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Halogenation of N-Substituted *para*-Quinone Monoimine and *para*-Quinone Monooxime Esters: V.* Chlorination and Bromination of *N*-Arylsulfonyl-1,4-benzoquinone Monoimines Dialkyl-Substituted in the Quinoid Ring

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Abstract—The direction of halogen addition to *N*-arylsulfonyl-1,4-benzoquinone monoimines dialkyl-substituted in the quinoid ring is governed by the steric factors: the size and position of the substituent, the halogen volume, and the position of the substituent at the nitrogen. The first stage of halogenation of *N*-arylsulfonyl-4-aminophenols with two alkyl substituents in the phenylsulfonyl ring largely occurs as electrophilic substitution.

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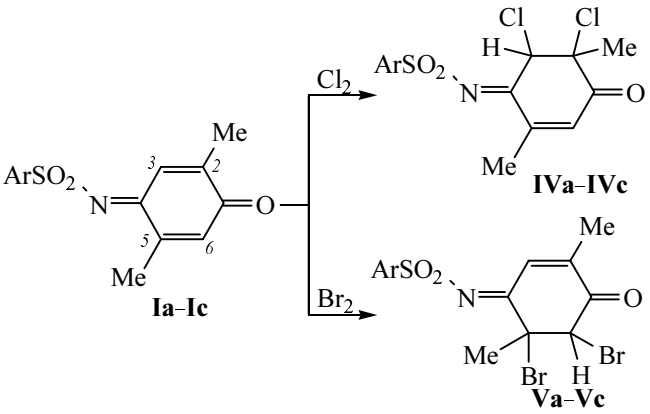
In [1] was reported on the halogenation of the *N*-arylsulfonyl-2(3)-methyl(2-chloro)-1,4-benzoquinone monoimines, and the principal factors were established influencing the direction of the halogen addition.

The goal of the present study was the elucidation of the extent to which the steric factor influenced the halogenation direction in the case of *para*-quinone monoimines with two alkyl substituents in the quinoid ring (varying of the size of the substituent in the quinoid ring and its position). The results should be compared with those obtained on the corresponding *para*-quinone monooximes esters. To this end the halogenation was carried out using *para*-quonone monoimines with various substituents (*i*-Pr, Me) in positions *2* and *5* of the quinoid ring of the *para*-quinone imines, with different positions of two methyl groups (*2, 5*; *2, 6*, and *3, 5*); the halogens employed had various atomic radii (Cl_2, Br_2).

The chlorination of quinone imines **Ia–Ic–IIIa–IIIc** was performed with gaseous chlorine, the bromination, with molecular bromine in various solvents ($CHCl_3$, AcOH, DMF–AcOH, 1 : 5) at different ratios of the initial substance and the halogen. Owing to the presence of a Me (*i*-Pr) group in the *ortho*-position with respect to the imine carbon atom these compounds exist as a single isomer.

In the halogenation of *N*-arylsulfonyl-2,5-dimethyl-1,4-benzoquinone imines **Ia–Ic** the direction of the halogen addition is governed mainly by the bulk of the halogen atom proper. The chlorination of quinone imines **Ia–Ic** occurred under more stringent conditions than with *N*-arylsulfonyl-2(3)-methyl-1,4-benzoquinone imines [1], at prolonged heating. The chlorine molecule in this instance added to the C=C bond having a substituent in the *ortho*-position with respect to the carbonyl carbon, namely to the *syn*-bond. It was already stated in [2, 3] that in the halogenation of *para*-quinone oximes esters the C=C bond in the *syn*-position to the substituent at the nitrogen atom was more reactive. Accordingly the chlorination of quinone imines **Ia–Ic** resulted in cyclohexene (hemiquinoid) structures: 4-arylsulfonylimino-3,6-dimethyl-5,6-dichloro-2-cyclphexen-1-ones **IVa–IVc** (Scheme 1).

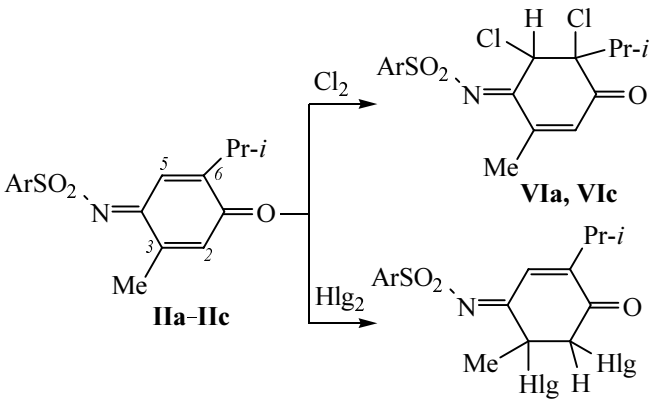
Scheme 1.



Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 3-$NO_2C_6H_4$ (**c**).

* For communication IV, see [1].

Scheme 2.



Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 3-$NO_2C_6H_4$ (**c**); Hlg = Cl (**VII**), Br (**VIII**).

The bromination proceeded easier, at slight short heating. The bulkier bromine molecule added to the a *anti*-bond C=C with a substituent in the *ortho*-position with respect to the imine carbon atom, consequently, to the more spatially accessible C=C bond of the quinoid ring, affording 4-arylsulfonylimino-2,5-dimethyl-5,6-dibromo-2-cyclohexen-1-ones **Va–Vc** (Scheme 1) (in quinone imine **I** the *syn*-bond C=C of the quinoid ring contained a Me group and suffered a steric hindrance from the $ArSO_2$ group).

