ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 2, pp. 231–236. © Pleiades Publishing, Ltd., 2008.
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# Comparison of Preparation Methods of *N*-Arylsulfinyl-1,4-benzoquinone Monoimines

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Received May 11, 2007

**Abstract**—Advantages and shortcomings were discussed of three procedures for preparation *N*-arylsulfinyl-1,4-benzoquinone imines: the reaction of arenesulfenyl chlorides with 1,4-benzoquinone oximes, the oxidation of *N*-arylthio-1,4-benzoquinone imines, and the reaction of arylsulfinyl chlorides with *p*-aminophenols followed by oxidation. A series of new *N*-arylsulfinyl-1,4-benzoquinone imines was obtained.

**DOI:** 10.1134/S1070428008020085

Stable *N*-arylsulfinyl-1,4-benzoquinone monoimines containing sulfur(IV) were formerly prepared by acylation of 1,4-benzoquinone monooximes with corresponding arenesulfenyl chlorides (method *a*) [1]. In [2, 3] a method of the synthesis of *N*-aryl(alkyl)sulfinyl-1,4-benzoquinone monoimines by oxidation of *N*-aryl(alkyl)-thio-1,4-benzoquinone imines with *m*-chloroperbenzoic acid was described (method *b*). The traditional and the most widely applied method of *N*-substituted 1,4-benzoquinone imines preparation is the oxidation of the corresponding N-substituted *p*-aminophenols [4]. The latter are as a rule obtained by reaction of the chlorides of the corresponding acids with *p*-aminophenols. Reactions were reported of arylsulfinyl chlorides with various aromatic amines giving arylsulfinylamides [5]. Several preparative procedures for arylsulfinyl chlorides were published [6]. Some *N*-arylsulfinyl-1,4-benzoquinone imines were produced by acylation of *p*-aminophenols followed by oxidation with $Pb(OAc)_4$ or $Ag_2O$ [7] (method *c*).

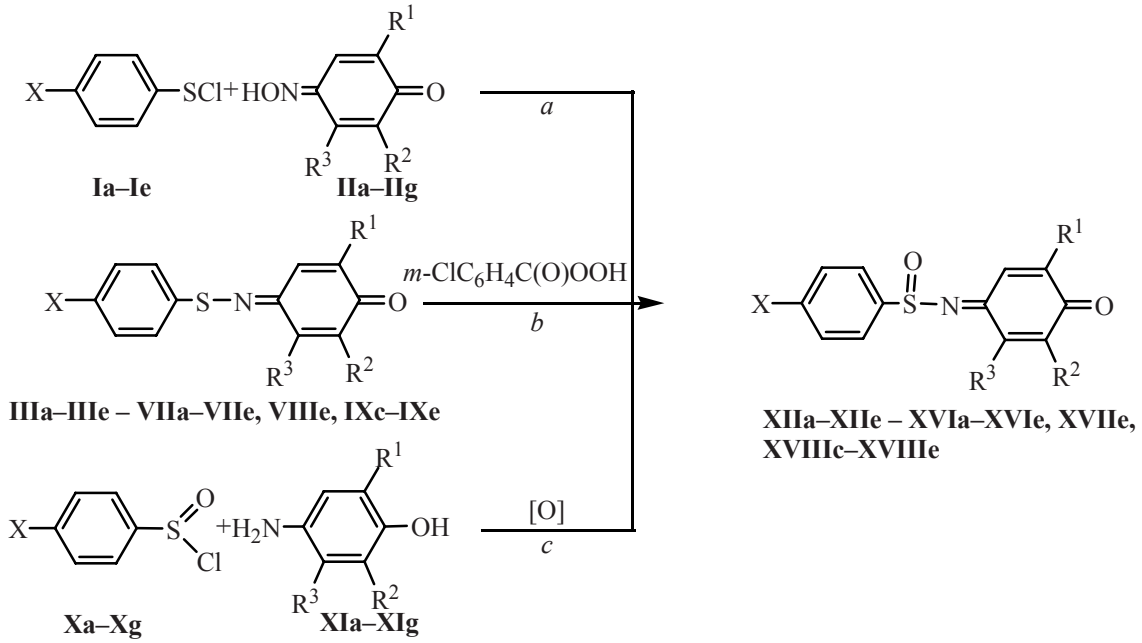
The target of the present study was synthesis of new N-arylsulfinyl-1,4-benzoquinone monoimines by the above cited methods and revealing their advantages and shortcomings in the preparation of certain N-arylsulfinyl-1,4-benzoquinone monoimines (see the scheme).

At application of method *a* to the synthesis of *N*-arylsulfinyl-1,4-benzoquinone monoimines a special attention should be paid to the temperature regime of the reaction (–10°C) and also to the quality of the solvent. The dried and distilled ethyl ether proved to be the most suitable solvent. This method is acceptable for preparation of any *N*-arylsulfinyl-1,4-benzoquinone imines, but the substances obtained require repeated recrystallization. The yields of reaction products were low (30–45%) except for benzoquinone imines **XIVe** and **XVIe** whose yields attained 65–70%. This method should not be used with 4-methoxyphenylsulfenylchloride due to the extremely low stability of the arising quinone imine.

In the synthesis of *N*-arylsulfinyl-1,4-benzoquinone monoimines by method *b* special requirements are presented to the purity of initial N-arylthio derivatives for in the presence of insignificant impurities the reaction product after oxidation is difficult to obtain in the individual state even after multiple recrystallizations. The case in point is diaryl disulfides that are very difficult to remove from the target compounds. The most suitable procedure for removal of the diaryl disulfide impurity is the reaction of arylthiols with *N*-chloro-1,4-benzoquinone monoimines [8].

