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Hydrohalogenation of *N*-[Arylsulfonylimino(phenyl)methyl]-1,4-benzoquinone Monoimines Having Alkyl Substituents in the Quinoid Ring

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Abstract—Hydrohalogenation of *N*-[arylsulfonylimino(phenyl)methyl]-2,5(3,5)-dimethyl-1,4-benzoquinone monoimines follows exclusively the 1,4-addition pattern, whereas *N*-[arylsulfonylimino(phenyl)methyl]-2,6-dimethyl-1,4-benzoquinone monoimines take up hydrogen halides according to the 6,3-addition scheme.

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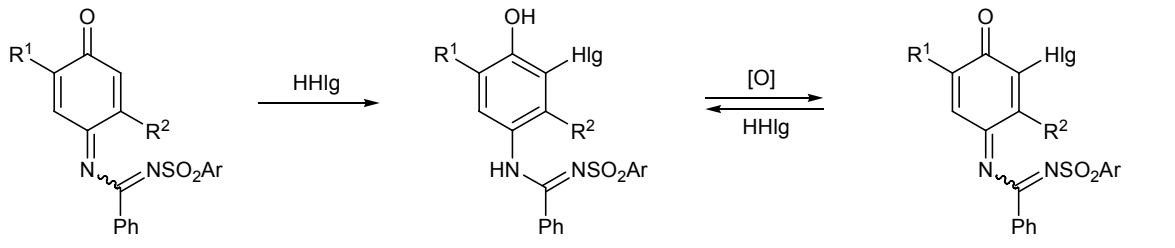
Hydrohalogenation of N-substituted *p*-quinone monoimines was studied in sufficient detail [1–9]. Hydrohalogenation of *N*-aryl- [1, 2], *N*-arylsulfonyl- [4, 5], *N*-aroyl-, *N*-acetyl- [6, 7], and some *N*-[arylsulfonylimino(phenyl)methyl]-1,4-benzoquinone monoimines was reported [8]. It was found that addition of the first hydrogen halide molecule to quinone imines possessing at least one vacant *ortho* position with respect to the carbonyl group generally follows the 1,4-addition pattern [1, 2, 4–8]. Only hydrochlorination of *N*-(4-methylphenyl)-1,4-benzoquinone imine occurred as 6,3-addition [3].

Successive hydrohalogenation–oxidation–hydrohalogenation gives different products, depending on the substituents on the nitrogen atom and in the quinoid ring and size of the halogen atom. Quinone imines having no substituents in the quinoid ring take up first two hydrogen halide molecules according to the 1,4-addition scheme, and the subsequent addition follows 6,3-addition pattern to produce 4-amino-*N*-arylsulfonyl-2,3,6-trichloro(or 2,6-dibromo)phenols [4, 5] and 4-amino-*N*-[arylsulfonylimino(phenyl)-methyl]-2,3,5,6-tetrachloro(or 2,3,6-tribromo)phenols [8]. The latter products contained the maximum possible number of chlorine atoms in the case of hydrochlorination.

We previously succeeded in effecting 6,3-addition of one hydrogen halide molecule in the hydrochlorination of 2,6-dimethyl-substituted *N*-arylsulfonyl- and *N*-[arylsulfonylimino(phenyl)methyl]-1,4-benzoqui-

Scheme 1.



Ia–Ic, **IIa–IIc**, **IIIa–IIIc** — **IVa–IVc**, **Va–Vc**, **VIa–VIc**, **VIIa–VIIc**, **VIIIa–VIIIc**, **IXa–IXc** — **Xa–Xc**, **XIa–XIc**, **XIIa–XIIc**, **XIIIa–XIIIc**, **XIVa–XIVc**, **XVa–XVc**

Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**); **I**, **IV**, **VII**, **X**, **XIII**, $R^1 = R^2 = Me$; **II**, **V**, **VIII**, **XI**, **XIV**, R^1 = *i*-Pr, R^2 = Me; **III**, **VI**, **IX**, **XII**, **XV**, R^1 = Me, R^2 = *i*-Pr; **IV**–**VI**, **X**–**XII**, Hlg = Cl; **VII**–**IX**, **XIII**–**XV**, Hlg = Br.

none imines [6, 8]. *N*-[Arylsulfonylimino(phenyl)-methyl]-2,6-dimethyl-1,4-benzoquinone imines are capable of taking up in succession two hydrogen chloride molecules, whereas their hydrobromination even under severe conditions was unsuccessful: only the initial compounds and their hydrolysis products were isolated [8]. Successive hydrohalogenation–oxidation–hydrohalogenation of *N*-arylsulfonyl- and *N*-aroyl(or acetyl)-2,5-dialkyl-1,4-benzoquinone monoimines afforded only products containing one halogen atom in the 6-position [6, 7, 9].

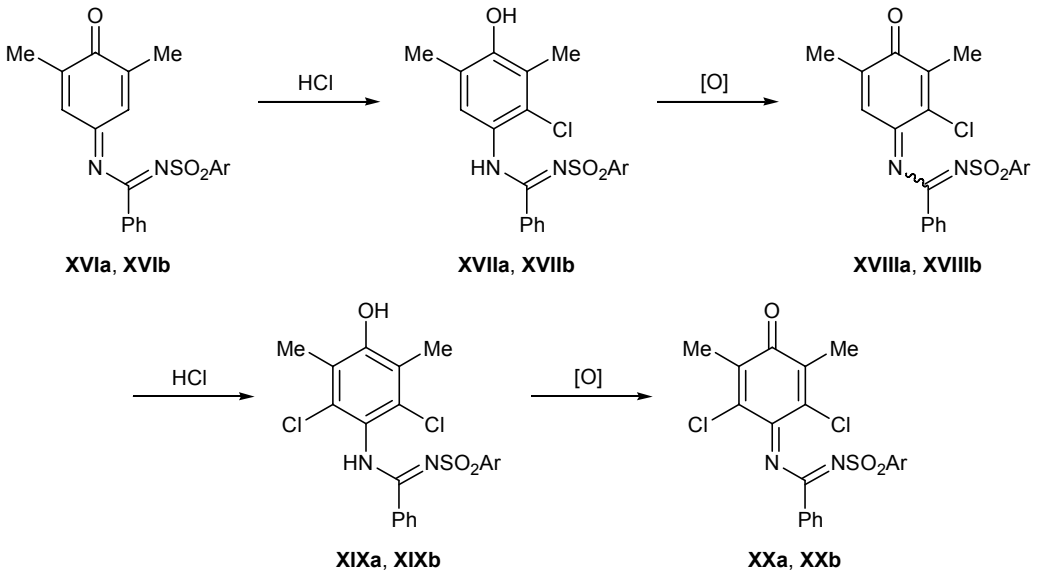
N-[Arylsulfonylimino(phenyl)methyl]-1,4-benzoquinone imines may be regarded as *N*-aroyl-1,4-benzoquinone imine derivatives in which the oxygen atom in the =NC=O carbonyl group is replaced by an arylsulfonylimino group ($ArSO_2N$=), i.e., these compounds are structurally analogous [10]. On the other hand, the redox potential of *N*-[arylsulfonylimino(phenyl)methyl]-1,4-benzoquinone imines is intermediate between those of *N*-arylsulfonyl- and *N*-aroyl-1,4-benzoquinone imines [11–13]. It is known that this parameter is important in the hydrhalogenation process; therefore, in many cases *N*-[arylsulfonylimino(phenyl)methyl]-1,4-benzoquinone imines exhibit reactivity typical of both *N*-arylsulfonyl- and *N*-aroyl-1,4-benzoquinone imines [14, 15].

The present work was aimed at studying hydrohalogenation of alkyl-substituted *N*-[arylsulfonylimino-(phenyl)methyl]-1,4-benzoquinone imines and obtaining their halogen derivatives containing the maximum possible number of halogen atoms in the quinoid ring. It should be noted that hydrohalogenation of *N*-[arylsulfonylimino(phenyl)methyl]-2,5-dialkyl-1,4-benzoquinone imines was not studied previously. Only hydrohalogenation of the corresponding *N*-phenyl-2,6(3,5)-dimethyl derivatives was reported [8].