In the halogenation of 2,5-dimethyl-substituted *para*-quinone monooximes esters [4] the products obtained resulted from halogen addition to each of the C=C bonds of the quinoid ring, therefore the chlorine and bromine molecules could add both to C^2=C^3 and C^5=C^6 bonds of the quinoid ring. The chlorination of 2,5-dimethyl-substituted quinone imines **Ia–Ic** affords only the products of addition to the C^2=C^3 bond, and the bromination, to the C^5=C^6 bond; it means that the addition direction is governed by the size of the halogen atom. The calculations by PM3 method demonstrated that in quinone imine **Ia** the difference in polarization of the C^2=C^3 and C^5=C^6 bonds (see the table) was less pronounced than in the corresponding 2,5-dimethyl-1,4-quinone monooxime ester [2]. Therefore the chlorine molecule adds across the less polarized and more active C^2=C^3 bond, and the bulkier bromine molecule, across the more sterically accessible C^5=C^6 bond; thus the steric factor is relatively more important for the regioselectivity of the halogen addition to quinone imines than to the corresponding *para*-quinone oximes esters, as is proved experimentally.

At the chlorination of *N*-arylsulfonyl-6-isopropyl-3-methyl-1,4-benzoquinone imines **IIa–IIc** the molecule of Cl_2 added to either of C=C bonds of the quinoid ring. This may be due to the presence of a bulkier substituent, *i*-Pr, at the C=C bond in the *syn*-position to the substituent at the nitrogen, and therefore addition to the C^5=C^6 bond is impeded. The addition of the bromine molecule as expected by analogy to quinone imines **Ia–Ic** occurred only at the more accessible C=C containing a Me substituent (Scheme 2).

The calculations by PM3 method showed that same as in 2,5-dimethyl-substituted quinone imine **Ia** in quinone imine **IIa** difference in the polarization of the bonds C^2=C^3 and C^5=C^6 (see the table) is less pronounced than in the corresponding *para*-quinone oxime ester [2]. Hence as in *para*-quinone imines **Ia–Ic** the steric factor governs the direction of the halogen addition.

The chlorination of *N*-arylsulfonyl-2-methyl-5-isopropyl-1,4-benzoquinone monoimines **IIIa–IIIc** occurred exclusively across the C^2=C^3 bond of the quinoid ring containing a Me group. At the bromination both products of Br_2 addition to either C=C bond of the quinoid ring were obtained. This fact is due to the presence in quinone imines **IIIa** and **IIIb** of the bulky isopropyl group at the C^5=C^6 bond in the *anti*-position with respect to $ArSO_2$ substituent. This bond, more sterically accessible in quinone imines **Ia–Ic** and **IIa–IIc**, is difficultly accessible for bulky bromine molecule in compounds **III** (Scheme 3). The PM3 calculations show that the difference in the polarization of the C=C bonds of the quinoid ring in quinone imine **IIIa** is comparable with the

Charges on atoms C^2, C^3, C^5, and C^6 of the quinoid ring in *N*-arylsulfonyl-1,4-benzoquinone monoimines dialkyl-substituted in the quinoid ring **Ia–IIIa** calculated by PM3 method

Compd. no.	qC^2	qC^3	Δq_1[a]	qC^5	qC^6	Δq_2[b]	Δq[c]
Ia	–0.164	–0.1022	0.0619	–0.1829	–0.0326	0.1503	0.0884
IIa	–0.1871	–0.0382	0.1489	–0.165	–0.0994	0.0656	0.0833
IIIa	–0.157	–0.1003	0.0562	–0.191	–0.0365	0.1545	0.0983

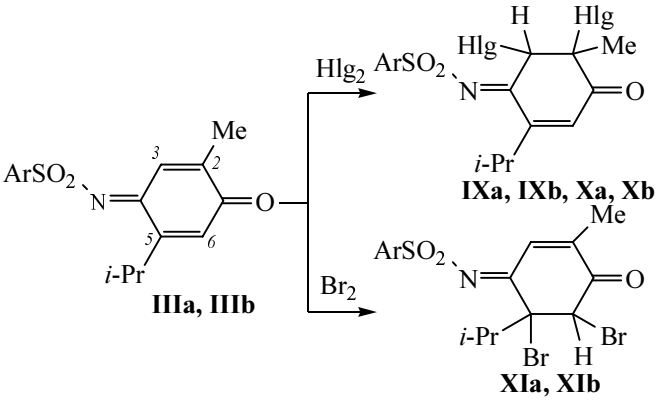
[a] $\Delta q_1 = |qC^2 - qC^3|$; [b] $\Delta q_2 = |qC^5 - qC^6|$; [c] $\Delta q = \Delta q_1 - \Delta q_2$.

corresponding values for quinone imines **Ia** and **IIa** (see the table), and the governing influence on the direction of the halogen addition to quinone imines **IIIa** and **IIIb** is also produced by the steric factor.

The halogenation of reduced forms of the corresponding quinone imines, 4-arylsulfonylamido-2,5-dimethylphenols **XIIa–XIIc**, 4-arylsulfonylamido-6-isopropyl-3-methylphenols **XIIIa–XIIIc**, and 4-arylsulfonylamido-5-isopropyl-2-methylphenols **XIVa–XIVc** gave the identical set of products (Scheme 4).