As oxidant in method *b* is used a mild reagent *m*-chloroperbenzoic acid. In the reaction it is reduced to *m*-chlorobenzoic acid that is easily removed from the reaction mixture by washing with 10% water solution of sodium hydrogen carbonate. The oxidant should be applied to the reaction mixture by small portions,and the reaction progress should be monitored by TLC.

In preparation of quinone imines **VIIa–VIIe, VIIIe**, and **IXc–IXe** by this method it was difficult to achieve a complete consumption of the initial thioquinone imine. The increased quantity of the oxidant resulted in the




**I, III–X, XII–XVIII**: X = MeO (**a**), Me (**b**), H (**c**), Cl (**d**), $NO_2$ (**e**); **II, XI**: $R^1 = R^2 = R^3 = H$ (**a**), $R^2$ = Me, $R^1 = R^3 = H$ (**b**), $R^1 = R^2$ = Me, $R^3 = H$ (**c**), $R^1 = R^3$ = Me, $R^2 = H$ (**d**), $R^1 = R^2 = t$-Bu, $R^3 = H$ (**e**), $R^1 = R^2 = i$-Pr, $R^3 = H$ (**f**), $R^1 = R^2$ = Cl, $R^3$ = H (**g**); **III, XII**: $R^1 = R^2 = R^3 = H$; **IV, XIII**: $R^2$ = Me, $R^1 = R^3 = H$; **V, XIV**: $R^1 = R^2$ = Me, $R^3 = H$; **VI, XV**: $R^1 = R^3$ = Me, $R^2 = H$; **VII, XVI**: $R^1 = R^2 = t$-Bu, $R^3 = H$; **VIII, XVII**: $R^1 = R^2 = i$-Pr, $R^3 = H$; **IX, XVIII**: $R^1 = R^2$ = Cl, $R^3 = H$.

formation of the corresponding N-arylsulfonyl derivative [2]. Frequently three products are present simultaneously in the reaction mixture: *N*-arylthio-, *N*-arylsulfinyl-, and *N*-arylsulfonyl-1,4-benzoquinone monoimines. This may result from the close values of the oxidation rate of these compounds and also by the operation of a redox disproportionation process of *N*-arylsulfinyl-1,4-benzoquinone monoimines.

The redox potential of N-arylthioquinone imines is significantly more negative that the potential of the corresponding *N*-arylsulfonyl-1,4-benzoquinone monoimines [9], and intermediate value corresponds to the N-arylsulfinyl derivatives, as shows the result of oxidation of N-arylthioquinone imines with 1 equiv of oxidant to N-arylsulfinyl derivatives and with 2 equiv of oxidant, to N-arylsulfonyl compounds [2]. The separation of *N*-arylthio-, *N*-arylsulfinyl-, and *N*-arylsulfonyl-1,4-benzoquinone monoimines is a difficult task due to their similar solubility in many solvents and to close values of their retention factors ($R_f$) hampering their chromatographic isolation on $SiO_2$. Therefore this method is unsuitable for preparation compounds with *i*-Pr, *t*-Bu groups and chlorine atoms in the positions *2* and *6* of the quinoid ring (**XVIa**–**XVIe, XVIIe**, and **XVIIIc**–**XVIIIe**). This method is most suitable for the synthesis of unsubstituted, mono- and disubstituted in the quinoid ring compounds (**XIIa–XIIe–XVa–XVe**). The yield of reaction products reach 65–85%.

In preparation of *N*-arylsulfinyl-1,4-benzoquinone monoimines by method *c* the solvent for the reaction significantly affects the course of the process.

It was shown formerly that the reaction of arylsulfinyl chlorides **Xa–Xe** with *p*-aminophenols **XIa–XIg** carried out in pyridine led to the formation of *N*-arylthio-1,4-benzoquinone monoimines. The intermediate unstable *N*-arylsulfinyl-4-aminophenols formed in this reaction eliminate an $H_2O$ molecule and suffer an intramolecular oxidation-reduction process resulting in transformation of sulfur (IV) into sulfur(II), and the aminophenol moiety into quinone imine [10].

In the reaction carried out in ether or dioxane in the presence of triethylamine the formed *N*-arylsulfinyl-4-aminophenols were not isolated from the reaction mixture and immediately were subjected to oxidation with silver oxide or lead tetraacetate. Yields of the target products were 50–60%.

This method of synthesis of *N*-arylsulfinyl-1,4-benzoquinone imines provides sufficiently pure reaction products. But stringent requirements with respect to the purity of initial compounds and quality of solvents, the labor-consuming procedure of preparation of initial

arylsulfinyl chlorides, and also an additional oxidation stage make this process less favorable that the oxidation of *N*-arylthio-1,4-benzoquinone imines that provides sufficiently pure reaction products in good yields except for compounds **XVIa**–**XVIe, XVIIe**, and **XVIIIc**–**XVIIIe**. In event of formation of difficultly removable disulfides method *a* can be applied based on the reaction between arenesulfenyl chlorides and *p*-benzoquinone monooximes.

The composition and structure of compounds obtained were proved by elemental analysis, IR and $^1$H NMR spectra. In the IR spectra of *N*-arylsulfinyl-1,4-benzoquinone imines a characteristic absorption band of S=O group was observed in the range 1070–1110 cm$^{-1}$, also appeared absorption bands in the region 1580–1600 (C=N) and 1640–1670 cm$^{-1}$ (C=O).