N-[Arylsulfonylimino(phenyl)methyl]-2,5-dialkyl-1,4-benzoquinone imines **Ia**–**Ic**, **IIa**–**IIc**, and **IIIa**–**IIIc** were synthesized by oxidation of the corresponding 2,5-dialkyl-4-amino-*N*-[arylsulfonylimino(phenyl)-methyl]phenols with lead tetraacetate in acetic acid. Hydrochlorination of 2,5-dimethyl- (**Ia**–**Ic**), 2-isopropyl-5-methyl- (**IIa**–**IIc**), and 5-isopropyl-2-methyl-1,4-benzoquinone imines (**IIIa**–**IIIc**) was carried out by passing gaseous hydrogen chloride through a solution of quinone imine **I**–**III** in chloroform, and their hydrobromination was performed in acetic acid by adding excess 40% hydrobromic acid. According to the ^{1}H NMR data, the only products were the corresponding 2,5-dialkyl-4-amino-*N*-[arylsulfonylimino(phenyl)-methyl]-6-halophenols **IV**–**IX** (Scheme 1). No 6,3-addition products were detected.

Aminophenols **IV**–**IX** were oxidized with lead tetraacetate in acetic acid to obtain the corresponding quinone imines **X**–**XV**. The ^{1}H NMR spectra of compounds **Xa**–**Xc**, **XIIa**–**XIIc**, **XIIIa**–**XIIIc**, and **XVa**–**XVc** contained a quartet due to 3-H in the region δ 6.38–6.48 ppm, while quinone imines **XIa**–**XIc** and **XIVa**–**XIVc** displayed a singlet from 5-H at δ 6.38–6.40 ppm. These data confirmed the assumed structure

Scheme 2.

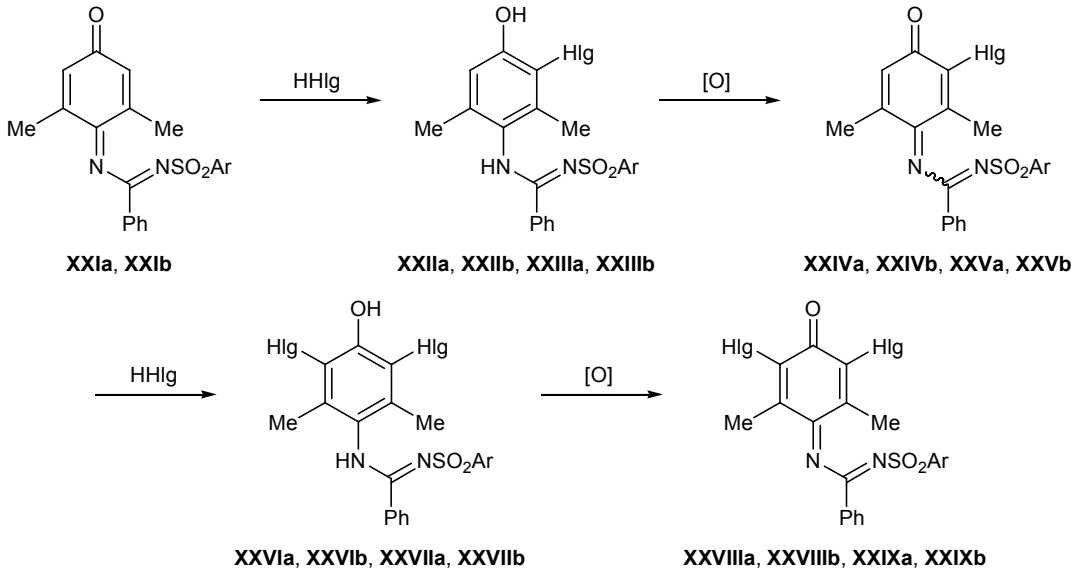


XVIa, **XVIb** **XVIIa**, **XVIIb** **XVIIIa**, **XVIIIb**

XIXa, **XIXb** **XXa**, **XXb**

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

Scheme 3.



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

of the products. In the ^{1}H NMR spectra of **XIa**–**XIc** and **XIVa**–**XIVc** we observed a broadened doublet at δ 1.04–1.06 ppm with a coupling constant *J* of 18.6–20.4 Hz due to protons in the isopropyl groups. Our attempt to subject quinone imines **X**–**XV** to further hydrohalogenation even under severe conditions (on heating in DMF) resulted in their reduction, and only the corresponding 6-halophenols **IV**–**IX** were isolated from the reaction mixtures (Scheme 1).

We also extended the substrate series via introduction of a donor or acceptor substituent into the *para*-position of the arylsulfonyl fragment in *N*-[arylsulfonylimino(phenyl)methyl]-2,6(3,5)-dimethyl-1,4-benzoquinone imines, expecting that such substitution could affect the hydrohalogenation process [3]. By consecutive hydrochlorination–oxidation–hydrochlorination of 2,6-dimethyl derivatives **XVIa** and **XVIb** we succeeded in adding two hydrogen chloride molecules (Scheme 2) and obtaining aminophenols **XVIIa**, **XVIIb**, **XIXa**, and **XIXb** and quinone imines **XVIIIa**, **XVIIIb**, **XXa**, and **XXb**. However, no hydrobromination of the same substrates occurred even under severe conditions, presumably for steric reasons. As a result, only the initial quinone imines and their hydrolysis products were isolated.

As might be expected, stepwise hydrohalogenation of 3,5-dimethyl-substituted analogs **XXIa** and **XXIb** afforded aminophenols **XXIIa**, **XXIIb**, **XXIIIa**, **XXIIIb**, **XXVIa**, **XXVIb**, **XXVIIa**, and **XXVIIb** and quinone imines **XXIVa**, **XXIVb**, **XXVa**, **XXVb**, **XXVIIIa**, **XXVIIIb**, **XXIXa**, and **XXIXb** (Scheme 3). Successful hydrohalogenation of the above substrates is ensured by the absence of substituents in both *ortho* positions of the quinoid ring, which are more reactive toward hydrogen halides as nucleophiles.

Thus hydrohalogenation of *N*-[arylsulfonylimino-(phenyl)methyl]-2,5-dialkyl-1,4-benzoquinone imines is strictly regioselective, and it follows exclusively the 1,4-addition pattern. We failed to introduce the second hydrogen halide molecule to obtain 6,3-addition products. Hydrochlorination of 2,6-dimethyl-substituted derivatives gives 6,3-addition products, and chlorine atoms can be introduced in both *ortho* positions with respect to the C=N carbon atom.

We found previously that introduction of methyl groups into the quinoid ring of quinone imines considerably reduces their redox potential [16] and that the magnitude of this reduction is larger for 2,6-dimethyl derivatives than for their 2,5-dimethyl analogs. The presence of a halogen atom in the quinoid ring increases the redox potential [17], but its effect is much weaker than the effect of methyl substituent. Therefore, the redox potential of quinone imines **X**–**XV** should be higher than that of quinone imines **XVIII**. As a result, reduction of quinone imines **X**–**XV** is more favorable than their hydrohalogenation. We can conclude that the hydrohalogenation of *N*-[arylsulfonylimino(phenyl)methyl]-1,4-benzoquinone imines is controlled by steric factors and competition between two processes, hydrohalogenation and reduction.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer (300 MHz) from solutions in $CDCl_3$. The chemical shifts were determined relative to tetramethylsilane. The reaction mixtures were analyzed by TLC on Silufol UV-254 plates; spots were applied as solutions in chloroform, benzene–hexane (10 : 1) was used as eluent, and the chromatograms were developed under UV light.

Initial *N*-[arylsulfonylimino(phenyl)methyl]-1,4-benzoquinone imines **Ia**–**Ic**, **IIa**–**IIc**, **IIIa**–**IIIc**, **XVIa**, **XVIb**, **XXIa**, and **XXIb** were synthesized by oxidation of the corresponding N-substituted *p*-aminophenols with lead tetraacetate in acetic acid [18]. 4-[Arylsulfonylimino(phenyl)methylamino]phenols were prepared in turn by acylation of 4-aminophenols with *N*-arylsulfonylbenzimidoyl chlorides in DMF–AcOH (1 : 3) in the presence of anhydrous sodium acetate according to the procedure described in [18].

***N*-(2,5-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(phenylsulfonyl)benzenecarboximidamide (Ia).** Yield 79%, mp 121–123°C; published data [19]: mp 120–121°C. ^{1}H NMR spectrum, δ, ppm: 1.94 d (3H, 5-Me, J = 1.2 Hz), 2.21 d (3H, 2-Me, J = 1.5 Hz), 6.42 q (1H, 6-H, J = 1.5 Hz), 6.61 q (1H, 3-H, J = 1.5 Hz), 7.42–8.19 m (10H, H_{arom}).

***N*-(2,5-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-methylphenylsulfonyl)benzenecarboximidamide (Ib).** Yield 84%, mp 134–136°C; published data [15]: mp 131.5–132°C. ^{1}H NMR spectrum, δ, ppm: 1.92 d (3H, 5-Me, J = 1.2 Hz), 2.23 d (3H, 2-Me, J = 1.5 Hz), 2.42 s (3H, **Me**C_6H_4), 6.38 q (1H, 6-H, J = 1.5 Hz), 6.61 q (1H, 3-H, J = 1.2 Hz), 7.28 d (2H, 3′-H, 5′-H, J = 8.7 Hz), 7.42–7.81 m (5H, C_6H_5), 7.85 d (2H, 2′-H, 6′-H, J = 8.7 Hz).