Inasmuch as the halogenation products of aminophenols are unlike the halogenation products of quinone imines it was presumable that in the first stage an electrophilic substitution occurred of the hydrogen in the *ortho*-position relative to the hydroxy group. It is also possible that in the first stage the aminophenol is oxidized by the halogen molecule, and then an addition occurs of the HHlg molecule liberated in the process of oxidation to the formed quinone imines (**Ia–Ic–IIIa–IIIc**; for **IIIc** Ar=3-$NO_2C_6H_4$). As a result arise the corresponding aminophenols **XVa–XVc–XXa–XXc**. The probability of this halogenation path is supported by hydrohalogenation of quinone imines **Ia–Ic–IIIa–IIIc** yielding aminophenols **XVa–XVc–XXa–XXc**. Aminophenols **XVa–XVc–XXa–XXc** in the course of halogenation under the action of the Hlg_2 molecule can be converted into the corresponding quinone imines **XXIa–XXIc–XXVIa–XXVIc**. This oxidation can also

Scheme 3.

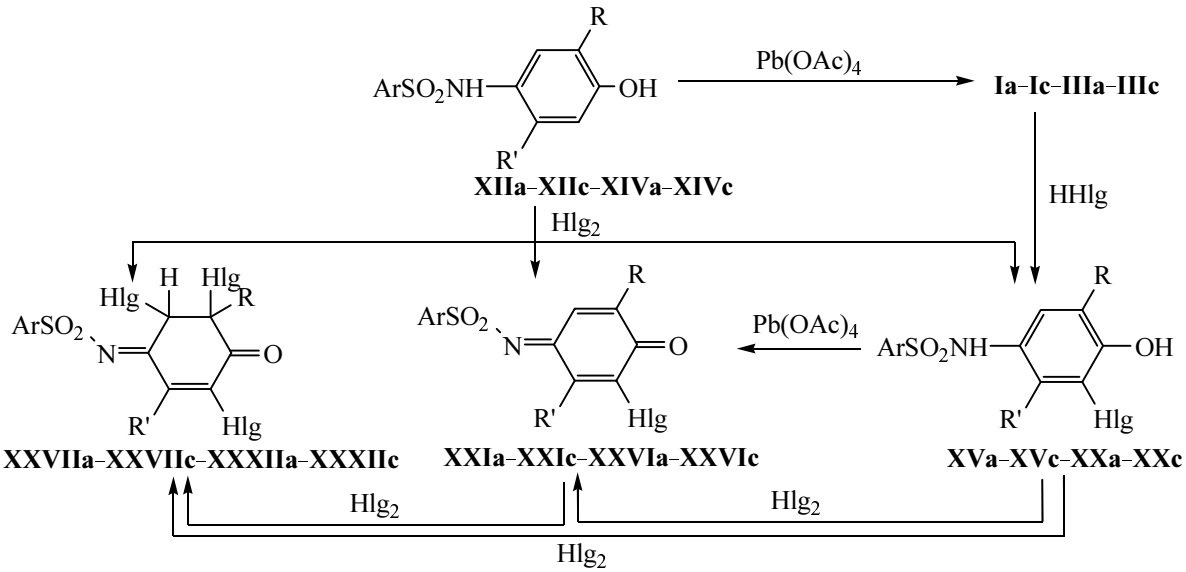


Ar = Ph (**a**), 4-MeC_6H_4 (**b**); Hlg = Cl (**IX**), Br (**X**).

be performed with the use of lead tetraacetate as oxidant (Scheme 4).

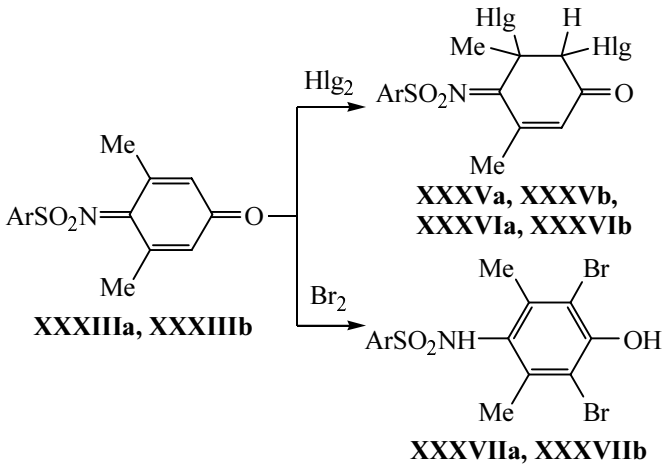
The formation of quinone imines **XXIa–XXIc–XXVIa–XXVIc** cannot be explained as oxidation of initial aminophenols **XIIa–XIIc–XIVa–XIVc** followed by halogen addition and dehydrohalogenation, since at the chlorination of quinone imines **Ia–Ic–IIIa–IIIc** the Cl_2 molecule adds to the C=C bond containing the Me group in the *ortho*-position with respect to carbonyl carbon, and then the dehydrochlorination cannot afford quinone imines **XXIa–XXIc–XXVIa–XXVIc** for the chlorine

Scheme 4.



Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 3-$NO_2C_6H_4$ (**c**); R = R' = Me (**XII, XV, XVI, XXI, XXII, XXVII, XXVIII**); R = *i*-Pr, R' = Me (**XIII, XVII, XVIII, XXIII, XXIV,XXIX, XXX**); R = Me, R' = *i*-Pr (**XIV, XIX, XX, XXV, XXVI, XXXI, XXXII**); Hlg = Cl (**XV, XVII, XIX, XXI, XXIII, XXV, XXVII, XXIX, XXXI**), Br (**XVI, XVIII, XX, XXII, XXIV, XXVI, XXVIII, XXX, XXXII**).