## EXPERIMENTAL

$^1$H NMR spectra were registered on a spectrometer Varian VXR-300 at operating frequency 300 MHz in $CDCl_3$ solutions, internal reference TMS. IR spectra were recorded on a spectrophotometer UR-20 from KBr pellets. Analysis of compounds obtained was done by TLS on Silufol UV-254 plates. Chloroform was used as solvent, eluent benzene–hexane, 10:1, development under UV irradiation.

Arenesulfenyl chlorides **Ia–Id** were obtained by procedure [11], **Ie** as in [12]. *N*-Arylthio-1,4-benzoquinone imines **IIIa–IIIe–VIa–VIe**, and **VIIIe** were synthesized by acylation of *p*-aminophenols **XIa–XIg** with appropriate arenesulfenyl chlorides **Ia–Ie** in the presence of triethylamine. In this process the formed *N*-arylthio-1,4-aminophenols were spontaneously oxidized by air oxygen giving the corresponding *N*-arylthio-1,4-benzoquinone imines.

***N*-Arylthio-1,4-benzoquinone imines IIa–IIe – VIIa–VIIe, VIIIe,** and **IXc–IXe).** To a dispersion of 2 mmol of *p*-aminophenol **XIa–XId** and **XIf** in 20 ml of anhydrous ethyl ether was added an equimolar quantity of an appropriate arylsulfenyl chloride **Ia–Ie** and of triethylamine. The separated precipitate of triethylamine hydrochloride was filtered off, and the filterate was evaporated in a vacuum of water jet pump. The residue obtained was washed with methanol and glacial acetic acid and recrystallized from the glacial acetic acid or from hexane. In the case of compounds **VIIa–VIIe** and **IXc–IXe** the precipitate obtained was oxidized with 2.5 mmol of iodosobenzene diacetate in acetic acid; the precipitate thus formed was recrystallized from the glacial acetic acid.

The characteristics of quinone imines **IIIa–IIIe** are reported in [13], of quinone imine **IVc, IVe**, and **VIe**, in [10], of quinone imines **IVd, VIa–VId**, in [2], of quinone imines **Ve** and **VIIe**, in [1].

***N*-[(4-Methoxyphenyl)thio]-2-methyl-1,4-benzoquinone imine (IVa).** Yield 23%, mp 114–115°C. $^1$H NMR spectrum, δ, ppm, *Z*-isomer, 34%: 6.97–7.57 d.d (4H, Ar, $J^O$ 8.7 Hz), 7.40–7.44 d.d (1H, H$^5$, $J_{3,5}$ 2.4, $J_{5,6}$ 9.9 Hz), 6.96 q [1H, H$^3$ *J*(2-Me, H$^3$) 1.8 Hz], 6.55 d (1H, H$^6$, $J_{5,6}$ 9.9 Hz), 3.84 s (3H, MeO), 2.01 d (3H, 2-Me, *J* 1.5 Hz); *E*-isomer, 66%: 6.97–7.57 d.d (4H, Ar, $J^O$ 8.7 Hz), 7.31 q [1H, H$^3$, *J*(2-Me, H$^3$) 1.2 Hz], 7.01–7.05 d.d (1H, H$^5$, $J_{3,5}$ 2.7, $J_{5,6}$ 9.9 Hz), 6.47 d (1H, H$^6$, $J_{5,6}$ 10.2 Hz), 3.84 s (3H, MeO), 2.09 d (3H, 2-Me, *J* 0.9 Hz). Found, %: N 5.02, 5.04; S 11.51, 11.57. $C_{14}H_{13}NO_2S$. Calculated, %: N 5.05; S 11.56.

***N*-[(4-Methylphenyl)thio]-2-methyl-1,4-benzoquinone imine (IVb).** Yield 59%, mp 86–87°C. $^1$H NMR spectrum, δ, ppm, *Z*-isomer, 36%: 7.24–7.53 d.d (4H, Ar, $J^O$ 8.1 Hz), 7.40–7.44 d.d (1H, H$^5$, $J_{3,5}$ 2.4, $J_{5,6}$ 9.9 Hz), 6.99 q [1H, H$^3$, *J*(2-Me, H$^3$) 1.5 Hz], 6.55 d (1H, H$^6$, $J_{5,6}$ 9.9 Hz), 2.39 s (3H, Me), 2.02 d (3H, 2-Me, *J* 1.2 Hz); *E*-isomer, 64%: 7.24–7.53 d.d (4H, Ar, $J^O$ 8.1 Hz), 7.31 q [1H, H$^3$, *J*(2-Me, H$^3$) 1.2 Hz], 7.04–7.08 d.d (1H, H$^5$, $J_{3,5}$ 3.0, $J_{5,6}$ 9.9 Hz), 6.47 d (1H, H$^6$, $J_{5,6}$ 9.6 Hz), 2.39 s (3H, Me), 2.09 d (3H, 2-Me, *J* 1.2 Hz). Found, %: N 5.26, 5.40; S 12.23, 12.31. $C_{14}H_{13}NOS$. Calculated, %: N 5.36; S 12.27.

***N*-[(4-Methoxyphenyl)thio]-2,6-dimethyl-1,4-benzoquinone imine (Va).** Yield 34%, mp 85–86°C. $^1$H NMR spectrum, δ, ppm: 6.97–7.56 d.d (4H, Ar, $J^O$ 8.4 Hz), 7.27 q (1H, H$^5$), 6.89 q [1H, H$^3$, *J*(2-Me, H$^3$) 1.2 Hz], 3.84 s (3H, MeO), 2.08 s (3H, 2-Me), 2.01 s (3H, 6-Me). Found, %: N 4.79, 4.84; S 10.91, 10.98. $C_{15}H_{15}NO_2S$. Calculated, %: N 4.81; S 11.00.

