	–	3.66 c (3H)
VIIIc	DMSO-d_6	6.40 d	7.19 d	6.46-7.94 m (6H)	7.60 c (4H), 7.65 c (4H)	9.94 br.s (1H), 9.37 br.s (1H), 8.22 br.s (1H)	–	3.67 c (3H)

EXPERIMENTAL

IR spectra were recorded on spectrophotometer UR-20 from KBr pellets. ^{1}H NMR spectra were registered on Varian VXR-300 instrument at operating frequency 300 MHz with TMS as reference.

Initial quinone imines **Ia–c, IIa–c, IIIa–c** were prepared by oxidation with lead tetraacetate the corresponding 2,4-diarenesulfonamidophenols as described in [78, 11].

***N*-Arylsulfonyl-2-arenesulfonamido-6-(2-hydroxy-1-naphthyl)-4-aminophenols (IVa–c).** To a solution of 1 mmol of quinone imine **Ia–c** in 5 ml of chloroform was added 1,1mmol of 2-naphthol, the mixture was heated to boiling, and 3–5 drops of boron trifluoride etherate was added. Then the mixture was left standing at room temperature for 24 h. The separated precipitate was filtered off and washed with a little of chloroform.

Compound **IVa** was prepared also along the above procedure from quinone imine **IIa** and double excess of 2-naphthol. The compound was purified from the reduction product by repeated recrystallizations from acetic acid.

***N*-Arylsulfonyl-2-arenesulfonamido-6-(2-methoxy-1-naphthyl)-4-aminophenols (VIIIa–c**) were prepared analogously to compounds **IVa–c** from quinone imines **Ia–c** and 2-methoxynaphthalene. The characteristics of compounds **VIIIa–c** are given in Table 1.

***N*-Arylsulfonyl-2-arenesulfonamido-6-(1-acetoxy-1,2-dihydro-2-oxo-1-naphthyl)-1,4-benzoquinone 4-imines (Va–c).** To a solution of 1 mmol of aminophenol **IVa–c** in 5 ml of acetic acid was added 2.2 mmol of lead tetraacetate, and the solution was heated to boiling. As a result the solution turned yellow. On cooling to room temperature 1 ml of ethylene glycol was added, the mixture was stirred for 5 min and was diluted with water. The separated yellow precipitate was filtered off and washed with methanol.

***N*-Arylsulfonyl-2-arenesulfonamido-6-(2-methoxy-1-naphthyl)-1,4-benzoquinone 4-imines (IXa–c).** To a mixture of 10 mmol of aminophenol **VIIIa–c** in 10 ml of acetic acid was added 11 mmol of lead tetraacetate, and the mixture was heated to dissolution of the initial compounds. The solution turned dark violet. To the cooled solution 2 ml of ethylene glycol was added, the mixture was stirred for 5 min, and left standing at room temperature for several hours. The precipitate of dark-violet crystals was filtered off and washed with methanol.

Reaction of quinone imines IIa–c, IIIa–c with 2-naphthol or 2-methoxynaphthalene, and of quinone imines Ia–c, IIa–c, IIIa–c with 1-naphthol. The reactions were carried out at the same conditions as reactions of quinone imines **Ia–c** with 2-naphthol and 2-methoxynaphthalene. As a result we obtained the corresponding reduced forms of quinone imines **Xa–c, VIa–c, VIIa–c** in 70–85% yield. The reaction products were identified by comparison of the IR spectra of compounds obtained with those of authentic samples.

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