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Reactions of Arylsulfinyl Chlorides and *N*-(Arylsulfonyl)arylsulfinimidoyl Chlorides with *p*-Aminophenols

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Abstract—In reactions of arylsulfinyl chlorides and *N*-(arylsulfonyl)arylsulfinimidoyl chlorides with *p*-aminophenols formed *N*-arylthio-1,4-benzoquinone imines, evidently through a stage of *N*-arylsulfinyl-4-aminophenols and *N*-(*N*-arylsulfonyl)arylsulfinylimidoyl-4-aminophenols that under the reaction conditions eliminate respectively H_2O and $ArSO_2NH_2$.

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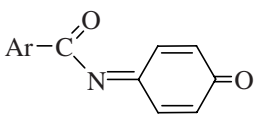
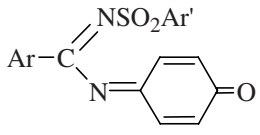
We thoroughly investigated formerly the structural features and reactivity of *N*-aroyl-1,4-benzoquinone monoimines **I**. *N*-(*N*-arylsulfonyl)arylimidoyl-1,4-benzoquinone monoimines **II** are their structural analogs with a similar reactivity [1].

Recently we prepared for the first time *N*-arylsulfinyl-1,4-benzoquinone monoimines **III** in reaction of arylsulfinyl chlorides with alkyl-substituted *p*-aminophenols in ethyl ether or dioxane followed by oxidation in situ of the formed *N*-arylsulfinyl-4-aminophenols with silver oxide or lead tetraacetate [2].

In this study we attempted to synthesize structural analogs of *N*-arylsulfinyl-1,4-benzoquinone monoimines **III**, *N*-(*N*-arylsulfonyl)aryl-sulfinylimidoyl-1,4-benzoquinone monoimines **IV**. An extensive literature exists on the synthesis and reactivity of *N*-(arylsulfonyl)aryl-sulfinylimidoyl chlorides **V** [3]. Based on published data we presumed a possible preparation of quinone imines **IV** by reaction of *N*-(arylsulfonyl)arylsulfinylimidoyl chlorides **V** with *p*-aminophenols **VI** with subsequent oxidation of formed *N*-(*N*-arylsulfonyl)aryl-sulfinyl-imidoyl-4-aminophenols **A**.



I



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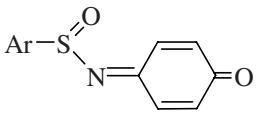
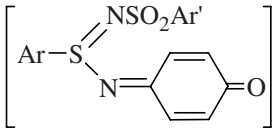


III



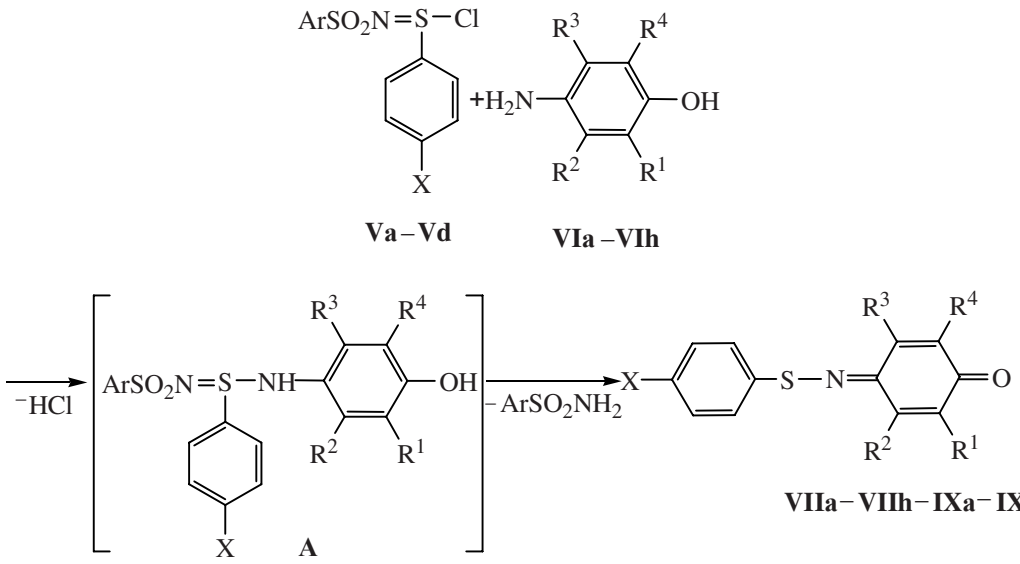
IV

However in the reaction of *N*-(arylsulfonyl)-arylsulfinylimidoyl chlorides **Va–Vd** with *p*-aminophenols **VIa–VIh** *N*-arylthio-1,4-benzoquinone monoimines **VIIa–VIIh–IXa–IXh** were obtained (Scheme 1). The reaction was carried out in ethyl ether, dioxane in the presence of triethylamine, and in pyridine. The best results were obtained in reactions performed in pyridine.