***N*-[(4-Methylphenyl)thio]-2,6-dimethyl-1,4-benzoquinone imine (Vb).** Yield 30%, mp 111–112°C. $^1$H NMR spectrum, δ, ppm: 7.23–7.52 d.d (4H, Ar, $J^O$ 8.1 Hz), 7.23 q (1H, H$^5$), 6.93 q [1H, H$^3$, *J*(2-Me, H$^3$) 1.2 Hz], 2.38 s (3H, Me), 2.08 d [3H, 2-Me, *J*(2-Me, H$^3$) 0.9 Hz], 2.01 d [3H, 6-Me, *J*(6-Me, H$^5$) 0.9 Hz]. Found, %: N 5.01, 5.07; S 11.54, 11.61. $C_{15}H_{15}NOS$. Calculated, %: N 5.09; S 11.64.

***N*-(Phenylthio)-2,6-dimethyl-1,4-benzoquinone imine (Vc).** Yield 29%, mp 147–148°C. $^1$H NMR spectrum, δ, ppm: 7.31–7.63 m (5H, Ph), 7.26 q (1H, H$^5$), 6.95 q (1H, H$^3$), 2.09 s (3H, 2-Me), 2.03 s (3H, 6-Me).

Found, %: N 5.33, 5.40; S 12.20, 12.31. $C_{14}H_{13}NOS$. Calculated, %: N 5.36; S 12.27.

***N*-[(4-Chlorophenyl)thio]-2,6-dimethyl-1,4-benzoquinone imine (Vd).** Yield 21%, mp 137–138°C. $^1$H NMR spectrum, δ, ppm: 7.38–7.56 d.d (4H, Ar, $J^O$ 8.7 Hz), 7.22 q [1H, H$^5$, $J$(H$^5$, 6-Me) 1.5 Hz], 6.93 q [1H, H$^3$, $J$(2-Me, H$^3$) 1.5 Hz], 2.09 d [3H, 2-Me, $J$(2-Me, H$^3$) 1.5 Hz], 2.03 d [3H, 6-Me, $J$(6-Me, H$^5$) 1.2 Hz]. Found, %: N 4.65, 4.77; S 10.71, 10.83. $C_{14}H_{12}ClNOS$. Calculated, %: N 4.74; S 10.84.

***N*-[(4-Methoxyphenyl)thio]-2,6-di-*tert*-butyl-1,4-benzoquinone imine (VIIa).** Yield 25%, mp 117–119°C. $^1$H NMR spectrum, δ, ppm: 6.97–7.58 d.d (4H, Ar, $J^O$ 8.7 Hz), 7.22 d (1H, H$^5$, $J_{3,5}$ 3.0 Hz), 6.86 d (1H, H$^3$, $J_{3,5}$ 2.7 Hz), 3.85 s (3H, MeO), 1.34 C (9H, 2-*t*-Bu), 1.28 s (9H, 6-*t*-Bu). Found, %: N 3.96, 3.99; S 8.85, 8.93. $C_{21}H_{27}NO_2S$. Calculated, %: N 3.92; S 8.96.

***N*-[(4-Methylphenyl)thio]-2,6-di-*tert*-butyl-1,4-benzoquinone imine (VIIb).** Yield 25%, mp 101–102°C. $^1$H NMR spectrum, δ, ppm: 7.24–7.54 d.d (4H, Ar, $J^O$ 8.4 Hz), 7.21 d (1H, H$^5$, $J_{3,5}$ 3.0 Hz), 6.89 d (1H, H$^3$, $J_{3,5}$ 2.7 Hz), 2.38 s (3H, Me), 1.34 C (9H, 2-*t*-Bu), 1.29 s (9H, 6-*t*-Bu). Found, %: N 3.81, 3.95; S 8.87, 8.90. $C_{21}H_{27}NOS$. Calculated, %: N 3.90; S 8.92.

***N*-(Phenylthio)-2,6-di-*tert*-butyl-1,4-benzoquinone imine (VIIc).** Yield 30%, mp 103–105°C. $^1$H NMR spectrum, δ, ppm: 7.31–7.65 m (5H, Ph), 7.21 d (1H, H$^5$, $J_{3,5}$ 2.7 Hz), 6.92 d (1H, H$^3$, $J_{3,5}$ 2.7 Hz), 1.34 s (9H, 2-*t*-Bu), 1.29 s (9H, 6-*t*-Bu). Found, %: N 3.97, 4.09; S 9.15, 9.32. $C_{20}H_{25}NOS$. Calculated, %: N 4.05; S 9.28.

***N*-[(4-Chlorophenyl)thio]-2,6-di-*tert*-butyl-1,4-benzoquinone imine (VIId).** Yield 22%, mp 112–113°C. $^1$H NMR spectrum, δ, ppm: 7.39–7.58 d.d (4H, Ar, $J^O$ 8.7 Hz), 7.17 d (1H, H$^5$, $J_{3,5}$ 2.7 Hz), 6.89 d (1H, H$^3$, $J_{3,5}$ 3.0 Hz), 1.34 s (9H, 2-*t*-Bu), 1.29 s (9H, 6-*t*-Bu). Found, %: N 3.51, 3.67; S 8.32, 8.45. $C_{20}H_{24}ClNOS$. Calculated, %: N 3.69; S 8.44.