***N*′-(4-Chlorophenylsulfonyl)-*N*-(2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzenecarboximidamide (Ic).** Yield 89%, mp 112–113°C. ^{1}H NMR spectrum, δ, ppm: 1.95 d (3H, 5-Me, J = 1.5 Hz), 2.24 d (3H, 2-Me, J = 1.5 Hz), 6.42 q (1H, 6-H, J = 1.5 Hz), 6.62 q (1H, 3-H, J = 1.2 Hz), 7.44–7.80 m (5H, C_6H_5), 7.48 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.93 d (2H, 2′-H, 6′-H, J = 8.4 Hz). Found, %: N 6.53, 6.76; S 7.59, 7.78. $C_{21}H_{17}ClN_2O_3S$. Calculated, %: N 6.78; S 7.77.

***N*-(5-Isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(phenylsulfonyl)benzenecarboximidamide (IIa).** Yield 81%, mp 125–125.5°C. ^{1}H NMR spectrum, δ, ppm: 1.02 d (6H, CH**Me**$_2$, J = 16.2 Hz), 2.19 d (3H, 2-Me, J = 1.2 Hz), 2.94–3.03 m (1H, C**H**Me_2), 6.35 s (1H, 6-H), 6.59 q (1H, 3-H, J = 1.2 Hz), 7.43–7.99 m (10H, H_{arom}). Found, %: N 7.00, 7.16; S 7.59, 7.78. $C_{23}H_{22}N_2O_3S$. Calculated, %: N 6.89; S 7.89.

***N*-(5-Isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-methylphenylsulfonyl)benzenecarboximidamide (IIb).** Yield 86%, mp 105–107°C; published data [15]: mp 102–104°C. ^{1}H NMR spectrum, δ, ppm: 1.01 d (6H, CH**Me**$_2$, J = 20.7 Hz), 2.20 d (3H, 2-Me, J = 0.9 Hz), 2.43 s (3H, **Me**C_6H_4), 2.93–3.02 m (1H, C**H**Me_2), 6.33 s (1H, 6-H), 6.59 q (1H, 3-H, J = 1.2 Hz), 7.29 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.42–7.79 m (5H, C_6H_5), 7.85 d (2H, 2′-H, 6′-H, J = 8.4 Hz).

***N*′-(4-Chlorophenylsulfonyl)-*N*-(5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene) benzenecarboximidamide (IIc).** Yield 88%, mp 123.5–124°C. ^{1}H NMR spectrum, δ, ppm: 1.01 d (6H, CH**Me**$_2$, J = 7.7 Hz), 2.22 d (3H, Me, J = 1.2 Hz), 2.92–3.01 m (1H, C**H**Me_2), 6.33 s (1H, 6-H), 6.59 q (1H, 3-H, J = 1.2 Hz), 7.29 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.46–7.79 m (5H, C_6H_5), 7.84 d (2H, 2′-H, 6′-H, J = 8.4 Hz). Found, %: N 5.87, 6.03; S 6.75, 6.94. $C_{25}H_{26}ClN_2O_3S$. Calculated, %: N 5.96; S 6.82.

***N*-(2-Isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(phenylsulfonyl)benzenecarboximidamide (IIIa).** Yield 79%, mp 122°C. ^{1}H NMR spectrum, δ, ppm: 1.26–1.33 d.d (6H, CH**Me**$_2$, J = 15.6 Hz), 1.93 d (3H, Me, J = 1.2 Hz), 3.17–3.26 m (1H, C**H**Me_2), 6.41 q (1H, 6-H, J = 1.5 Hz), 6.59 s (1H, 3-H), 7.43–7.99 m (10H, H_{arom}). Found, %: N 6.87, 7.03; S 7.75, 7.96. $C_{23}H_{22}N_2O_3S$. Calculated, %: N 6.89; S 7.89.

***N*-(2-Isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-methylphenylsulfonyl)benzenecarboximidamide (IIIb).** Yield 87%, mp 85–86°C; published data [15]: mp 78–80°C. ^{1}H NMR spectrum, δ, ppm: 1.27–1.33 d.d (6H, CH**Me**$_2$, J = 5.1 Hz), 1.91 d (3H, 5-Me, J = 1.2 Hz), 2.42 s (3H, **Me**C_6H_4), 3.18–3.27 m (1H, C**H**Me_2), 6.37 q (1H, 6-H, J = 1.5 Hz), 6.58 s (1H, 3-H), 7.29 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.42–7.79 m (5H, C_6H_5), 7.86 d (2H, 2′-H, 6′-H, J = 8.4 Hz).

***N*′-(4-Chlorophenylsulfonyl)-*N*-(2-isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzenecarboximidamide (IIIc).** Yield 91%, mp 140–141°C. ^{1}H NMR spectrum, δ, ppm: 1.27–1.34 d.d (6H, CH**Me**$_2$, J = 5.7 Hz), 1.95 d (3H, 5-Me, J = 1.5 Hz), 3.17–3.26 m (1H, C**H**Me_2), 6.42 q (1H, 6-H, J =

1.5 Hz), 6.59 s (1H, 3-H), 7.44–7.79 m (5H, C_6H_5), 7.49 d (2H, 3′-H, 5′-H, J = 9.0 Hz), 7.93 d (2H, 2′-H, 6′-H, J = 9.0 Hz). Found, %: N 6.18, 6.32; S 7.25, 7.36. $C_{23}H_{21}SlN_2O_3S$. Calculated, %: N 6.35; S 7.27.

***N*-(3,5-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-methylphenylsulfonyl)benzenecarboximidamide (XVIa).** Yield 88%, mp 169–170°C; published data [14]: mp 172–174°C. ^{1}H NMR spectrum, δ, ppm: 2.05 s (6H, 3-Me, 5-Me), 2,43 s (3H, **Me**C_6H_4), 6.73 br.s (2H, 2-H, 6-H), 7.30 d (2H, 3′-H, 5′-H, J = 8.7 Hz), 7.40–7.82 m (5H, C_6H_5), 7.86 d (2H, 2′-H, 6′-H, J = 8.7 Hz).

***N*′-(4-Chlorophenylsulfonyl)-*N*-(3,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzenecarboximidamide (XVIb).** Yield 84%, mp 175–177°C; published data [14]: mp 175–177°C. ^{1}H NMR spectrum, δ, ppm: 2.07 s (6H, Me), 6.74 s (2H, 2-H, 6-H), 7.42–7.81 m (5H, C_6H_5), 7.49 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.92 d (2H, 2′-H, 6′-H, J = 8.1 Hz)..

***N*-(2,6-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-methylphenylsulfonyl)benzenecarboximidamide (XXIa).** Yield 79%, mp 131–132°C; published data [14]: mp 122–124°C. ^{1}H NMR spectrum, δ, ppm: 2.08 s (6H, 2-Me, 6-Me), 2.43 s (3H, **Me**C_6H_4), 6.49 s (2H, 3-H, 5-H), 7.32 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.44–7.79 m (5H, C_6H_5), 7.86 d (2H, 2′-H, 6′-H, J = 8.1 Hz).

***N*′-(4-Chlorophenylsulfonyl)-*N*-(2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzenecarboximidamide (XXIb).** Yield 82%, mp 173–175°C; published data [14]: mp 175–176°C. ^{1}H NMR spectrum, δ, ppm: 2.10 s (6H, Me), 6.51 s (2H, 3-H, 5-H), 7.47–7.78 m (5H, C_6H_5), 7.48 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.93 d (2H, 2′-H, 6′-H, J = 8.4 Hz).

Hydrochlorination of *N*-[arylsulfonylimino(phenyl)methyl]-1,4-benzoquinone imines (*general procedure*). Dry gaseous hydrogen chloride was passed over a period of 25–35 min through a solution of 0.01 mol of quinone imine **I**–**III**, **X**–**XII**, **XVI**, **XVIII**, **XXI**, or **XXIV** in 5 ml of anhydrous chloroform. The solution turned lighter, and a colorless solid separated. The precipitate was filtered off, washed with a small amount of acetic acid, dried, and recrystallized from acetic acid.

***N*-(3-Chloro-4-hydroxy-2,5-dimethylphenyl)-*N*′-(phenylsulfonyl)benzenecarboximidamide (IVa).** Yield 85%, mp 210°C. Found, %: Cl 8.49, 8.66; N 6.53, 6.70; S 7.49, 7.75. $C_{21}H_{19}ClN_2O_3S$. Calculated, %: Cl 8.54; N 6.75; S 7.73.