Evidently the formed in the reaction unstable compound **A,** *N*-(*N*-arylsulfonyl)arylsulfinylimidoyl-4-aminophenol, suffered arylsulfamide elimination as was experimentally proved by isolating from the reaction mixture also the corresponding arylsulfamides.

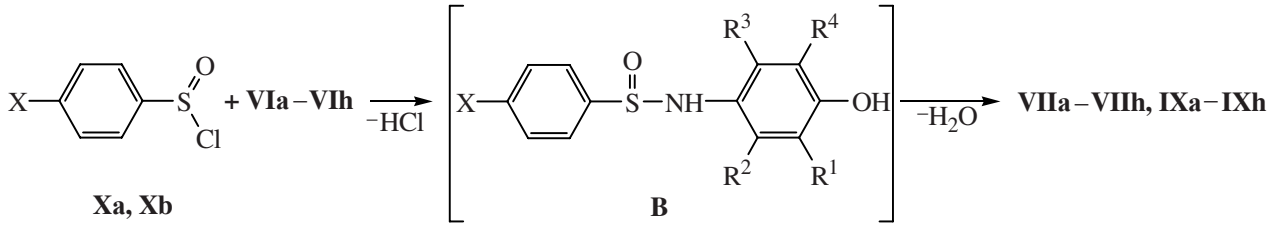
Thus we discovered a new unusual preparation method for *N*-arylthio-1,4-benzoquinone monoimines **VII–IX**: as a result of an intramolecular redox process the tetravalent sulfur in compound **A** is reduced into bivalent, and the aminophenol moiety is oxidized to quinone imine. Note the high purity of compounds obtained and the absence of disulfide impurities which are difficult to remove from *N*-arylthio-1,4-benzoquinone monoimines in preparation by the other traditional methods [4, 5].

Scheme 1.



V, Ar = Ph (**a, b, c**), 4-ClC_6H_4 (**d**); X = H (**a**), Cl (**b**), NO_2 (**c, d**); **VI–IX**, $R^1 = R^4$ = Me, $R^2 = R^3$ = H (**a**); $R^1 = R^4$ = H, $R^2 = R^3$ = Me (**b**); $R^1 = R^3$ = Me, $R^2 = R^4$ = H (**c**); R^1 = *i*-Pr, R^3 = Me, $R^2 = R^4$ = H (**d**); R^1 = Me, $R^2 = R^3 = R^4$ = H (**e**); R^2 = Me, $R^1 = R^3 = R^4$ = H (**f**); $R^1 = R^4$ = Cl, $R^2 = R^3$ = H (**g**); R^1 = Me, R^3 = *i*-Pr, $R^2 = R^4$ = H (**h**); X = H (**VII**), Cl (**VIII**), NO_2 (**IX**).

Scheme 2.



X = H (**a**), NO_2 (**b**).

A similar intramolecular redox process occurs also with *N*-arylsulfinyl-4-aminophenols **B** when the reaction of arylsulfinyl chlorides with *p*-aminophenols is carried out not in ethyl ether or dioxane but in pyridine (Scheme 2). In this event unstable compound **B** eliminates an H_2O molecule and undergoes the intramolecular redox process involving tetravalent sulfur reduction into bivalent and aminophenol moiety oxidation into quinone imine.

N-arylthio-1,4-benzoquinone imines **VIIa–VIId**, **VIIg, VIIh, VIIIa–VIIIh, IXa, IXb**, and **IXg** obtained were identical to those described in publications [4–6]. The structure of newly prepared quinone imines **VIIe**, **VIIf, IXc–IXf,** and **IXh** was proved by elemental analyses and ^{1}H NMR spectra.

Thus the investigation performed established that in reactions of *p*-aminophenols with arylsulfinyl chlorides and N-(aryl-sulfonyl)arylsulfinylimidoyl chlorides first formed the corresponding unstable *N*-arylsulfinyl-4-aminophenols and *N*-(*N*-arylsulfonyl)arylsulfinyl-imidoyl-4-aminophenols which we failed to isolate in the individual state. Then an intramolecular redox process occurred involving water or arylsulfamide elimination leading to the formation of N-arylthio-1,4-benzoquinone imines.

