Reactivity of *N*-Arylsulfonyl-1,4-benzoquinone Imines. Reaction with Hydrazoic Acid

A. P. Avdeenko and Yu.V. Menafova

Donbass State Machine-Building Academy, ul. Shkadinova 72, Kramatorsk, 84313 Ukraine
*e-mail: chimist@dgma.donetsk.ua*

Abstract—*N*-Arylsulfonyl-2-halo-1,4-benzoquinone imines react with hydrazoic acid in boiling acetic acid via two pathways: the 1,4-addition and nucleophilic replacement of the halogen atom by an azido group, followed by the 1,4-addition of HN_3. In the reaction of *N*-arylsulfonyl-2,6-dihalo-1,4-benzoquinone imines with hydrazoic acid, both halogen atoms are replaced by azido groups, while *N*-*p*-tolylsulfonyl-2-methyl-1,4-benzoquinone imine takes up HN_3 molecule according to the 1,4-addition pattern.

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It has been shown [1, 2] that *N*-arylsulfonyl-1,4-benzoquinone imines having no substituent in the quinoid ring react with sodium azide in acetic acid according to the 1,4-additin pattern, yielding 4-arylsulfonylamino-2-azidophenols. On heating in boiling acetic acid, the latter undergo intramolecular oxida-

tion–reduction with elimination of nitrogen and formation of 2-amino-*N*-arylsulfonyl-1,4-benzoquinone imines [2]. *N*-Arylsulfonyl-2-chloro-1,4-benzoquinone imines also react with hydrazoic acid at room temperature, following the 1,4-addition scheme. Nucleophilic replacement of the chlorine atom was not

Scheme 1.
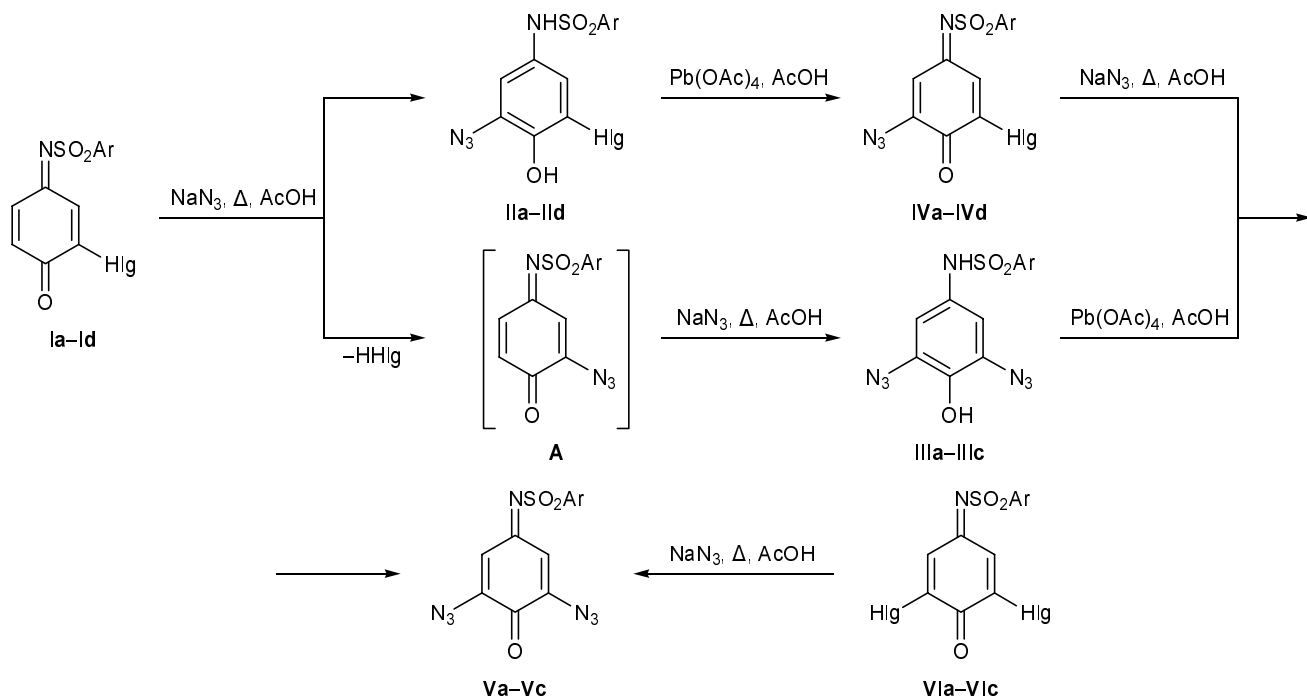
I, II, IV, Ar = Ph (**a**), 4-MeC₆H₄ (**b, d**), 4-ClC₆H₄ (**c**); Hlg = Cl (**a–c**), Br (**d**); **III, V**, Ar = Ph (**a**), 4-MeC₆H₄ (**b**), 4-ClC₆H₄ (**c**);
VI, Ar = Ph (**a**), 4-MeC₆H₄ (**b, c**); Hlg = Cl (**a, b**), Br (**c**).