***N*-(3-Chloro-4-hydroxy-2,5-dimethylphenyl)-*N*′-(4-methylphenylsulfonyl)benzenecarboximidamide (IVb).** Yield 77%, mp 213–215°C. Found, %: Cl 8.11, 8.27; N 6.60, 6.77; S 7.25, 7.43. $C_{22}H_{21}ClN_2O_3S$. Calculated, %: Cl 8.27; N 6.63; S 7.48.

***N*-(3-Chloro-4-hydroxy-2,5-dimethylphenyl)-*N*′-(4-chlorophenylsulfonyl)benzenecarboximidamide (IVc).** Yield 60%, mp 232°C. Found, %: Cl 15.67, 15.82; N 6.13, 6.24; S 7.09, 7.25. $C_{21}H_{18}Cl_2N_2O_3S$. Calculated, %: Cl 15.78; N 6.23; S 7.14.

***N*-(3-Chloro-4-hydroxy-5-isopropyl-2-methylphenyl)-*N*′-(phenylsulfonyl)benzenecarboximidamide (Va).** Yield 98%, mp 183–184°C. Found, %: Cl 8.11, 8.26; N 6.30, 6.54; S 7.19, 7.38. $C_{23}H_{23}ClN_2O_3S$. Calculated, %: Cl 8.00; N 6.32; S 7.24.

***N*-(3-Chloro-4-hydroxy-5-isopropyl-2-methylphenyl)-*N*′-(4-methylphenylsulfonyl)benzenecarboximidamide (Vb).** Yield 96%, mp 172–174°C. Found, %: Cl 7.55, 7.69; N 6.20, 6.47; S 7.13, 7.25. $C_{24}H_{25}ClN_2O_3S$. Calculated, %: Cl 7.76; N 6.13; S 7.02.

***N*-(3-Chloro-4-hydroxy-5-isopropyl-2-methylphenyl)-*N*′-(4-chlorophenylsulfonyl)benzenecarboximidamide (Vc).** Yield 89%, mp 176–178°C. Found, %: Cl 14.70, 14.93; N 5.88, 6.12; S 6.75, 6.83. $C_{23}H_{22}Cl_2N_2O_3S$. Calculated, %: Cl 14.85; N 5.87; S 6.72.

***N*-(3-Chloro-4-hydroxy-2-isopropyl-5-methylphenyl)-*N*′-(phenylsulfonyl)benzenecarboximidamide (VIa).** Yield 88%, mp 168–170°C. Found, %: Cl 7.88, 8.06; N 6.13, 6.35; S 7.42, 7.56. $C_{23}H_{23}ClN_2O_3S$. Calculated, %: Cl 8.00; N 6.32; S 7.24.

***N*-(3-Chloro-4-hydroxy-2-isopropyl-5-methylphenyl)-*N*′-(4-methylphenylsulfonyl)benzenecarboximidamide (VIb).** Yield 74%, mp 176–177°C. Found, %: Cl 7.48, 7.66; N 6.00, 6.27; S 7.15, 7.39. $C_{24}H_{25}ClN_2O_3S$. Calculated, %: Cl 7.76; N 6.13; S 7.02.

***N*-(3-Chloro-4-hydroxy-2-isopropyl-5-methylphenyl)-*N*′-(4-chlorophenylsulfonyl)benzenecarboximidamide (VIc).** Yield 62%, mp 167–169°C. Found, %: Cl 14.84, 15.06; N 6.02, 6.33; S 6.59, 6.78. $C_{23}H_{22}Cl_2N_2O_3S$. Calculated, %: Cl 14.85; N 5.87; S 6.72.

***N*-(2-Chloro-4-hydroxy-3,5-dimethylphenyl)-*N*′-(4-methylphenylsulfonyl)benzenecarboximidamide (XVIIa).** Yield 59%, mp 262°C. Found, %: Cl 8.01, 8.34; N 6.72, 6.95; S 7.15, 7.34. $C_{22}H_{21}ClN_2O_3S$. Calculated, %: Cl 8.27; N 6.53; S 7.48.

***N*-(2-Chloro-4-hydroxy-3,5-dimethylphenyl)-*N*′-(4-chlorophenylsulfonyl)benzenecarboximidamide**

(XVIIb). Yield 77%, mp 222–224°C. Found, %: Cl 15.28, 15.43; N 6.09, 6.37; S 7.51, 7.77. $C_{21}H_{18}Cl_2N_2O_3S$. Calculated, %: Cl 15.78; N 6.23; S 7.14.

***N*-(2,6-Dichloro-4-hydroxy-3,5-dimethylphenyl)-*N′*-(4-methylphenylsulfonyl)benzenecarboximidamide (XIXa).** Yield 77%, mp 230–232°C. Found, %: Cl 15.01, 15.22; N 6.08, 6.34; S 6.97, 7.14. $C_{22}H_{20}Cl_2N_2O_3S$. Calculated, %: Cl 15.30; N 6.05; S 6.92.

***N′*-(4-Chlorophenylsulfonyl)-*N*-(2,6-dichloro-4-hydroxy-3,5-dimethylphenyl)benzenecarboximidamide (XIXb).** Yield 68%, mp 268.5–269°C. Found, %: Cl 21.68, 21.83; N 5.49, 5.67; S 6.30, 7.42. $C_{21}H_{17}Cl_3N_2O_3S$. Calculated, %: Cl 21.98; N 5.79; S 6.63.

***N*-(3-Chloro-4-hydroxy-2,6-dimethylphenyl)-*N′*-(4-methylphenylsulfonyl)benzenecarboximidamide (XXIIa).** Yield 66%, mp 28°C. Found, %: Cl 8.31, 8.54; N 6.39, 6.52; S 7.19, 6.48. $C_{22}H_{21}ClN_2O_3S$. Calculated, %: Cl 8.27; N 6.53; S 7.48.

***N*-(3-Chloro-4-hydroxy-2,6-dimethylphenyl)-*N′*-(4-chlorophenylsulfonyl)benzenecarboximidamide (XXIIb).** Yield 76%, mp 276–27°C. Found, %: Cl 15.62, 15.79; N 5.98, 6.19; S 7.23, 7.44. $C_{21}H_{18}Cl_2N_2O_3S$. Calculated, %: Cl 15.78; N 6.23; S 7.14.

***N*-(3,5-Dichloro-4-hydroxy-2,6-dimethylphenyl)-*N′*-(4-methylphenylsulfonyl)benzenecarboximidamide (XXVIa).** Yield 71%, mp 29°C. Found, %: Cl 15.02, 15.27; N 6.30, 6.47; S 6.49, 6.68. $C_{22}H_{20}Cl_2N_2O_3S$. Calculated, %: Cl 15.30; N 6.05; S 6.92.

***N′*-(4-Chlorophenylsulfonyl)-*N*-(3,5-dichloro-4-hydroxy-2,6-dimethylphenyl)benzenecarboximidamide (XXVIb).** Yield 78%, mp 305–307°C. Found, %: Cl 21.62, 21.80; N 5.37, 5.69; S 6.24, 6.51. $C_{21}H_{17}Cl_3N_2O_3S$. Calculated, %: Cl 21.98; N 5.79; S 6.63.

Chloro-substituted *N*-[arylsulfonylimino(phenyl)methyl]-1,4-benzoquinone imines X–XII, XVIII, XX, XXIV, and XXVIII (*general procedure*). Lead tetraacetate, 6.5 mmol, was added at room temperature under vigorous stirring to 5 mmol of aminophenol **IV**–**VI**, **XVII**, **XIX**, **XXII**, or **XXVI** in 10 ml of acetic acid. The reaction was accompanied by heat evolution, so that the mixture was cooled. When the reaction was complete, 2 ml of ethylene glycol was added, the mixture was stirred for 2 min, and the yellow precipitate was filtered off, washed with methanol, dried, and recrystallized from acetic acid.

***N*-(3-Chloro-2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N′*-(phenylsulfonyl)benzenecarboximidamide (Xa).** Yield 96%, mp 173–174°C. ^{1}H NMR spectrum, δ, ppm: 2.14 d (3H, 5-Me, J = 1.2 Hz), 2.37 s (3H, 2-Me), 6.48 q (1H, 6-H, J = 1.8 Hz), 7.43–7.98 m (10H, H_{arom}). Found, %: Cl 8.40, 8.56; N 6.43, 6.77; S 7.29, 7.45. $C_{21}H_{17}ClN_2O_3S$. Calculated, %: Cl 8.59; N 6.78; S 7.77.