EXPERIMENTAL

^{1}H NMR spectra were registered on a spectrometer Varian VXR-300 at operating frequency 300 MHz from solutions in deuterochloroform, internal reference TMS.

TLC was carried out on Silufol UV-254 plates using chloroform as solvent, eluent benzene–hexane, 10:1, spots visualized under UV irradiation.

N-Arylthio-1,4-benzoquinone imines VIIa–VIIh–IXa–IXh. To a dispersion of 2 mmol of *p*-aminophenol **VIa–VIh** in 20 ml of anhydrous ethyl ether was added an equimolar quantity of the corresponding arylsulfinyl chloride and triethylamine. The separated precipitate of triethylamine hydrochloride was filtered off, the filtrate was evaporated under a vacuum of a water-jet pump. The precipitate obtained was washed with methanol and glacial acetic acid, and recrystallized from the glacial acetic acid or hexane.

The characteristics of quinone imines **VIIa, VIIb–IXa, IXb** are published in [5], those of **VIIc, VIId, VIIh, VIIIa–VIIIf**, and **VIIIh** in [6], **VIIg–IXg** in [4].

***N*-Phenylthio-2-methyl-1,4-benzoquinone imine (VIIe).** Yield 52%, mp 116–118°C. ^{1}H NMR spectrum, δ, ppm, *Z*-isomer (32%): 7.30–7.64 m (5H, Ph), 7.39–7.43 d.d [1H, H^5, *J*(H^{3,5}) 3.0, *J*(H^{5,6}) 9.9 Hz], 7.01 q (1H, H^3), 6.56 d [1H, H^6, *J*(H^{5,6}) 9.9 Hz], 2.03 d (3H, C^{2}H$_3$, *J* 1.5 Hz); *E*-isomer (68%): 7.30–7.64 m (5H, Ph), 7.06–7.10 d.d [1H, H^5, *J*(H^{3,5}) 3.0, *J*(H^{5,6}) 9.9 Hz], 7.30 q (1H, H^3), 6.49 d [1H, H^6, *J*(H^{5,6}) 9.6 Hz], 2.09 d (3H, C^{2}H$_3$, *J* 1.2 Hz). Found, %: N 6.08, 6.10; S 13.92, 14.01. $C_{13}H_{11}NOS$. Calculated, %: N 6.11; S 13.98.

***N*-Phenylthio-3-methyl-1,4-benzoquinone imine (VIIf).** Yield 61%, mp 124–125°C. ^{1}H NMR spectrum, δ, ppm: 7.30–7.63 m (5H, Ph), 7.40 d [1H, H^5, *J*(H^{5,6}) 10.2 Hz], 6.47–6.51 d.d [1H, H^6, *J*(H^{2,6}) 1.8, *J*(H^{5,6}) 9.9 Hz], 6.39 q (1H, H^2), 2.26 d (3H, C^{3}H$_3$, *J* 1.2 Hz). Found, %: N 6.01, 6.08; S 13.74, 13.97. $C_{13}H_{11}NOS$. Calculated, %: N 6.11; S 13.98.

***N*-4-Nitrophenylthio-2,5-dimethyl-1,4-benzoquinone imine (IXc).** Yield 60%, mp 224–225°C. ^{1}H NMR spectrum, δ, ppm: 7.75–8.32 d.d (4H, Ar, J_O 9.0 Hz), 7.19 d (1H, H^3), 6.42 q (1H, H^6), 2.29 d (3H, C^{5}H$_3$, *J* 1.2 Hz), 2.09 d (3H, C^{2}H$_3$, *J* 1.5 Hz). Found, %: N 9.60, 9.78; S 11.08, 11.25. $C_{14}H_{12}N_2O_3S$. Calculated, %: N 9.72; S 11.12.

***N*-4-Nitrophenylthio-6-isopropyl-3-methyl-1,4-benzoquinone imine (IXd).** Yield 57%, mp 154–155°C. ^{1}H NMR spectrum, δ, ppm: 7.76–8.32 d.d (4H, Ar, J_O 9.0 Hz), 7.09 d (1H, H^5), 6.41 q (1H, H^2), 3.07–3.16 m (1H, CH in *i*-Pr), 2.29 d [3H, C^{3}H$_3$, *J* 0.9 Hz], 1.18 d (6H, Me in *i*-Pr, *J* 6.9 Hz). Found, %: N 8.71, 8.86; S 10.01, 10.16. $C_{16}H_{16}N_2O_3S$. Calculated, %: N 8.85; S 10.13.