Scheme 2.
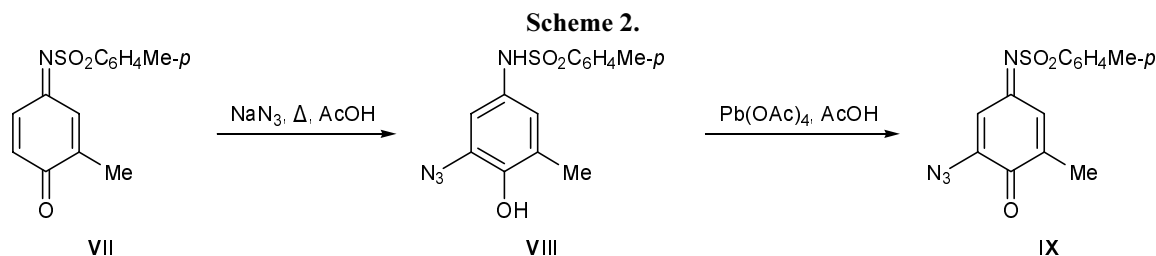
observed [2], though azide ion is a stronger nucleophile than Hlg⁻.

We examined reactions of some substituted *N*-arylsulfonyl-1,4-benzoquinone imines with hydrazoic acid at elevated temperature and revealed new reaction pathways. *N*-Arylsulfonyl-2-halo-1,4-benzoquinone imines **Ia–Id** reacted with sodium azide in acetic acid to give mixtures of two products, 2-azido-6-halo-4-arylsulfonylaminophenols **IIa–IId** and 2,6-diazido-4-arylsulfonylaminophenols **IIIa–IIIc** (Scheme 1). Presumably, compounds **IIIa–IIIc** are formed via initial nucleophilic substitution of the halogen atom to afford intermediate quinone imine **A** which was not detected in the reaction mixture. Quinone imine **A** takes up hydrazoic acid according to the 1,4-addition scheme, yielding compounds **IIIa–IIIc**.

Thus the reaction of *N*-arylsulfonyl-2-halo-1,4-benzoquinone imines with hydrazoic acid takes two concurrent pathways: 1,4-addition to give compounds **IIa–IId** and nucleophilic replacement of the halogen atom, followed by 1,4-addition of HN₃ molecule, with formation of diazidophenols **IIIa–IIIc**.

The obtained mixtures of compounds **IIa–IId** and **IIIa–IIIc** were viscous materials which did not crystallize. Therefore, compounds **IIa–IId** and **IIIa–IIIc** were not isolated as individual substances. Oxidation of mixtures **II/III** with lead tetraacetate in acetic acid gave crystalline mixtures of 2-azido-*N*-arylsulfonyl-6-halo-1,4-benzoquinone imines **IVa–IVd** and 2,6-diazido-*N*-arylsulfonyl-1,4-benzoquinone imines **Va–Vc**, which confirmed the proposed reaction scheme. Quinone imines **Va–Vc** were also synthesized by the action of hydrazoic acid on *N*-arylsulfonyl-2,6-dihalo-1,4-benzoquinone imines **VIa–VIc**, i.e., nucleophilic replacement of both halogen atoms in quinone imines **VI** occurred.

The chlorine atom in quinone imines **I** is replaced by azido group more readily than bromine. This follows from relatively high concentration of quinone imine **IVd** in its mixture with compound **Vb**. As a result, we succeeded in isolating pure quinone imine **IVd** by several recrystallizations of mixture **IVd/Vb**.

We can conclude that 1,4-addition is the main pathway in the reaction with quinone imine **Id** (Hlg = Br).