***N*-(3-Chloro-2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N′*-(4-methylphenylsulfonyl)benzenecarboximidamide (Xb).** Yield 85%, mp 158–160°C. ^{1}H NMR spectrum, δ, ppm: 2.00 d (3H, 5-Me, J = 1.8 Hz), 2.38 s (3H, 2-Me), 2.43 s (3H, **Me**C_6H_4), 6.45 q (1H, 6-H, J = 1.5 Hz), 7.31 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.42–7.79 m (5H, C_6H_5), 7.84 d (2H, 2′-H, 6′-H, J = 8.1 Hz),. Found, %: Cl 8.09, 8.26; N 6.33, 6.57; S 7.29, 7.44. $C_{22}H_{19}ClN_2O_3S$. Calculated, %: Cl 8.30; N 6.56; S 7.51.

***N*-(3-Chloro-2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N′*-(4-chlorophenylsulfonyl)benzenecarboximidamide (Xc).** Yield 94%, mp 168–170°C. ^{1}H NMR spectrum, δ, ppm: 2.03 d (3H, 5-Me, J = 1.5 Hz), 2.10 s (3H, 2-Me), 6.48 q (1H, 6-H, J = 1.5 Hz), 7.44–7.78 m (5H, C_6H_5), 7.48 d (2H, 3′-H, 5′-H, J = 8.7 Hz), 7.92 d (2H, 2′-H, 6′-H, J = 8.7 Hz). Found, %: Cl 15.69, 15.82; N 6.30, 6.47; S 7.19, 7.34. $C_{21}H_{16}Cl_2N_2O_3S$. Calculated, %: Cl 15.85; N 6.26; S 7.17.

***N*-(3-Chloro-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N′*-(phenylsulfonyl)benzenecarboximidamide (XIa).** Yield 78%, mp 168.5–170°C. ^{1}H NMR spectrum, δ, ppm: 1.04 d (6H, CH**Me**$_2$, J = 20.4 Hz), 2.35 s (3H, Me), 2.99–3.08 m (1H, C**H**Me$_2$), 6.41 s (1H, 6-H), 7.43–7.97 m (10H, H_{arom}). Found, %: Cl 7.69, 7.84; N 6.01, 6.35; S 7.29, 7.58. $C_{23}H_{21}ClN_2O_3S$. Calculated, %: Cl 8.04; N 6.35; S 7.27.

***N*-(3-Chloro-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N′*-(4-methylphenylsulfonyl)benzenecarboximidamide (XIb).** Yield 41%, mp 146–148°C. ^{1}H NMR spectrum, δ, ppm: 1.03 d (6H, CH**Me**$_2$, J = 22.8 Hz), 2.36 s (3H, 2-Me), 2.43 s (3H, **Me**C_6H_4), 2.96–3.07 m (1H, C**H**Me$_2$), 6.39 s (1H, 6-H), 7.30 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.42–7.79 m (5H, C_6H_5), 7.84 d (2H, 2′-H, 6′-H, J = 8.4 Hz). Found, %: Cl 7.53, 7.89; N 5.62, 5.84; S 6.91, 7.08. $C_{24}H_{23}ClN_2O_3S$. Calculated, %: Cl 7.79; N 6.16; S 7.05.

***N*-(3-Chloro-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N′*-(4-chlorophenylsulfonyl)benzenecarboximidamide (XIc).** Yield 53%,

mp 141–143°C. ^{1}H NMR spectrum, δ, ppm: 1.05 d (6H, CH**Me**$_2$, *J* = 18.3 Hz), 2.39 s (3H, Me), 3.00–3.10 m (1H, C**H**Me$_2$), 6.41 s (1H, 6-H), 7.44–7.79 m (5H, C_6H_5), 7.47 d (2H, 3′-H, 5′-H, *J* = 8.7 Hz), 7.92 d (2H, 2′-H, 6′-H, *J* = 8.7 Hz). Found, %: Cl 14.80, 15.22; N 5.36, 5.74; S 6.81, 6.97. $C_{23}H_{20}Cl_2N_2O_3S$. Calculated, %: Cl 14.92; N 5.89; S 6.75.

***N*-(3-Chloro-2-isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(phenylsulfonyl)benzenecarboximidamide (XIIa).** Yield 78%, mp 128–130°C. ^{1}H NMR spectrum, δ, ppm: 1.52 d (6H, CH**Me**$_2$, *J* = 7.2 Hz), 1.98 d (3H, Me, *J* = 1.2 Hz), 3.72–3.82 m (1H, C**H**Me$_2$), 6.42 q (1H, 6-H, *J* = 1.2 Hz), 7.44–8.02 m (10H, H_{arom}). Found, %: Cl 7.79, 8.14; N 6.25, 6.49; S 7.53, 7.80. $C_{23}H_{21}ClN_2O_3S$. Calculated, %: Cl 8.04; N 6.35; S 7.27.

***N*-(3-Chloro-2-isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-methylphenylsulfonyl)benzenecarboximidamide (XIIb).** Yield 75%, mp 153–154°C. ^{1}H NMR spectrum, δ, ppm: 1.52 d (6H, CH**Me**$_2$, *J* = 6.9 Hz), 1.96 d (3H, 5-Me, *J* = 1.2 Hz), 2.43 s (3H, **Me**C_6H_4), 3.72–3.82 m (1H, C**H**Me$_2$), 6.38 q (1H, 6-H, *J* = 1.2 Hz), 7.31 d (2H, 3′-H, 5′-H, *J* = 7.8 Hz), 7.43–7.78 m (5H, C_6H_5), 7.88 d (2H, 2′-H, 6′-H, *J* = 7.8 Hz). Found, %: Cl 7.51, 7.83; N 6.05, 6.49; S 7.22, 7.53. $C_{24}H_{23}ClN_2O_3S$. Calculated, %: Cl 7.79; N 6.16; S 7.05.

***N*-(3-Chloro-2-isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-chlorophenylsulfonyl)benzenecarboximidamide (XIIc).** Yield 72%, mp 159°C. ^{1}H NMR spectrum, δ, ppm: 1.52 d (6H, CH**Me**$_2$, *J* = 6.9 Hz), 2.00 d (3H, Me, *J* = 1.8 Hz), 3.72–3.82 m (1H, C**H**Me$_2$), 6.43 q (1H, 6-H, *J* = 1.8 Hz), 7.44–7.77 m (5H, C_6H_5), 7.68 d (2H, 3′-H, 5′-H, *J* = 8.4 Hz), 7.88 d (2H, 2′-H, 6′-H, *J* = 8.4 Hz). Found, %: Cl 14.50, 14.73; N 5.62, 5.81; S 6.79, 6.94. $C_{24}H_{20}Cl_2N_2O_3S$. Calculated, %: Cl 14.92; N 5.89; S 6.75.

***N*-(2-Chloro-3,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-methylphenylsulfonyl)benzenecarboximidamide (XVIIIa).** Yield 56%, mp 194–196°C. ^{1}H NMR spectrum, δ, ppm: 1.99 d (3H, 5-Me, *J* = 1.5 Hz), 2.29 s (3H, 3-Me), 2,42 s (3H, **Me**C_6H_4), 6.54 q (1H, 6-H, *J* = 1.8 Hz), 7.30 d (2H, 3′-H, 5′-H, *J* = 8.1 Hz), 7.41–7.82 m (5H, C_6H_5), 7.87 d (2H, 2′-H, 6′-H, *J* = 8.1 Hz). Found, %: Cl 8.32, 8.51; N 6.04, 6.37; S 7.49, 7.63. $C_{22}H_{19}ClN_2O_3S$. Calculated, %: Cl 8.30; N 6.56; S 7.51.

***N*-(2-Chloro-3,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-chlorophenylsulfonyl)benzenecarboximidamide (XVIIIb).** Yield 78%, mp 193–195°C. ^{1}H NMR spectrum, δ, ppm: 2.02 d (3H, 5-Me, *J* = 1.5 Hz), 2.30 s (3H, 3-Me), 6.56 q (1H, 6-H, *J* = 1.8 Hz), 7.42–7.81 m (5H, C_6H_5), 7.50 d (2H, 3′-H, 5′-H, *J* = 8.4 Hz), 7.94 d (2H, 2′-H, 6′-H, *J* = 8.4 Hz). Found, %: Cl 15.60, 15.73; N 6.29, 6.48; S 7.05, 7.32. $C_{21}H_{16}Cl_2N_2O_3S$. Calculated, %: Cl 15.85; N 6.26; S 7.17.