***N*-[(4-Nitrophenyl)thio]-2,6-diisopropyl-1,4-benzoquinone imine (VIIIe).** Yield 25%, mp 144–146°C. $^1$H NMR spectrum, δ, ppm: 7.79–8.31 d.d (4H, Ar, $J^O$ 9.0 Hz), 7.11 d.d [1H, H$^5$, $J_{3,5}$ 0.9, $J$(H$^5$, 6-CH) 2.4 Hz], 6.92 d.d [1H, H$^3$, $J_{3,5}$ 0.9, $J$(2-CH, H$^3$) 2.7 Hz], 3.08–3.22 m (2H, 2,6-*i*-Pr), 1.19 d (6H, 2-*i*-Pr, $J$ 6.9 Hz), 1.17 d (6H, 6-*i*-Pr, $J$ 7.5 Hz). Found, %: N 7.65, 7.79; S 8.73, 8.89. $C_{18}H_{20}N_2O_3S$. Calculated, %: N 7.73; S 8.85.

***N*-(Phenylthio)-2,6-dichloro-1,4-benzoquinone imine (IXc).** Yield 29%, mp 186°C. $^1$H NMR spectrum, δ, ppm: 7.71 d (1H, H$^5$, $J$ 2.4 Hz), 7.39–7.64 m (5H, Ph), 7.41 d (1H, H$^3$, $J$ 2.4 Hz). Found, %: N 4.51, 4.63; S 10.55, 10.67. $C_{12}H_7Cl_2NOS$. Calculated, %: N 4.64; S 10.61.

***N*-[(4-Chlorophenyl)thio]-2,6-dichloro-1,4-benzoquinone imine (IXd).** Yield 32%, mp 168°C. $^1$H NMR spectrum, δ, ppm: 7.68 d (1H, H$^5$, $J$ 2.7 Hz), 7.44–7.58 d.d (4H, Ar, $J^O$ 8.7 Hz), 7.41 d (1H, H$^3$, $J$ 2.7 Hz). Found, %: N 4.11, 4.15; S 9.41, 9.52. $C_{12}H_6Cl_3NOS$. Calculated, %: N 4.16; S 9.53.

***N*-[(4-Nitrophenyl)thio]-2,6-dichloro-1,4-benzoquinone imine (IXe).** Yield 30%, mp 262°C. $^1$H NMR spectrum, δ, ppm: 7.79–8.35 d.d (4H, Ar, $J^O$ 9.0 Hz), 7.68 d (1H, H$^5$, $J$ 2.7 Hz), 7.48 d (1H, H$^3$, $J$ 2.4 Hz). Found, %: N 8.01, 8.11; S 9.17, 9.26. $C_{12}H_6Cl_2N_2O_3S$. Calculated, %: N 8.07; S 9.24.

Arylsulfinyl chlorides **Xa–Xe** were prepared by procedure [6].

***N*-Arylsulfinyl-1,4-benzoquinone imines XIIa–XIId–XIVa–XIVe, XVIa–XVIe, XVIIe, and XVIIIc–XVIIIe.** *a*. The preparation of quinone imines by acylating with arenesulfenyl chlorides **Ia–Ie** the corresponding 1,4-benzoquinone oximes **IIa–IIg** was described in [1].

*b*. The oxidation of *N*-arylthio-1,4-benzoquinone imines with *m*-chloroperbenzoic acid was reported in [2].

*c*. In 20 ml of ethyl ether 5 mmol of *p*-aminophenol **XIa–XIc, XIe–XIg** was dispersed, and 5.5 mmol of triethylamine was added. To this dispersion was added at stirring 5.5 mmol of an appropriate sulfinyl chloride **Xa–Xe**. The formed thick mass 10 min later was filtered off, washed with water and a little methanol. On drying the precipitate was dissolved in 30 ml of acetone, and at stirring 5.5 mmol of silver oxide was added. After 30 min the reaction mixture was filtered through a silica gel bed, the filtrate was evaporated, and the residue was recrystallized from petroleum ether of bp 40–60°C.

***N*-arylsulfinyl-2,5-dimethyl-1,4-benzoquinone imines XVa–XVe.** *a*. To a solution of 5 mmol of 2,5-dimethyl-4-aminophenol in 10 ml of dioxane was added at stirring 5.5 mmol of triethylamine and then was charged 5.5 mmol of an appropriate arylsulfinyl chloride **Xa–Xe**. The stirring was continued for 15 min, then at cooling 6 mmol of lead tetraacetate was added, and the separated yellow precipitate was quickly filtered off, the filtrate was evaporated, and the residue was recrystallized from petroleum ether of bp 40–60°C.

The characteristics of quinone imines **XIIId, XIVa, XIVb, XIVd, XVa–XVd** are described in [2], of quinone imines **XIVe** and **XVIe**, in [1].

***N*-[(4-Methoxyphenyl)sulfinyl]-1,4-benzoquinone imine (XIIa).** Yield 32% (*a*), 73% (*b*), 56% (*c*), mp 89–90°C. $^1$H NMR spectrum, δ, ppm: 8.48–8.52 d.d (1H, $H^5$, $J_{3,5}$ 3.0, $J_{5,6}$ 9.9 Hz), 7.04–7.74 d.d (4H, Ar, $J^O$ 9.0 Hz), 7.01–7.05 d.d (1H, $H^3$, $J_{3,5}$ 2.1, $J_{2,3}$ 9.9 Hz), 6.57–6.61 d.d (2H, $H^{2,6}$, $J_{2,6}$ 2.4, $J_{2,3}$ 9.3 Hz), 3.87 s (3H, MeO). Found, %: N 4.89, 4.97; S 11.31, 11.50. $C_{13}H_{11}NO_3S$. Calculated, %: N 5.01; S 11.48.