Scheme 5.



Ar = Ph (**a**), 4-MeC_6H_4 (**b**); Hlg = Cl (**XXXV**), Br (**XXXVI**).

atom in this case should be in the position *3* of the quinoid ring.

The addition of a Hlg_2 molecule to quinone imines **XXIa–XXIc–XXVIa–XXVIc** furnished relatively stable products of cyclohexene structure **XXVIIa–XXVIIc–XXXIIa–XXXIIc**. The chlorination of quinone imines **XXIa–XXIc–XXVIa–XXVIc** occurred only under rigid conditions: at prolonged boiling. In the presence of $AlCl_3$ or LiCl the process is considerably accelerated, and the chlorination is completed within several minutes. In the presence of HCl the chlorination of quinone imines **XXIa–XXIc, XXIIIa–XXIIIc**, and **XXVa–XXVc** proceeded even faster. The special role of HCl in the chlorination of quinoid systems was formerly mentioned in [5].

The composition and structure of compounds synthesized **Ia–Ic–XXXIIa–XXXIIc** were proved by elemental analysis, IR, ^1H and ^{13}C NMR spectra. ^1H NMR spectra were measured only for compounds of quinoid and cyclohexene structures because they are more informative. In the ^1H NMR spectra of hemiquinoid structures **IVa–IVc**, **VIa, VIc, IXa, IXb, Xa**, and **Xb** the signal from H^2 atom appears in the region δ 6.43–6.65 ppm character-istic of hydrogen atoms at the C=C bond of the quinoid ring, the signal from H^5, in the region δ 6.12–6.38 ppm common for hydrogen atoms attached to an sp^3-hybridized carbon atom in the *ortho*-position with respect to the imine carbon. In the spectra of compounds **Va–Vc, VIIa–VIIb, VIIIa–VIIIc**, **XIa**, and **XIb** the signal from H^6 is observed in the region δ 4.51–4.87 ppm common for hydrogen atoms attached to an sp^3-hybridized carbon atom in the *ortho*-position relative to the carbonyl carbon. For compounds **IVa–VIa, VIIc, IXa, Xa, XXVIIa–XXIXa, XXXIa,** and **XXXIIa** in order to prove the presence of sp^3-hybridized carbon atoms in the cyclohexene ring we registered ^{13}C NMR spectra.

The experiments performed suggest a conclusion that the governing factor regulating the direction of the halogen addition to 2,5-dialkyl-substituted *para*-quinone monoimines is the steric factor; hence, the main influence is exerted by the size of the halogen atom and the bulk of the substituent in the quinoid ring. At equal size of the substituents at both C=C bond of the quinoid ring the point of the halogen addition is determined by the charge distribution in the quinoid ring: The halogen adds to the less polar C=C bond.

The comparison of halogenation processes of quinone monoimines **Ia–Ic, IIa–IIc, IIIa,** and **IIIb** with those of the corresponding 2,5-dialkyl-1,4-benzoquinone monooximes esters [2] shows that in both cases the principal factor governing the direction of halogen addition is the steric factor.

To compare the halogenation of 2,6(3,5)-dimethyl-substituted N-arylsulfonyl-1,4-benzoquinone monoimines and the corresponding *para*-quinone monooximes esters we carried out the halogenation of *N*-arylsulfonyl-3,5-dimethyl-1,4-benzoquinone monoimines **XXXIIIa** and **XXXIIIb** and N-arylsulfonyl-2,6-dimethyl-1,4-benzoquinone monoimines **XXXIVa** and **XXXIVb**. In contrast to the *para*-quinone oximes esters in the solutions of quinone imines **XXXIVa** and **XXXIVb** due to the lower energy barrier to the nitrogen atom inversion a process of *Z*,*E*-isomerization was observed, and in solutions of quinone imines **XXXIIIa** and **XXXIIIb** occurred degenerate *Z*,*E*-isomerization fast on the NMR time scale [6].

The chlorination of quinone imines **XXXIIIa**, **XXXIIIb**, **XXXIVa**, and **XXXIVb** was performed with gaseous chlorine, the bromination, with molecular bromine in $CHCl_3$, AcOH, DMF–AcOH, 1:5, at various temperatures and different ratios of the initial compound to halogen.

The chlorination of quinone imines **XXXIIIa** and **XXXIIIb** in $CHCl_3$ and AcOH at the molar ratio substrate–halogen from 1:1 to 1:3 gave rise to 4-arylsulfonylimino-3,5-dimethyl-5,6-dichloro-2-cyclohexen-1-ones **XXXVa** and **XXXVb**, the bromination in a mixture DMF–AcOH, 1:5, provided compounds with the similar structure **XXXVIa** and **XXXVIb**. The bromination in $CHCl_3$ and AcOH afforded as the main products 4-arylsulfonylamido-5,6-dibromo-3,5-dimethylphenols **XXXVIIa** and **XXXVIIb** (Scheme 5). Hence, as in the case of halogenation of *N*-arylsulfonyl-3-methyl-1,4-

benzoquinone monoimines [1] the obvious effect of the solvent nature on the bromination process was observed.