***N*-(2,6-Dichloro-3,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-methylphenylsulfonyl)benzenecarboximidamide (XXa).** Yield 70%, mp 172–173°C. ^{1}H NMR spectrum, δ, ppm: 2.10 s (3H, 3-Me), 2.24 s (3H, 5-Me), 2.42 s (3H, **Me**C_6H_4), 7.29 d (2H, 3′-H, 5′-H, *J* = 8.7 Hz), 7.42–7.79 m (5H, C_6H_5), 7.87 d (2H, 2′-H, 6′-H, *J* = 8.7 Hz). Found, %: Cl 15.09, 15.32; N 6.18, 6.47; S 6.51, 6.89. $C_{22}H_{18}Cl_2N_2O_3S$. Calculated, %: Cl 15.37; N 6.07; S 6.95.

***N*′-(4-Chlorophenylsulfonyl)-*N*-(2,6-dichloro-3,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzenecarboximidamide (XXb).** Yield 74%, mp 175–176°C. ^{1}H NMR spectrum, δ, ppm: 2.26 s (6H, Me), 7.43–7.79 m (5H, C_6H_5), 7.47 d (2H, 3′-H, 5′-H, *J* = 9.0 Hz), 7.91 d (2H, 2′-H, 6′-H, *J* = 9.0 Hz). Found, %: Cl 22.10, 22.34; N 5.78, 5.91; S 6.73, 6.82. $C_{21}H_{15}Cl_3N_2O_3S$. Calculated, %: Cl 22.08; N 5.81; S 6.66.

***N*-(3-Chloro-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-methylphenylsulfonyl)benzenecarboximidamide (XXIVa).** Yield 88%, mp 159–160°C. ^{1}H NMR spectrum, δ, ppm: 2.10 d (3H, 6-Me, *J* = 0.9 Hz), 2.25 s (3H, 2-Me), 2.44 s (3H, **Me**C_6H_4), 6.61 q (1H, 5-H, *J* = 1.2 Hz), 7.32 d (2H, 3′-H, 5′-H, *J* = 8.4 Hz), 7.44–7.76 m (5H, C_6H_5), 7.84 d (2H, 2′-H, 6′-H, *J* = 8.4 Hz). Found, %: Cl 8.09, 8.34; N 6.58, 6.71; S 7.51, 7.76. $C_{22}H_{19}ClN_2O_3S$. Calculated, %: Cl 8.30; N 6.56; S 7.51.

***N*-(3-Chloro-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-chlorophenylsulfonyl)benzenecarboximidamide (XXIVb).** Yield 78%, mp 170–171°C. ^{1}H NMR spectrum, δ, ppm: 2.11 d (3H, 6-Me, *J* = 1.2 Hz), 2.29 s (3H, 2-Me), 6.63 q (1H, 5-H, *J* = 1.2 Hz), 7.45–7.76 m (5H, C_6H_5), 7.67 d (2H, 3′-H, 5′-H, *J* = 8.4 Hz), 7.86 d (2H, 2′-H, 6′-H, *J* = 8.4 Hz). Found, %: Cl 15.69, 15.84; N 6.07, 6.19; S 7.22, 7.43. $C_{21}H_{16}Cl_2N_2O_3S$. Calculated, %: Cl 15.85; N 6.26; S 7.17.

***N*-(3,5-Dichloro-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-methylphenylsulfonyl)benzenecarboximidamide (XXVIIIa).** Yield 53%, mp 216–218°C. ^{1}H NMR spectrum, δ, ppm: 2.26 s (6H, 2-Me, 6-Me), 2.44 s (3H, **Me**C_6H_4), 7.32 d (2H,

3′-H, 5′-H, J = 8.4 Hz), 7.44–7.76 m (5H, C_6H_5), 7.84 d (2H, 2′-H, 6′-H, J = 8.4 Hz). Found, %: Cl 15.09, 15.32; N 6.18, 6.47; S 6.51, 6.89. $C_{22}H_{18}Cl_2N_2O_3S$. Calculated, %: Cl 15.37; N 6.07; S 6.95.

***N′*-(4-Chlorophenylsulfonyl)-*N*-(3,5-dichloro-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzenecarboximidamide (XXVIIIb).** Yield 81%, mp 218–220°C. ^{1}H NMR spectrum, δ, ppm: 2.29 s (6H, Me), 7.46–7.75 m (5H, C_6H_5), 7.69 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.86 d (2H, 2′-H, 6′-H, J = 8.4 Hz). Found, %: Cl 21.87, 22.09; N 5.64, 5.83; S 6.21, 6.49. $C_{21}H_{15}Cl_3N_2O_3S$. Calculated, %: Cl 22.08; N 5.81; S 6.66.

Hydrobromination of *N*-[arylsulfonylimino(phenyl)methyl]-1,4-benzoquinone imines (*general procedure*). A solution of 0.01 mol of quinone imine **I**–**III**, **XIII**–**XV**, **XXI**, or **XXV** in 10 ml of acetic acid was heated to 50–60°C, and 2 ml of 40% hydrobromic acid was added in portions under stirring. The mixture turned lighter and was diluted with water, and the colorless precipitate was filtered off and recrystallized from acetic acid.

***N*-(3-Bromo-4-hydroxy-2,5-dimethylphenyl)-*N′*-(phenylsulfonyl)benzenecarboximidamide (VIIa).** Yield 63%, mp 210–212°C. Found, %: Br 17.40, 17.63; N 6.25, 6.41; S 6.58, 6.79. $C_{21}H_{19}BrN_2O_3S$. Calculated, %: Br 17.39; N 6.10; S 6.98.

***N*-(3-Bromo-4-hydroxy-2,5-dimethylphenyl)-*N′*-(4-methylphenylsulfonyl)benzenecarboximidamide (VIIb).** Yield 79%, mp 190–191°C. Found, %: Br 16.53, 16.77; N 5.32, 5.49; S 6.08, 6.31. $C_{22}H_{21}BrN_2O_3S$. Calculated, %: Br 16.88; N 5.92; S 6.77.

***N*-(3-Bromo-4-hydroxy-2,5-dimethylphenyl)-*N′*-(4-chlorophenylsulfonyl)benzenecarboximidamide (VIIc).** Yield 58%, mp 270–272°C. Found, %: Br 15.79, 16.03; N 5.44, 5.62; S 6.38, 6.50. $C_{21}H_{18}BrClN_2O_3S$. Calculated, %: Br 16.18; N 5.67; S 6.49.

***N*-(3-Bromo-4-hydroxy-5-isopropyl-2-methylphenyl)-*N′*-(phenylsulfonyl)benzenecarboximidamide (VIIIa).** Yield 93%, mp 152–154°C. Found, %: Br 16.07, 16.29; N 5.42, 5.63; S 6.19, 6.37. $C_{23}H_{23}BrN_2O_3S$. Calculated, %: Br 16.39; N 5.75; S 6.58.

***N*-(3-Bromo-4-hydroxy-5-isopropyl-2-methylphenyl)-*N′*-(4-methylphenylsulfonyl)benzenecarboximidamide (VIIIb).** Yield 84%, mp 156–158°C. Found, %: Br 15.61, 15.84; N 5.67, 5.90; S 6.24, 6.43. $C_{24}H_{25}BrN_2O_3S$. Calculated, %: Br 15.94; N 5.59; S 6.39.

***N*-(3-Bromo-4-hydroxy-5-isopropyl-2-methylphenyl)-*N′*-(4-chlorophenylsulfonyl)benzenecarboximidamide (VIIIc).** Yield 86%, mp 155–156°C. Found, %: Br 15.09, 15.31; N 5.42, 5.67; S 6.24, 6.38. $C_{23}H_{22}BrClN_2O_3S$. Calculated, %: Br 15.31; N 5.37; S 6.14.

***N*-(3-Bromo-4-hydroxy-2-isopropyl-5-methylphenyl)-*N′*-(phenylsulfonyl)benzenecarboximidamide (IXa).** Yield 73%, mp 153°C. Found, %: Br 16.44, 16.62; N 5.37, 5.49; S 6.78, 6.90. $C_{23}H_{23}BrN_2O_3S$. Calculated, %: Br 16.39; N 5.75; S 6.58.

***N*-(3-Bromo-4-hydroxy-2-isopropyl-5-methylphenyl)-*N′*-(4-methylphenylsulfonyl)benzenecarboximidamide (IXb).** Yield 70%, mp 147–149°C. Found, %: Br 15.70, 15.83; N 5.41, 5.69; S 6.07, 6.31. $C_{24}H_{25}BrN_2O_3S$. Calculated, %: Br 15.94; N 5.59; S 6.39.

***N*-(3-Bromo-4-hydroxy-2-isopropyl-5-methylphenyl)-*N′*-(4-chlorophenylsulfonyl)benzenecarboximidamide (IXc).** Yield 72%, mp 149.5–150°C. Found, %: Br 15.42, 15.66; N 5.19, 5.38; S 6.06, 6.27. $C_{23}H_{22}BrClN_2O_3S$. Calculated, %: Br 15.31; N 5.37; S 6.14.