***N*-[(4-Methylphenyl)sulfinyl]-1,4-benzoquinone imine (XIIb).** Yield 39% (*a*), 82% (*b*), 59% (*c*), mp 87–88°C. $^1$H NMR spectrum, δ, ppm: 8.49–8.54 d.d (1H, $H^5$, $J_{3,5}$ 2.1, $J_{5,6}$ 9.9 Hz), 7.35–7.70 d.d (4H, Ar, $J^O$ 8.4 Hz), 7.01–7.05 d.d (1H, $H^3$, $J_{3,5}$ 2.8, $J_{2,3}$ 8.7 Hz), 6.56–6.60 d.d (2H, $H^{2,6}$, $J_{2,6}$ 2.4, $J_{2,3}$ 9.6 Hz), 2.43 s (3H, Me). Found, %: N 5.23, 5.34; S 12.11, 12.23. $C_{13}H_{11}NO_2S$. Calculated, %: N 5.32; S 12.18.

***N*-(Phenylsulfinyl)-1,4-benzoquinone imine (XIIc).** Yield 45% (*a*), 74% (*b*), 54% (*c*), mp 82–83°C. $^1$H NMR spectrum, δ, ppm: 8.51–8.55 d.d (1H, $H^5$, $J_{3,5}$ 3.0, $J_{5,6}$ 9.6 Hz), 7.55–7.83 m (5H, Ph), 7.02–7.06 d.d (1H, $H^3$, $J_{3,5}$ 2.4, $J_{2,3}$ 9.6 Hz), 6.57–6.61 d.d (2H, $H^{2,6}$, $J_{2,6}$ 2.7, $J_{2,3}$ 10.2 Hz). Found, %: N 5.59, 5.65; S 12.81, 12.91. $C_{12}H_9NO_2S$. Calculated, %: N 5.62; S 12.86.

***N*-[(4-Chlorophenyl)sulfinyl]-1,4-benzoquinone imine (XIId).** Yield 42% (*a*), 84% (*b*), 55% (*c*), mp 117–119°C. $^1$H NMR spectrum, δ, ppm: 8.46–8.51 d.d (1H, $H^5$, $J_{3,5}$ 2.7, $J_{5,6}$ 9.9 Hz), 7.52–7.77 d.d (4H, Ar, $J^O$ 9.0 Hz), 7.01–7.05 d.d (1H, $H^3$, $J_{3,5}$ 2.7, $J_{2,3}$ 9.9 Hz), 6.58–6.61 d.d (2H, $H^{2,6}$, $J_{2,3}$ 10.5 Hz). Found, %: N 4.93, 4.97; S 11.21, 11.33. $C_{12}H_8ClNO_2S$. Calculated, %: N 4.98; S 11.30.

***N*-[(4-Nitrophenyl)sulfinyl]-1,4-benzoquinone imine (XIIe).** Yield 30% (*a*), 71% (*b*), 59% (*c*), mp 109–110°C. $^1$H NMR spectrum, δ, ppm: 8.45–8.49 d.d (1H, $H^5$, $J_{3,5}$ 2.7, $J_{5,6}$ 9.9 Hz), 8.02–8.43 d.d (4H, Ar, $J^O$ 8.7 Hz), 7.02–7.06 d.d (1H, $H^3$, $J_{3,5}$ 2.7, $J_{2,3}$ 9.9 Hz), 6.59–6.64 d.d (2H, $H^{2,6}$, $J_{2,6}$ 2.4, $J_{2,3}$ 9.9 Hz). Found, %: N 9.46, 9.55; S 10.76, 10.89. $C_{12}H_8N_2O_4S$. Calculated, %: N 9.52; S 10.90.

***N*-[(4-Methoxyphenyl)sulfinyl]-2-methyl-1,4-benzoquinone imine (XIIIa).** Yield 30% (*a*), 82% (*b*), 60% (*c*), mp 99–100°C. $^1$H NMR spectrum, δ, ppm, *Z*-isomer, 48%: 8.25 q (1H, $H^3$), 7.03–7.74 d.d (4H, Ar, $J^O$ 9.0 Hz), 6.95–6.99 d.d (1H, $H^5$, $J_{3,5}$ 2.7, $J_{5,6}$ 9.9 Hz), 6.57 d (1H, $H^6$, $J_{5,6}$ 9.9 Hz), 3.86 s (3H, MeO), 2.08 br.s (3H, 2-Me); *E*-isomer, 52%: 8.38–8.43 d.d (1H, $H^5$, $J_{3,5}$ 2.4, $J_{5,6}$ 10.2 Hz), 7.03–7.74 d.d (4H, Ar, $J^O$ 9.0 Hz), 6.88 q (1H, $H^3$), 6.57 d (1H, $H^6$, $J_{5,6}$ 9.9 Hz), 3.86 s (3H, MeO), 2.03 br.s (3H, 2-Me). Found, %: N 4.59, 4.72; S 10.80, 10.94. $C_{14}H_{13}NO_3S$. Calculated, %: N 4.77; S 10.93.