As might be expected on the basis of theoretical considerations and our experimental results, 2-methyl-*N*-4-tolylsulfonyl-1,4-benzoquinone imine (**VII**) reacted with sodium azide in acetic acid according to the 1,4-addition scheme with formation of 2-azido-6-methyl-4-*p*-tolylsulfonylaminophenol (**VIII**). Oxidation of the latter with lead tetraacetate in acetic acid gave 2-azido-6-methyl-*N*-4-tolylsulfonyl-1,4-benzoquinone imine (**IX**) (Scheme 2).

The structure of compounds **IVa–IVd**, **Va–Vc**, **VIII**, and **IX** was confirmed by the analytical and spectral (IR and ¹H NMR) data. *N*-*p*-Tolylsulfonyl quinone imines **IVb** and **IVd** showed in the ¹H NMR spectra double sets of signals from the 3-H and 5-H protons in the quinoid ring (four doublets), which corresponded to the *Z* and *E* isomers with respect to the azido group. An analogous ¹H NMR pattern was typical of quinone imine **IX**. The ¹H NMR spectra of quinone imines **Va–Vc** contained two doublets from the quinoid 3-H and 5-H protons, indicating degenerate *Z,E* isomerization (topomerization) with respect to the C=N bond. Signals from the other protons were fully consistent with the proposed structures.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer from samples prepared as KBr pellets. The ¹H NMR spectra were measured on a Varian VXR-300 instrument at 300 MHz using chloroform-*d* as solvent and tetramethylsilane as internal reference. The reaction mixtures were analyzed by thin-layer chromatography on Silufol UV-254 plates; samples were applied as solutions in chloroform, benzene–hexane (10:1, by volume) was used as eluent, and spots were visualized under UV light.

Compounds **Ia–Id** and **VII** were synthesized by oxidation of the corresponding aminophenols with lead tetraacetate in acetic acid [3]. The initial compounds were recrystallized, and the solvents were dried and distilled prior to use.

Reaction of *N*-arylsulfonyl-1,4-benzoquinone imines Ia–Id, VIa–VIc, and VII with hydrazoic acid (*general procedure*). Quinone imine **Ia–Id**, **VIa–VIc**, or **VII**, 5 mmol, was dissolved in 10 ml of glacial acetic acid, the solution was heated to the boiling point, and 20 mmol of sodium azide was added under stirring. The solution turned red. In the reaction with compounds **Ia–Id**, the mixture was cooled, a few milliliters of water was added, and a viscous noncrystallizable material separated. It was a mixture of compounds **IIa–IId** and **IIIa–IIIc**. Yield quantitative. In the reaction with quinone imines **VIa–VIc**, the reaction mixture was cooled, and quinone imines **Va–Vc** separated from the solution as a dark red solid which was recrystallized from acetic acid.

Compound **Va**. Yield 30% (from **Ia–Ic**) or 70% (from **VIa–VIc**), mp 112–115°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 7.57–8.00 m (5H, H$_{arom}$), 7.61 d (5-H), 6.42 d (3-H, $J_{3,5}$ = 2.1 Hz). Found, %: S 9.61, 9.74. C$_{12}$H$_7$N$_7$O$_3$S. Calculated, %: S 9.73.

Compound **Vb**. Yield 20% (from **Ia–Ic**), 15% (from **VIa–VIc**), or 87% (from **Id**); mp 115–116°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 7.35–7.88 d.d (4H, H$_{arom}$), 7.63 d (5-H), 6.41 d (3-H, $J_{3,5}$ = 2.1 Hz), 2.46 s (3H, MeC$_6$H$_4$). Found, %: S 9.35, 9.43. C$_{13}$H$_9$N$_7$O$_3$S. Calculated, %: S 9.33.

Compound **Vc**. Yield 30% (from **Ia–Ic**) or 76% (from **VIa–VIc**), mp 117–118°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 7.52–7.93 d.d (4H, H$_{arom}$), 7.55 d (5-H), 6.39 (3-H, $J_{3,5}$ = 2.7 Hz). Found, %: S 8.64, 8.67. C$_{12}$H$_9$ClN$_7$O$_3$S. Calculated, %: S 8.73.