***N*-(3-Bromo-4-hydroxy-2,6-dimethylphenyl)-*N′*-(4-methylphenylsulfonyl)benzenecarboximidamide (XXIIIa).** Yield 73%, mp 260.5–262°C. Found, %: Br 16.42, 16.70; N 5.89, 6.14 S 6.39, 6.58. $C_{22}H_{21}BrN_2O_3S$. Calculated, %: Br 16.88; N 5.92; S 6.77.

***N*-(3-Bromo-4-hydroxy-2,6-dimethylphenyl)-*N′*-(4-chlorophenylsulfonyl)benzenecarboximidamide (XXIIIb).** Yield 74%, mp 250–251°C. Found, %: Br 16.03, 16.29; N 5.75, 5.94; S 6.32, 6.48. $C_{21}H_{18}BrClN_2O_3S$. Calculated, %: Br 16.18; N 5.67; S 6.49.

***N*-(3,5-Dibromo-4-hydroxy-2,6-dimethylphenyl)-*N′*-(4-methylphenylsulfonyl)benzenecarboximidamide (XXVIIa).** Yield 91%, mp 273–274°C. Found, %: Br 28.73, 28.94; N 5.16, 5.33; S 5.41, 5.60. $C_{22}H_{20}Br_2N_2O_3S$. Calculated, %: Br 28.94; N 5.07; S 5.81.

***N′*-(4-Chlorophenylsulfonyl)-*N*-(3,5-dibromo-4-hydroxy-2,6-dimethylphenyl)benzenecarboximidamide (XXVIIb).** Yield 95%, mp 290–291.5°C. Found, %: Br 27.60, 27.82; N 4.53, 4.79; S 5.61, 5.88. $C_{21}H_{17}Br_2ClN_2O_3S$. Calculated, %: Br 27.90; N 4.89; S 5.60.

Bromo-substituted *N*-[arylsulfonylimino-(phenyl)methyl]-1,4-benzoquinone imines XIII–XV, XXV, and XXIX (*general procedure*). Lead tetraacetate, 6.5 mmol, was added under vigorous stirring at room temperature to 5 mmol of aminophenol **VII–IX**, **XXIII**, or **XXVII** in 10 ml of acetic acid. The reaction was accompanied by heat evolution, so that the mixture was cooled. When the reaction was complete, 2 ml of ethylene glycol was added, and the mixture was stirred for 2 min. The yellow precipitate was filtered off, washed with methanol, dried, and recrystallized from acetic acid.

***N*-(3-Bromo-2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(phenylsulfonyl)benzenecarboximidamide (XIIIa).** Yield 87%, mp 210.5–212°C. ^{1}H NMR spectrum, δ, ppm: 2.02 d (3H, 5-Me, J = 1.2 Hz), 2.41 s (3H, 2-Me), 6.47 q (1H, 6-H, J = 1.5 Hz), 7.43–7.97 m (10H, H_{arom}). Found, %: Br 17.42, 17.69; N 5.33, 5.68; S 7.29, 7.44. $C_{21}H_{17}BrN_2O_3S$. Calculated, %: Br 17.47; N 6.13; S 7.01.

***N*-(3-Bromo-2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-methylphenylsulfonyl)benzenecarboximidamide (XIIIb).** Yield 79%, mp 190–191.5°C. ^{1}H NMR spectrum, δ, ppm: 2.00 d (3H, 5-Me, J = 1.5 Hz), 2.41 s (3H, 2-Me), 2.43 s (3H, **Me**C_6H_4), 6.43 q (1H, 6-H, J = 1.8 Hz), 7.31 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.43–7.78 m (5H, C_6H_5), 7.84 d (2H, 2′-H, 6′-H, J = 8.1 Hz). Found, %: Br 16.82, 17.04; N 5.69, 5.94; S 6.83, 7.02. $C_{22}H_{19}BrN_2O_3S$. Calculated, %: Br 16.95; N 5.94; S 6.80.

***N*-(3-Bromo-2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-chlorophenylsulfonyl)benzenecarboximidamide (XIIIc).** Yield 99%, mp 225.5–227°C. ^{1}H NMR spectrum, δ, ppm: 2.04 d (3H, 5-Me, J = 1.5 Hz), 2.44 s (3H, 2-Me), 6.47 q (1H, 6-H, J = 1.5 Hz), 7.44–7.78 m (5H, C_6H_5), 7.50 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.44–7.78 m (5H, Ph), 7.92 d (2H, 2′-H, 6′-H, J = 8.4 Hz). Found, %: Br 16.09, 16.34; N 5.68, 5.92; S 6.33, 6.52. $C_{21}H_{16}BrClN_2O_3S$. Calculated, %: Br 16.25; N 5.70; S 6.52.

***N*-(3-Bromo-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(phenylsulfonyl)benzenecarboximidamide (XIVa).** Yield 85%, mp 157–159°C. ^{1}H NMR spectrum, δ, ppm: 1.04 d (6H, CH**Me**$_2$, J = 10.2 Hz), 2.40 s (3H, Me), 2.99–3.09 m (1H, C**H**Me$_2$), 6.40 q (1H, 6-H, J = 0.9 Hz), 7.43–7.97 m (10H, H_{arom}). Found, %: Br 16.58, 16.82; N 5.44, 5.79; S 6.23, 6.50. $C_{23}H_{21}BrN_2O_3S$. Calculated, %: Br 16.46; N 5.77; S 6.61.

***N*-(3-Bromo-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-methylphenylsulfonyl)benzenecarboximidamide (XIVb).** Yield 91%, mp 136–138°C. ^{1}H NMR spectrum, δ, ppm: 1.03 d (6H, CH**Me**$_2$, J = 18.6 Hz), 2.41 s (3H, 2-Me), 2.43 s (3H, **Me**C_6H_4), 2.99–3.08 m (1H, C**H**Me$_2$), 6.38 q (1H, 6-H, J = 1.2 Hz), 7.31 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.42–7.78 m (5H, C_6H_5), 7.84 d (2H, 2′-H, 6′-H, J = 8.1 Hz). Found, %: Br 16.12, 16.49; N 5.73, 5.88; S 6.27, 6.59. $C_{24}H_{23}BrN_2O_3S$. Calculated, %: Br 16.00; N 5.61; S 6.42.

***N*-(3-Bromo-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-chlorophenylsulfonyl)benzenecarboximidamide (XIVc).** Yield 95%, mp 157–158°C. ^{1}H NMR spectrum, δ, ppm: 1.04 d (6H, CH**Me**$_2$, J = 10.5 Hz), 2.43 s (3H, Me), 3.01–3.10 m (1H, C**H**Me$_2$), 6.40 q (1H, 6-H, J = 1.2 Hz), 7.43–7.78 m (5H, C_6H_5), 7.50 d (2H, 3′-H, 5′-H, J = 8.7 Hz), 7.92 d (2H, 2′-H, 6′-H, J = 8.7 Hz). Found, %: Br 15.26, 15.49; N 5.27, 5.63; S 6.01, 6.30. $C_{23}H_{20}BrClN_2O_3S$. Calculated, %: Br 15.37; N 5.39; S 6.17.

***N*-(3-Bromo-2-isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(phenylsulfonyl)benzenecarboximidamide (XVa).** Yield 75%, mp 134–136°C. ^{1}H NMR spectrum, δ, ppm: 1.52–1.56 d.d (6H, CH**Me**$_2$, J = 7.5 Hz), 1.98 d (3H, Me, J = 1.2 Hz), 3.74–3.84 m (1H, C**H**Me$_2$), 6.40 q (1H, 6-H, J = 0.9 Hz), 7.44–8.02 m (10H, H_{arom}). Found, %: Br 16.08, 16.34; N 5.29, 5.50; S 6.71, 6.93. $C_{23}H_{21}BrN_2O_3S$. Calculated, %: Br 16.46; N 5.77; S 6.61.

***N*-(3-Bromo-2-isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-methylphenylsulfonyl)benzenecarboximidamide (XVb).** Yield 88%, mp 94°C. ^{1}H NMR spectrum, δ, ppm: 1.52–1.56 d.d (6H, CH**Me**$_2$, J = 9.6 Hz), 1.96 d (3H, 5-Me, J = 1.2 Hz), 2.42 s (3H, **Me**C_6H_4), 3.74–3.83 m (1H, C**H**Me$_2$), 6.38 q (1H, 6-H, J = 1.2 Hz), 7.43–7.78 m (5H, C_6H_5), 7.47 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.88 d (2H, 2′-H, 6′-H, J = 8.1 Hz). Found, %: Br 15.87, 16.04; N 5.39, 5.62; S 6.37, 6.50. $C_{24}H_{23}BrN_2O_3S$. Calculated, %: Br 16.00; N 5.61; S 6.42.