***N*-[(4-Methylphenyl)sulfinyl]-2-methyl-1,4-benzoquinone imine (XIIIb).** Yield 34% (*a*), 70% (*b*), 53% (*c*), mp 68–69°C. $^1$H NMR spectrum, δ, ppm, *Z*-isomer, 51%: 8.28 q (1H, $H^3$), 7.33–7.69 d.d (4H, Ar, $J^O$ 8.4 Hz), 6.95–6.98 d.d (1H, $H^5$, $J_{3,5}$ 1.5, $J_{5,6}$ 9.9 Hz), 6.56 d (1H, $H^6$, $J_{5,6}$ 9.9 Hz), 2.42 s (3H, Me), 2.07 br.s (3H, 2-Me); *E*-isomer, 49%: 8.41–8.45 d.d (1H, $H^5$, $J_{3,5}$ 1.5, $J_{5,6}$ 9.6 Hz), 7.33–7.69 d.d (4H, Ar, $J^O$ 8.4 Hz), 6.83 q (1H, $H^3$), 6.56 d (1H, $H^6$, $J_{5,6}$ 9.9 Hz), 2.42 s (3H, Me), 2.02 br.s (3H, 2-Me). Found, %: N 5.01, 5.09; S 11.46, 11.57. $C_{14}H_{13}NO_2S$. Calculated, %: N 5.05; S 11.56.

***N*-(Phenylsulfinyl)-2-methyl-1,4-benzoquinone imine (XIIIc).** Yield 45% (*a*), 66% (*b*), 51% (*c*), mp 80°C. $^1$H NMR spectrum, δ, ppm, *Z*-isomer, 54 %: 8.30 q (1H, $H^3$), 7.54–7.82 m (5H, Ph), 6.96–6.98 d.d (1H, $H^5$, $J_{3,5}$ 2.1, $J_{5,6}$ 9.9 Hz), 6.56 d (1H, $H^6$, $J_{5,6}$ 9.9 Hz), 2.08 br.s (3H, 2-Me); *E*-isomer, 46%: 8.42–8.47 d.d (1H, $H^5$, $J_{3,5}$ 2.1, $J_{5,6}$ 10.2 Hz), 7.54–7.82 m (5H, Ph), 6.88 q (1H, $H^3$), 6.56 d (1H, $H^6$, $J_{5,6}$ 9.9 Hz), 2.03 br.s (3H, 2-Me). Found, %: N 5.25, 5.31; S 12.13, 12.21. $C_{13}H_{11}NO_2S$. Calculated, %: N 5.32; S 12.18.

***N*-[(4-Nitrophenyl)sulfinyl]-2-methyl-1,4-benzoquinone imine (XIIIe).** Yield 31% (*a*), 65% (*b*), 52% (*c*), mp 115–116°C. $^1$H NMR spectrum, δ, ppm, *Z*-isomer, 52%: 8.25 q (1H, $H^3$), 8.01–8.42 d.d (4H, Ar, $J^O$ 9.0 Hz), 6.95–6.99 d.d (1H, $H^5$, $J_{3,5}$ 1.5, $J_{5,6}$ 9.6 Hz), 6.59d (1H, $H^6$, $J_{5,6}$ 9.0 Hz), 2.09 br.s (3H, 2-Me); *E*-isomer, 48%: 8.42–8.46 d.d (1H, $H^5$, $J_{3,5}$ 1.5, $J_{5,6}$ 9.6 Hz), 8.01–8.42 d.d (4H, Ar, $J^O$ 9.0 Hz), 6.88 q (1H, $H^3$), 6.59 d (1H, $H^6$, $J_{5,6}$ 9.0 Hz), 2.05 br.s (3H, 2-Me). Found, %: N 9.01, 9.13; S 10.29, 10.37. $C_{13}H_{10}N_2O_4S$. Calculated, %: N 9.09; S 10.40.

***N*-(Phenylsulfinyl)-2,6-dimethyl-1,4-benzoquinone imine (XIVc).** Yield 70% (*a*), 67% (*b*), 50% (*c*), mp 50–52°C. $^1$H NMR spectrum, δ, ppm: 8.21 br.s (1H, $H^5$), 7.53–7.82 m (5H, Ph), 6.82 br.s (1H, $H^3$), 2.08 br.s (3H, 2-Me), 2.02 br.s (3H, 6-Me). Found, %: N 4.93, 4.99; S 11.44, 11.59. $C_{14}H_{13}NO_2S$. Calculated, %: N 5.05; S 11.56.

***N*-[(4-Nitrophenyl)sulfinyl]-2,5-dimethyl-1,4-benzoquinone imine (XVe).** Yield 42% (*a*), 85% (*b*), 53% (*c*), mp 153–155°C. $^1$H NMR spectrum, δ, ppm: 8.20 q [1H, $H^3$, $J$(2-Me, $H^3$) 1.5 Hz], 8.02–8.43 d.d (4H, Ar, $J^O$ 9.0 Hz), 6.47 q [1H, $H^6$, $J$($Me^5$, $H^6$) 1.5 Hz], 2.12 d [3H, 2-Me, $J$(2-Me, $H^3$) 1.5 Hz], 2.07 d [3H, $Me^5$,

$J$(Me$^5$, H$^6$) 1.5 Hz]. Found, %: N 8.53, 8.70; S 9.87, 9.99. $C_{14}H_{12}N_2O_4S$. Calculated, %: N 8.69; S 9.95.

***N*-[(4-Methoxyphenyl)sulfinyl]-2,6-di-*tert*-butyl-1,4-benzoquinone imine (XVIa).** Yield 40% (*a*), 67% (*b*), 50% (*c*), mp 66–69°C. $^1$H NMR spectrum, δ, ppm: 8.08 d (1H, H$^5$, $J_{3,5}$ 1.2 Hz), 7.03–7.76 d.d (4H, Ar, $J^O$ 8.7 Hz), 6.77 d (1H, H$^3$, $J_{3,5}$ 1.2 Hz), 3.86 s (3H, MeO), 1.30 br.s (9H, 2-*t*-Bu), 1.26 br.s (9H, 6-*t*-Bu). Found, %: N 3.64, 3.71; S 8.55, 8.61. $C_{21}H_{27}NO_3S$. Calculated, %: N 3.75; S 8.58.