***N*-4-Nitrophenylthio-2-methyl-1,4-benzoquinone imine (IXe).** Yield 53%, mp 161–163°C. ^{1}H NMR spectrum, δ, ppm, *Z*-isomer (38%): 7.78–8.32 d.d (4H, Ar, J_o 9.3 Hz), 7.37–7.41 d.d [1H, H^5, *J*(H^{3,5}) 3.0, *J*(H^{5,6}) 10.2 Hz], 7.08 q (1H, H^3), 6.62 d [1H, H^6, *J*(H^{5,6}) 9.6 Hz], 2.07 d (3H, C^{2}H$_3$, *J* 1.2 Hz); *E*-isomer (62%): 7.78–8.32 d.d (4H, Ar, J_o 9.3 Hz), 7.12–7.17 d.d [1H, H^5, *J*(H^{3,5}) 3.0, *J*(H^{5,6}) 9.9 Hz], 7.28 q (1H, H^3), 6.55 d [1H, H^6, *J*(H^{5,6}) 9.9 Hz], 2.12 d (3H, C^{2}H$_3$, *J* 1.5 Hz). Found, %: N 10.07, 10.24; S 11.69, 11.83. $C_{13}H_{10}N_2O_3S$. Calculated, %: N 10.21; S 11.69.

***N*-4-Nitrophenylthio-3-methyl-1,4-benzoquinone imine (IXf).** Yield 56%, mp 164–165°C. ^{1}H NMR spectrum, δ, ppm: 7.76–8.33 d.d (4H, Ar, J_O 9.0 Hz), 7.38 d [1H, H^5, *J*(H^{5,6}) 10.2 Hz], 6.53–6.57 d.d [1H, H^6, *J*(H^{2,6}) 2.1, *J*(H^{5,6}) 10.2 Hz], 6.45 q (1H, H^2), 2.32 d (3H, C^{3}H$_3$, *J* 1.2 Hz). Found, %: N 10.07, 10.20; S 11.58, 11.72. $C_{13}H_{10}N_2O_3S$. Calculated, %: N 10.21; S 11.69.

***N*-4-Nitrophenylthio-5-isopropyl-2-methyl-1,4-benzoquinone imine (IXh).** Yield 65%, mp 155–157°C. ^{1}H NMR spectrum, δ, ppm: 7.75–8.33 d.d (4H, Ar, J_o 9.0 Hz), 7.22 d (1H, H^3, *J* 1.5 Hz), 6.40 q (1H, H^6), 3.41–3.50 m (1H, CH in *i*-Pr), 2.09 d (3H, C^{2}H$_3$, *J* 1.5 Hz), 1.24 d (6H, Me in *i*-Pr, *J* 6.9 Hz). Found, %: N 8.71, 8.96; S 10.10, 10.26. $C_{16}H_{16}N_2O_3S$. Calculated, %: N 8.85; S 10.13.

Reaction of *p*-aminophenols VIa–VIh with arylsulfinyl chlorides and *N*-(arylsulfonyl)arylsulfinylimidoyl chlorides. *a.* To a solution of 1 mmol of *p*-aminophenol **VIa–VIh** in 2 ml of pyridine was added 1 mmol of an appropriate arylsulfinyl chloride **Xa** or **Xb** or *N*-(arylsulfonyl)arylsulfinylimidoyl chloride **Va** or **Vd**. The solution was heated at 60–70°C. After 30 min the reaction mixture was cooled and poured on ice mixed with HCl. The arising oily substance crystallized on addition of a little AcOH. The formed precipitate of *N*-arylthio-1,4-benzoquinone imines **VIIa–VIIh–IXa–IXh** was recrystallized from acetic acid. The *N*-arylthio-1,4-benzoquinone imines obtained were identical to known authentic compounds (the same ^{1}H NMR spectra and mp, no mp depression on mixing with authentic samples).

b. To a solution of 1 mmol of *p*-aminophenol **VIa–VIc, VIe**, and **VIh** in 5 ml of dioxane were added at room temperature equimolar amounts of *N*-(arylsulfonyl)arylsulfinylimidoyl chlorides **Va–Vd** and triethylamine. After 30 min 20–25 ml of water was added to the reaction mixture. The arising oily substance crystallized on addition of a little AcOH. The formed

precipitate of *N*-arylthio-1,4-benzoquinone imines **VIIa, VIIIa, IXa–IXc, IXe**, and **IXh** was recrystallized from acetic acid.

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