***N*-(3-Bromo-2-isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-chlorophenylsulfonyl)benzenecarboximidamide (XVc).** Yield 79%, mp 132–133°C. ^{1}H NMR spectrum, δ, ppm: 1.47–1.51 d.d (6H, CH**Me**$_2$, J = 10.5 Hz), 2.00 d (3H, Me, J = 1.6 Hz), 3.73–3.84 m (1H, C**H**Me$_2$), 6.42 q (1H, 6-H, J = 1.5 Hz), 7.44–7.77 m (5H, C_6H_5), 7.49 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.94 d (2H, 2′-H, 6′-H, J = 8.1 Hz). Found, %: Br 14.92, 15.20; N 5.37, 5.64; S 6.11, 6.38. $C_{23}H_{20}BrClN_2O_3S$. Calculated, %: Br 15.37; N 5.39; S 6.17.

***N*-(3-Bromo-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-methylphenylsulfonyl)benzenecarboximidamide (XXVa).** Yield 83%, mp 188–189°C. ^{1}H NMR spectrum, δ, ppm: 2.09 d (3H, 6-Me, J = 1.2 Hz), 2.30 s (3H, 2-Me), 2.44 s (3H, **Me**C_6H_4), 6.65 q (1H, 5-H, J = 1.2 Hz), 7.32 d (2H, 3′-H, 5′-H, J = 8.7 Hz), 7.44–7.77 m (5H, C_6H_5), 7.85 d (2H, 2′-H, 6′-H, J = 8.7 Hz). Found, %: Br 16.89, 17.14; N 5.83, 6.02; S 6.59, 6.84. $C_{22}H_{19}BrN_2O_3S$. Calculated, %: Br 16.95; N 5.94; S 6.80.

***N*-(3-Bromo-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-chlorophenylsulfonyl)benzenecarboximidamide (XXVb).** Yield 93%, mp 208–209.5°C. ^{1}H NMR spectrum, δ, ppm: 2.10 d (3H, 6-Me, J = 1.2 Hz), 2.31 s (3H, 2-Me), 6.63 q (1H, 5-H, J = 1.2 Hz), 7.45–7.76 m (5H, C_6H_5), 7.66 d (2H, 3′-H, 5′-H, J = 9.0 Hz), 7.85 d (2H, 2′-H, 6′-H, J = 9.0 Hz). Found, %: Br 15.90, 16.24; N 5.71, 5.89; S 6.23, 6.40. $C_{21}H_{16}BrClN_2O_3S$. Calculated, %: Br 16.25; N 5.70; S 6.52.

***N*-(3,5-Dibromo-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N*′-(4-methylphenylsulfonyl)-benzenecarboximidamide (XXIXa).** Yield 79%, mp 234–236°C. ^{1}H NMR spectrum, δ, ppm: 2.30 s (6H, 2-Me, 6-Me), 2.44 s (3H, **Me**C_6H_4), 7.32 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.44–7.76 m (5H, C_6H_5), 7.84 d (2H, 2′-H, 6′-H, J = 8.4 Hz). Found, %: Br 29.09, 29.34; N 5.17, 5.48; S 5.93, 6.11. $C_{22}H_{18}Br_2N_2O_3S$. Calculated, %: Br 29.04; N 5.09; S 5.83.

***N*′-(4-Chlorophenylsulfonyl)-*N*-(3,5-dibromo-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-benzenecarboximidamide (XXIXb).** Yield 84%, mp 238–240°C. ^{1}H NMR spectrum, δ, ppm: 2.34 s (6H, Me), 7.46–7.76 m (5H, C_6H_5), 7.52 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.92 d (2H, 2′-H, 6′-H, J = 8.4 Hz). Found, %: Br 28.17, 28.39; N 4.75, 4.93; S 5.61, 5.80. $C_{21}H_{15}Br_2ClN_2O_3S$. Calculated, %: Br 28.00; N 4.91; S 5.62.

REFERENCES

1. Adams, R. and Looker, J.H., *J. Am. Chem. Soc*., 1951, vol. 73, p. 1145; Adams, R. and Looker, J.H., *J. Am. Chem. Soc*., 1951, vol. 73, p. 1149; Adams, R. and Reifschneider, W., *Bull. Soc. Chim. Fr*., 1958, p. 23.
2. Adams, R. and Nagarkatti, A.S., *J. Am. Chem. Soc*., 1950, vol. 72, p. 4601; Adams, R. and Colgrove, R.S., *J. Am. Chem. Soc*., 1954, vol. 76, p. 3584; Markava, E.Ya., Kanepe, D.V., Liepin'sh, E.E., and Freimanis, Ya.F., *Zh. Org. Khim*., 1980, vol. 16, p. 2362; Burmistrov, K.S. and Toropin, N.V., *Zh. Org. Khim*., 1985, vol. 21, p. 1544; Toropin, N.V., Burmistrov, K.S., Burmistrov, S.I., and Zaichenko, N.L., *Zh. Org. Khim*., 1986, vol. 22, p. 999; Burmistrov, K.S., Toropin, N.V., and Burmistrov, S.I., *Zh. Org. Khim*., 1993, vol. 29, p. 1170.
3. Toropin, N.V. and Burmistrov, K.S., *Zh. Org. Khim*., 1983, vol. 19, p. 1546; Burmistrov, K.S. and Yurchenko, A.G., *Zh. Org. Khim*., 1985, vol. 21, p. 575.
4. Avdeenko, A.P. and Velichko, N.V., *Zh. Org. Khim*., 1993, vol. 29, p. 1167.
5. Avdeenko, A.P. and Velichko, N.V., *Zh. Org. Khim*., 1992, vol. 28, p. 1257.
6. Avdeenko, A.P., Konovalova, S.A., and Ludchenko, O.N., *Russ. J. Org. Chem*., 2009, vol. 45, p. 1799; Avdeenko, A.P., Konovalova, S.A., Ludchenko, O.N., Palamarchuk, G.V., and Shishkin, O.V., *Russ. J. Org. Chem*., 2009, vol. 45, p. 1651.
7. Avdeenko, A.P., Konovalova, S.A., Ludchenko, O.N., Ledeneva, O.P., and Vakulenko, A.V., *Russ. J. Org. Chem*., 2011, vol. 47, p. 214.
8. Avdeenko, A.P., Marchenko, I.L., and Konovalova, S.A., *Russ. J. Org. Chem*., 2001, vol. 37, p. 72.
9. Avdeenko, A.P. and Konovalova, S.A., *Russ. J. Org. Chem*., 2006, vol. 42, p. 669.
10. Avdeenko, A.P., Pirozhenko, V.V., Yagupol'skii, L.M., and Marchenko, I.L., *Russ. J. Org. Chem*., 2001, vol. 37, p. 991.
11. 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.
12. Petrova, S.A., Burmistrov, K.S., Kolodyazhnyi, M.V., and Ksenzhek, O.S., *Elektrokhimiya*, 1979, vol. 15, p. 1666.
13. Avdeenko, A.P., Burmistrov, K.S., Dubina, V.L., and Skripets, V.I., *Ukr. Khim. Zh*., 1980, vol. 46, p. 1081.
14. Avdeenko, A.P., Konovalova, S.A., Roman'kov, D.A., Burmistrov, K.S., Nichvoloda, V.M., Shishkin, O.V., Zubatyuk, R.I., and Palamarchuk, G.V., *Russ. J. Org. Chem*., 2009, vol. 45, p. 48.
15. Avdeenko, A.P., Konovalova, S.A., Roman'kov, D.A., Ludchenko, O.N., and Marchenko, I.L., *Russ. J. Org. Chem*., 2009, vol. 45, p. 383.
16. Dubina, V.L. and Burmistrov, K.S., *Zh. Org. Khim*., 1977, vol. 13, p. 378; Burmistrov, K.S. and Burmistrov, S.I., *Zh. Org. Khim*., 1980, vol. 16, p. 1487.
17. Burmistrov, K.S., Toropin, N.V., and Burmistrov, S.I., *Ukr. Khim. Zh*., 1983, vol. 49, p. 1208.
18. Avdeenko, A.P., Burmistrov, K.S., Dubina, V.L., and Skripets, V.I., *Ukr. Khim. Zh*., 1980, vol. 46, p. 1081.
19. Avdeenko, A.P., Pirozhenko, V.V., Konovalova, S.A., Roman'kov, D.A., Palamarchuk, G.V., and Shishkin, O.V., *Russ. J. Org. Chem*., 2009, vol. 45, p. 408.