***N*-[(4-Methylphenyl)sulfinyl]-2,6-di-*tert*-butyl-1,4-benzoquinone imine (XVIb).** Yield 32% (*a*), 69% (*b*), 58% (*c*), mp 60°C. $^1$H NMR spectrum, δ, ppm: 8.12 d (1H, H$^5$, $J_{3,5}$ 1.8 Hz), 7.34–7.72 d.d (4H, Ar, $J^O$ 8.4 Hz), 6.76 d (1H, H$^3$, $J_{3,5}$ 1.8 Hz), 2.42 s (3H, Me), 1.30 br.s (9H, 2-*t*-Bu), 1.25 br.s (9H, 6-*t*-Bu). Found, %: N 3.65, 3.74; S 8.47, 8.61. $C_{21}H_{27}NO_2S$. Calculated, %: N 3.73; S 8.54.

***N*-(Phenylsulfinyl)-2,6-di-*tert*-butyl-1,4-benzoquinone imine (XVIc).** Yield 44% (*1*), 66% (*b*), 58% (*c*), mp 100–102°C. $^1$H NMR spectrum, δ, ppm: 8.14 br.s (1H, H$^5$), 7.54–7.85 m (5H, Ph), 6.76 br.s (1H, H$^3$), 1.31 br.s (9H, 2-*t*-Bu), 1.27 br.s (9H, 6-*t*-Bu). Found, %: N 3.73, 3.85; S 8.71, 8.82. $C_{20}H_{25}NO_2S$. Calculated, %: N 3.87; S 8.87.

***N*-[(4-Chlorophenyl)sulfinyl]-2,6-di-*tert*-butyl-1,4-benzoquinone imine (XVId).** Yield 45% (*a*), 71% (*b*), 54% (*c*), mp 75–78°C. $^1$H NMR spectrum, δ, ppm: 7.53–7.97 d.d (4H, Ar, $J^O$ 8.4 Hz), 7.88 br.s (1H, H$^5$), 6.67 br.s (1H, H$^3$), 1.33 br.s (9H, 2-*t*-Bu), 1.26 br.s (9H, 6-*t*-Bu). Found, %: N 3.41, 3.43; S 8.02, 8.13. $C_{20}H_{24}ClNO_2S$. Calculated, %: N 3.54; S 8.10.

***N*-[(4-Nitrophenyl)sulfinyl]-2,6-diisopropyl-1,4-benzoquinone imine (XVIIe).** Yield 34% (*a*), 65% (*b*), 51% (*c*), mp 84–88°C. $^1$H NMR spectrum, δ, ppm: 8.03–8.42 d.d (4H, Ar, $J^O$ 8.7 Hz), 8.09 br.s (1H, H$^5$), 6.72 br.s. (1H, H$^3$), 3.05–3.22 m (2H, 2,6-CH *i*-Pr), 1.19 d (6H, 2-*i*-Pr, $J$ 7.5 Hz), 1.16 d (6H, 6-*i*-Pr, $J$ 7.2 Hz). Found, %: N 7.32, 7.44; S 8.39, 8.52. $C_{18}H_{20}N_2O_4S$. Calculated, %: N 7.40; S 8.47.

***N*-(Phenylsulfinyl)-2,6-dichloro-1,4-benzoquinone imine (XVIIIc).** Yield 40% (*a*), 69% (*b*), 53% (*c*), mp 77–80°C. $^1$H NMR spectrum, δ, ppm: 8.86 d (1H, H$^5$, $J_{3,5}$ 2.1 Hz), 7.56–7.82 m (5H, Ph), 7.28 d (1H, H$^3$, $J_{3,5}$ 2.4 Hz). Found, %: N 4.31, 4.43; S 9.91, 10.03. $C_{12}H_7Cl_2NO_2S$. Calculated, %: N 4.40; S 10.08.

***N*-[(4-Chlorophenyl)sulfinyl]-2,6-dichloro-1,4-benzoquinone imine (XVIIId).** Yield 30% (*a*), 65% (*b*), 50% (*c*), mp 146–148°C. $^1$H NMR spectrum, δ, ppm: 8.80 d (1H, H$^5$, $J_{3,5}$ 1.8 Hz), 7.53–7.76 d.d (4H, Ar, $J^O$ 8.4 Hz), 7.26 d (1H, H$^3$, $J_{3,5}$ 2.4 Hz). Found, %: N 4.12, 4.24; S 9.46, 9.53. $C_{12}H_6Cl_3NO_2S$. Calculated, %: N 4.19; S 9.58.

***N*-[(4-Nitrophenyl)sulfinyl]-2,6-dichloro-1,4-benzoquinone imine (XVIIIe).** Yield 33% (*a*), 67% (*b*), 56% (*c*), mp 155–158°C. $^1$H NMR spectrum, δ, ppm: 8.77 d (1H, H$^5$, $J_{3,5}$ 2.1 Hz), 8.01–8.44 d.d (4H, Ar, $J^O$ 8.7 Hz), 7.28 d (1H, H$^3$, $J_{3,5}$ 2.4 Hz). Found, %: N 7.63, 7.69; S 8.71, 8.85. $C_{12}H_6Cl_2N_2O_4S$. Calculated, %: N 7.71; S 8.83.

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