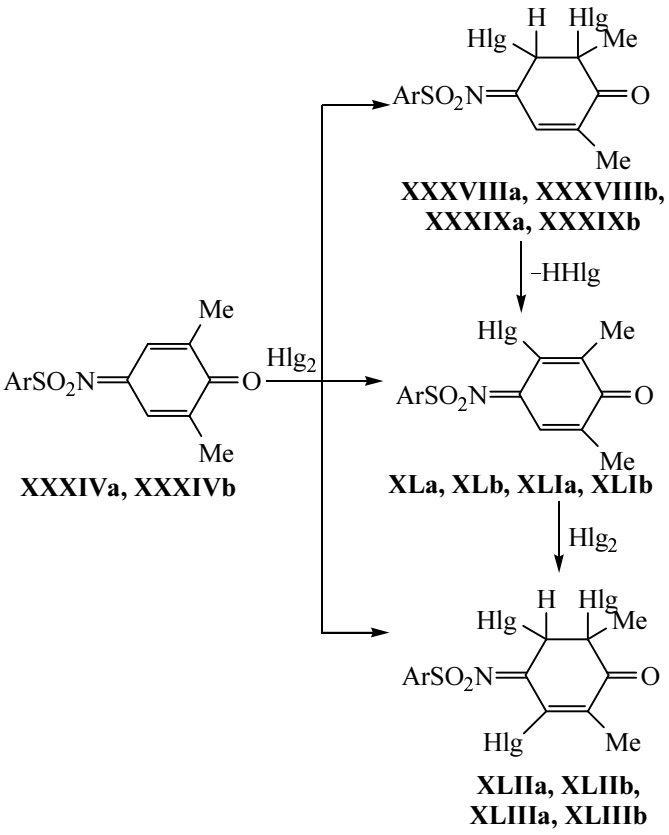
The structure of compounds **XXXVa, XXXVb, XXXVIa**, and **XXXVIb** was established from the ^{1}H and ^{13}C NMR spectra. According to ^{1}H NMR spectra the cyclohexene structures **XXXVa, XXXVb, XXXVIa**, and **XXXVIb** exist in solution in the form of a single isomer, and the chemical shifts of signals from atoms H^2, H^5 and Me groups indicate that the substituent $ArSO_2$ at the nitrogen is turned in the direction of the C=C bond of the quinoid ring in spite of the presence of Me. This fact permits a conclusion that Cl and Me at the sp^3-hybridized C^5 are is a greater steric obstacle for $ArSO_2$ group than Me at sp^2-hybridized carbon atom.

The halogenation of quinone imines **XXXIVa** and **XXXIVb** depending on conditions of the experiment afforded compounds **XXXVIIIa, XXXVIIIb–XLIIIa, XLIIIb** (Scheme 6).

The main halogenation products of quinone imines **XXXIVa** and **XXXIVb** at any ratios substrate–halogen in $CHCl_3$, AcOH, or in the mixture DMF–AcOH, 1:5, were quinone imines **XLa, XLb, XLIa, XLIb**, and 4-arylsulfonylimino-3,5,6-trihalo-2,6-dimethyl-2-cyclohexen-1-ones **XLIIa, XLIIb, XLIIIa**, and **XLIIIb** which resulted from further halogenation of quinone imines **XLa, XLb** and **XLIa, XLIb** respectively.

4-Arylsulfonylimino-5,6-dihalo-2,6-dimethyl-2-cyclohexen-1-ones **XXXVIIIa, XXXVIIIb, XXXIXa**, and **XXXIXb** are very unstable. Chlorine derivatives **XXXVIIIa** and **XXXVIIIb** already in the course of the reaction eliminate an HCl molecule and convert into quinone imines **XLa** and **XLb**. Therefore we failed to isolate individual compounds of cyclohexene structure **XXXVIIIa** and **XXXVIIIb**, they were obtained only in mixture with quinone imines **XLa** and **XLb**. Bromine derivatives **XXXIXa** and **XXXIXb** were isolated as individual substances, but on storage within several days they suffered dehydrobromination and transformed into the corresponding quinone imines **XLIa** and **XLIb**. Compounds **XXXVIIIa, XXXVIIIb, XXXIXa,** and **XXXIXb** as show ^{1}H NMR spectra exist as mixtures of *Z*- and *E*-isomers. The spectrum contains two identical sets of signals. The signal from H^3 atom appears in the spectrum as a quartet, and that of atom H^5, as a doublet. As already mentioned in [1] the occurrence of the *Z,E*-isomerization in solution of cyclohexene structures affects their stability. Similarly to the products of the halogen addition to *N*-arylsulfonyl-2-chloro(methyl)-1,4-benzo-quinone monoimines [1] hemiquinoid compounds **XXXVIIIa, XXXVIIIb,**

Scheme 6.