In the reaction with quinone imine **VII**, a pink crystalline product was isolated from the reaction mixture by precipitation with water. The precipitate was filtered off, dried, and recrystallized from benzene. Yield of 2-azido-6-methyl-4-*p*-tolylsulfonylaminophenol (**VIII**) 90%, mp 120–122°C (frcomp.). Found, %: S 9.96, 9.99. C$_{14}$H$_{14}$N$_4$O$_3$S. Calculated, %: S 10.06.

Oxidation of phenol mixtures IIa–IId/IIIa–IIIc (*general procedure*). Lead tetraacetate, 1.3 g, was added under stirring and cooling with cold water to a suspension of 1 g of mixture **IIa–IId/IIIa–IIIc** in 5 ml of glacial acetic acid. A few drops of ethylene glycol was then added, and the dark red crystals (mixture **IVa–IVd/Va–Vc**) were filtered off, washed with a small amount of acetic acid, dried in air, and recrystallized from acetic acid. According to the ^{1}H NMR data, diazido derivatives **V** were the major components of mixtures **IVa/Va**, **IVb/Vb**, and **IVc/Vc**, while com-

pound **IVd** predominated in mixture **IVd/Vb**. By several recrystallization of mixture **IVd/Vb** from octane we isolated pure quinone imine **IVd**.

Compound **IVd**. Yield 70%, mp 113–115°C (decomp.). ^{1}H NMR spectrum, δ, ppm: *Z* isomer (65%): 7.35–7.88 d.d (4H, H$_{arom}$), 7.62 d (3-H), 7.41 (5-H, $J_{3,5}$ = 2.4 Hz), 2.47 s (3H, MeC$_6$H$_4$); *E* isomer (35%): 7.35–7.88 d.d (4H, H$_{arom}$), 8.71 d (5-H), 6.44 d (3-H, $J_{3,5}$ = 2.7 Hz), 2.46 s (3H, MeC$_6$H$_4$).

Compound **IVb**: ^{1}H NMR spectrum, δ, ppm: *Z* isomer (55%): 7.35–7.90 d.d (4H, H$_{arom}$), 7.63 d (3-H), 7.19 d (5-H, $J_{3,5}$ = 2.1 Hz), 2.48 s (3H, MeC$_6$H$_4$); *E* isomer (45%): 7.35–7.90 d.d (4H, H$_{arom}$), 8.46 d (5-H), 6.42 d (3-H, $J_{3,5}$ = 2.4 Hz), 2.46 s (3H, MeC$_6$H$_4$). Found, %: S 7.82, 7.89. C$_{12}$H$_6$BrClN$_4$O$_3$S. Calculated, %: S 7.97.

Reaction of hydrazoic acid with mixtures of azido quinone imines IVa–IVd and diazido quinone imines Va–Vc (*general procedure*). Sodium azide, 0.5 g, was added under stirring to a solution of 1 g of mixture **IVa–IVd/Va–Vc** in 5 ml of acetic acid, heated to the boiling point. After cooling, diazido derivatives **Va–Vc** separated from the mixture as a dark red solid. The precipitate was filtered off, washed with a large amount of water, and dried in air. The products were identical to samples obtained by reactions of quinone imines **VIa–VIc** with hydrazoic acid.

2-Azido-6-methyl-*N*-4-tolylsulfonyl-1,4-benzoquinone imine (IX) was obtained by oxidation of compound **VIII** with lead tetraacetate in acetic acid at room temperature according to the procedure described in [1]. The orange precipitate of compound **IX** was filtered off, washed with acetic acid, dried in air, and recrystallized from octane. Yield 83%, mp 115–117°C (decomp.). ^{1}H NMR spectrum, δ, ppm: *Z* isomer (62%): 7.35–7.89 d.d (4H, H$_{arom}$), 7.56 d (3-H), 6.78 q (5-H, $J_{3,5}$ = 2.4 Hz), 2.46 s (3H, MeC$_6$H$_4$), 2.08 d (3H, 2-Me, J = 1.5 Hz); *E* isomer (38%): 7.35–7.89 d.d (4H, H$_{arom}$), 8.01 q (5-H), 6.36 d (3-H, $J_{3,5}$ = 2.4 Hz), 2.46 s (3H, MeC$_6$H$_4$), 1.16 d (3H, 2-Me, J = 1.5 Hz). Found, %: S 10.05, 10.09. C$_{14}$H$_{12}$N$_4$O$_3$S. Calculated, %: S 10.13.

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