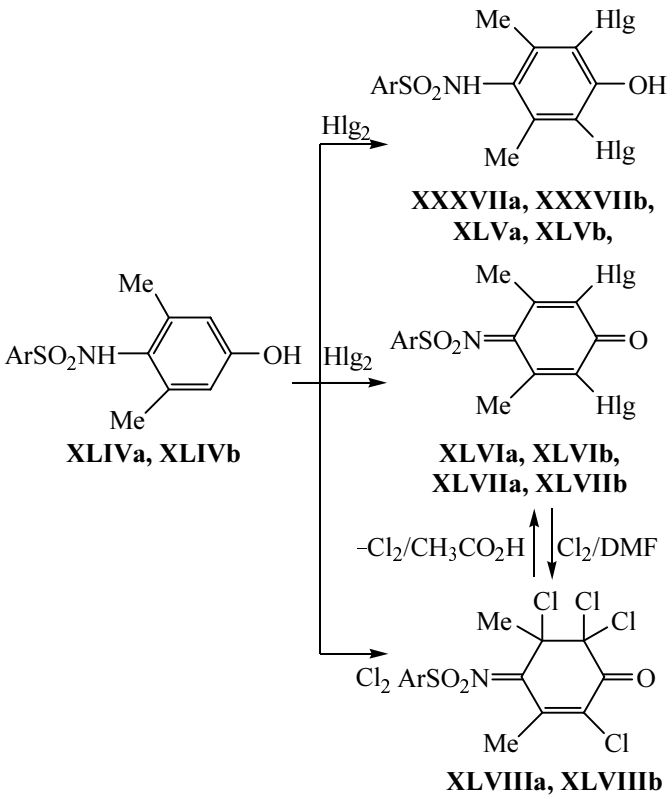


Ar = Ph (**a**), 4-MeC_6H_4 (**b**); Hlg = Cl (**XXXVIII, XL, XLII**), Br (**XXXIX, XLI, XLIII**).

XXXIXa, and **XXXIXb** due to the isomerization can occur into the isomeric form where no steric hindrance exists for the dehydrohalogenation process. Therefore they suffer fast dehydrohalogenation affording quinone imines **XLa, XLb, XLIa,** and **XLIb** which are the main halogenation products obtained from quinone imines **XXXIV**a and **XXXIVb**.

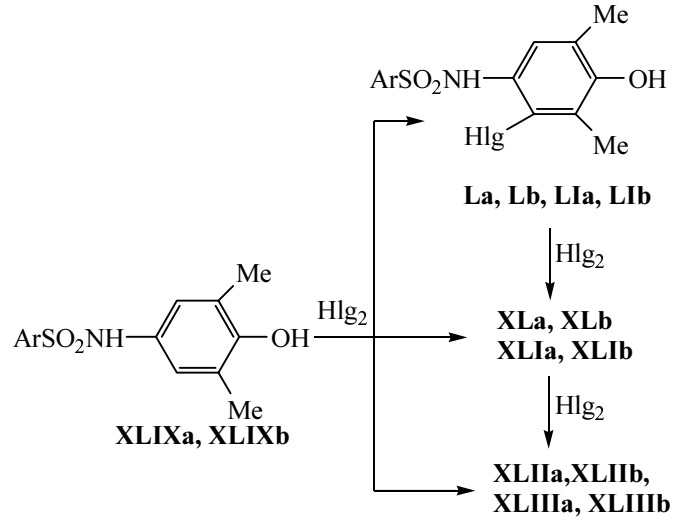
By halogenation of 4-arylsulfonylamido-3,5-dimethylphenols **XLIVa** and **XLIVb** were mainly obtained 4-arylsulfonylamido-2,6-dihalo-3,5-dimethylphenols **XXXVIIa, XXXVIIb, XLVa**, and **XLVb** (Scheme 7). At the halogenation in DMF we isolated *N*-arylsulfonyl-2,6-dihalo-3,5-dimethyl-1,4-benzoquinone monoimines **XLVIa, XLVIb, XLVIIa**, and **XLVIIb**, and at the use of considerable excess of chlorine (ratio substrate–chlorine 1:5) 4-arylsulfonylimino-3,5-dimethyl-2,5,6,6-tetrachloro-2-cyclohexen-1-ones **XLVIIIa** and **XLVIIIb** were obtained. In acetic acid cyclohexene structures **XLVIIIa** and **XLVIIIb** eliminated a Cl_2 molecule and turned into quinone imines **XLVIa** and **XLVIb**.

Scheme 7.



Ar = Ph (**a**), 4-MeC_6H_4 (**b**); Hlg = Cl (**XLV, XLVI**), Br (**XXXVII, XLVII**).

Scheme 8.



Ar = Ph (**a**), 4-MeC_6H_4 (**b**); Hlg = Cl (**L**), Br (**LI**).

The halogenation of 4-arylsulfonylamido-2,6-dimethylphenols **XLIXa** and **XLIXb** depending on the solvent nature gave rise to 4-arylsulfonylamido-3-halo-2,6-dimethylphenols **La** and **Lb**, **LI**a and **LIb** (in chloroform), quinone imines **XLa, XLb, XLIa,** and **XLIb** (in AcOH, in the mixture DMF–AcOH, 1:5), and to hemiquinoid structures **XLIIa, XLIIb, XLIIIa**, and **XLIIIb** (in the mixture DMF–AcOH, 1:5) (Scheme 8).

The analysis of processes occurring in conformity to Schemes 7 and 8 suggests a conclusion that the halogenation of aminophenols **XLIXa** and **XLIXb** proceeds as follows: the initial oxidation–addition of HHlg; further oxidation and addition of Hlg_2. At the same time the halogenation of aminophenols **XLIVa** and **XLIVb** occurs mostly analogously to that of 4-arylsulfonylamido-3-methylphenols [1], namely, predominantly by the mechanism of the electrophilic substitution, but another sequence of reactions is also possible: oxidation with a Hlg_2 molecule followed by the hydrohalogenation.

In the halogenation of *N*-arylsulfonyl-2,6(3,5)-dimethyl-1,4-benzoquinone monoimines **XXXIIIa**, **XXXIIIb**, **XXXIVa**, and **XXXIVb** (Schemes 5 and 6) in the first stage a halogen molecule adds to afford a cyclohexene structures **XXXVa, XXXVb, XXXVIa**, **XXXVIb** and **XXXVIIIa, XXXVIIIb, XXXIXa, XXXIXb**. In the case of 3,5-dimethyl-substituted derivatives the cyclohexene structures **XXXVa, XXXVb, XXXVIa**, **XXXVIb** are stable, in the case of 2,6-dimethyl-substituted compounds structures **XXXVa, XXXVb, XXXVIa**, **XXXVIb** rapidly undergo dehydrohalogenation affording quinone imines **XLa, XLb, XLIa, XLIb**. As in the case of cyclohexene structures generated from *N*-arylsulfonyl-2-methyl-1,4-benzoquinone monoimines [1], the fast dehydrohalogenation in this instance is due to the occurrence of the *Z,E*-isomerization leading to *E*-isomer where the steric hindrance to dehydrohalogenation is lacking. Therefore the different sets of halogenation products obtained from quinone imines **XXXIIIa**, **XXXIIIb** and **XXXIVa**, **XXXIVb** are due to dissimilar stability of the hemiquinoid structures formed after addition of the first halogen molecule. The difference in the halogenation products of quinone imines **XXXIIIa**, **XXXIIIb**, **XXXIVa**, and **XXXIVb** and their reduced forms **XLIVa**, **XLIVb**, **XLIXa** and **XLIXb** can be respectively explained by an assumption that in the halogenation of aminophenols **XLIVa**, **XLIVb**, **XLIXa** and **XLIXb** in the first stage might occur an electrophilic substitution of a hydrogen by a halogen atom or oxidation of the initial aminophenol with a Hlg_2 molecule into quinone imine with its subsequent hydrohalogenation.

The composition and structure of synthesized compounds **XXXIIIa**, **XXXIIIb** – **LIa, LIb** were proved by elemental analysis , IR, ^1H and ^{13}C NMR spectroscopy.

To confirm the structure of compounds **XXXVa**, **XXXVIa, XLIIa, XLIIIa, XLVIIa, XLVIIIa** we registered their ^{13}C NMR spectra.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer UR-20 from samples pelletized with KBr. ^1H and ^{13}C NMR spectra were registered on a spectrometer Varian VXR-300 at operating frequencies 300 and 75.4 MHz respectively relative to TMS from solutions in $CDCl_3$.

Reaction mixtures were analyzed by TLC on Silufol UV-254 plates(eluent benzene–ethyl acetate, 10:1, development under UV irradiation).

Quinone imines Ia–Ic–IIIa–IIIc, XXXIIIa, XXXIIIb, XXXIVa, and XXXIVb, and aminophenols XIIa–XIIc–XIVa–XIVc, XLIVa, XLIVb, XLIXa, XLIXb were obtained by procedures described in [7].

***N*-Phenylsulfonyl-2,5-dimethyl-1,4-benzoquinone monoimine (Ia).** Yield 91%, mp 135–136°C. ^1H NMR spectrum, δ, ppm: 7.96 q (1H, H^3), 6.54 q (1H, H^6), 2.12 d (3H, Me^2), 2.04 d [3H, Me^5, $J(Me^2, H^3)$ 1.5, $J(Me^5, H^6)$ 1.5 Hz], 7.56–8.04 m (5H, Ph). Found, %: N 5.11; 5.15. $C_{14}H_{13}NO_3S$. Calculated, %: N 5.09.

***N*-Tosyl-2,5-dimethyl-1,4-benzoquinone monoimine (Ib).** Yield 85%, mp 116–117°C. ^1H NMR spectrum, δ, ppm: 7.96 q (1H, H^3), 6.54 q (1H, H^6), 2.11 d (3H, Me^2), 2.03 d [3H, Me^5, $J(Me^2, H^3)$ 1.5, $J(Me^5, H^6)$ 1.2 Hz], 7.36–7.91 d.d (4H in Ts), 2.47 s (3H, Me in Ts). Found, %: N 5.00; 4.92. $C_{15}H_{15}NO_3S$. Calculated, %: N 4.84.

***N*-(3-Nitrophenylsulfonyl)-2,5-dimethyl-1,4-benzoquinone monoimine (Ic).** Yield 82%, mp 172–173°C. ^1H NMR spectrum, δ, ppm: 7.88 q (1H, H^3), 6.58 q (1H, H^6), 2.15 d (3H, Me^2), 2.05 d [3H, Me^5, $J(Me^2, H^3)$ 1.2, $J(Me^5, H^6)$ 1.5 Hz], 7.80–8.88 m (4H in Ar). Found, %: N 8.65, 8.72. $C_{14}H_{12}N_2O_5S$. Calculated, %: N 8.75.

***N*-Phenylsulfonyl-6-isopropyl-3-methyl-1,4-benzoquinone monoimine (IIa).** Yield 87%, mp 82–84°C. ^1H NMR spectrum, δ, ppm: 7.87 d (1H, H^5), 6.64 q (1H, H^2), 3.07 m [1H, $(CH)^6$], 2.03 d (3H, Me^3), 1.16 d {6H, Me_2 in *i*-Pr, $J(H^2, Me^3)$ 1.5, $J[H^5, (CH)^6]$ 1.2 Hz}, 7.56–8.07 m (5H, Ph). Found, %: N 4.65, 4.76. $C_{16}H_{17}NO_3S$. Calculated, %: N 4.62.

***N*-Tosyl-6-isopropyl-3-methyl-1,4-benzoquinone monoimine (IIb).** Yield 85%, mp 116–118°C. ^1H NMR spectrum, δ, ppm: 7.89 d (1H, H^5), 6.52 q (1H, H^2), 3.08 m [1H, $(CH)^6$], 2.03 d (3H, Me^3), 1.18 d {6H, Me_2 in *i*-Pr, $J(H^2, Me^3)$ 1.5, $J[H^5, (CH)^6]$ 1.2 Hz}, 7.36–7.92 d.d (4H in Ts), 2.47 s (3H, Me in Ts). Found, %: N 4.35, 4.45. $C_{17}H_{19}NO_3S$. Calculated, %: N 4.41.

***N*-(3-Nitrophenylsulfonyl)-6-isopropyl-3-methyl-1,4-benzoquinone monoimine (IIc).** Yield 81%, mp 106–108°C. ^1H NMR spectrum, δ, ppm: 7.81 d (1H, H^5), 6.57 q (1H, H^2), 3.11 m [1H, $(CH)^6$], 2.04 d (3H, Me^3), 1.20 d {6H, Me_2 in *i*-Pr, $J(H^2, Me^3)$ 1.2, $J[H^5, (CH)^6]$ 1.2 Hz}, 7.80–8.88 m (4H in Ar). Found, %: N 7.95, 8.02. $C_{16}H_{16}N_2O_5S$. Calculated, %: N 8.04.

***N*-Phenylsulfonyl-5-isopropyl-2-methyl-1,4-benzoquinone monoimine (IIIa).** Yield 85%, mp 112–113°C. ^1H NMR spectrum, δ, ppm: 7.98 q (1H, H^3), 6.51 d (1H, H^6), 3.04 m [1H, $(CH)^5$], 2.12 d (3H, Me^2), 1.09 d {6H, Me_2 in *i*-Pr, $J(Me^2, H^3)$ 1.5, $J[(CH)^5, H^6]$ 0.9 Hz}, 7.56–8.03 m (5H, Ph). Found, %: N 4.55, 4.59. $C_{16}H_{17}NO_3S$. Calculated, %: N 4.62.

***N*-Tosyl-5-isopropyl-2-methyl-1,4-benzoquinone monoimine (IIIb).** Yield 82%, mp 121–122°C. ^1H NMR spectrum, δ, ppm: 7.98 q (1H, H^3), 6.50 d (1H, H^6), 3.04 m [1H, $(CH)^5$], 2.12 d (3H, Me^2), 1.08 d {6H, Me_2 in *i*-Pr, $J(Me^2, H^3)$ 1.5, $J[(CH)^5, H^6]$ 0.9 Hz}, 7.37–7.89 d.d (4H in Ts), 2.47 s (3H, Me in Ts). Found, %: N 4.31, 4.42. $C_{17}H_{19}NO_3S$. Calculated, %: N 4.41.

***N*-(3-Nitrophenylsulfonyl)-5-isopropyl-2-methyl-1,4-benzoquinone monoimine (IIIc).** Yield 79%, mp 84–86°C. ^1H NMR spectrum, δ, ppm: 7.89 q (1H, H^3), 6.54 d (1H, H^6), 3.00 m [1H, $(CH)^5$], 2.15 d (3H, Me^2), 1.10 d {6H, $(Me)_2$ in *i*-Pr, $J(Me^2, H^3)$ 1.2, $J[(CH)^5, H^6]$ 0.9 Hz}, 7.83–8.87 m (4H in Ar). Found, %: N 7.89, 7.95. $C_{16}H_{16}N_2O_5S$. Calculated, %: N 8.04.

2,5-Dimethyl-4-phenylsulfonylamidophenol (XIIa). Yield 88%, mp 176–177°C. Found, %: N 4.88, 4.95. $C_{14}H_{15}NO_3S$. Calculated, %: N 5.05.

2,5-Dimethyl-4-tosylamidophenol (XIIb). Yield 83%, mp 172–173°C. Found, %: N 4.68, 4.75. $C_{15}H_{17}NO_3S$. Calculated, %: N 4.81.

2,5-Dimethyl-4-(3-nitrophenylsulfonyl)-amidophenol (XIIc). Yield 78%, mp 155–156°C. Found, %: N 8.48, 8.59. $C_{14}H_{14}N_2O_5S$. Calculated, %: N 8.69.

6-Isopropyl-3-methyl-4-phenylsulfonyl-amidophenol (XIIIa). Yield 91%, mp 200–202°C. Found, %: N 4.45, 4.57. $C_{16}H_{19}NO_3S$. Calculated, %: N 4.59.

6-Isopropyl-3-methyl-4-tosylamidophenol (XIIIb). Yield 87%, mp 200–201°C. Found, %: N 4.32, 4.40. $C_{17}H_{21}NO_3S$. Calculated, %: N 4.38.

6-Isopropyl-3-methyl-4-(3-nitrophenylsulfonyl)-amidophenol (XIIIc). Yield 83%, mp 140–141°C. Found, %: N 7.82, 7.95. $C_{16}H_{18}N_2O_5S$. Calculated, %: N 7.99.

5-Isopropyl-2-methyl-4-phenylsulfonylamidophenol (XIVa). Yield 94%, mp 179–180°C. Found, %: N 4.49, 4.59. $C_{16}H_{19}NO_3S$. Calculated, %: N 4.59.

5-Isopropyl-2-methyl-4-tosylamidophenol (XIVb). Yield 89%, mp 173–174°C. Found, %: N 4.29, 4.35. $C_{17}H_{21}NO_3S$. Calculated, %: N 4.38.

5-Isopropyl-2-methyl-4-(3-nitrophenylsulfonyl)-amidophenol (XIVc). Yield 78%, mp 137–139°C. Found, %: N 7.80, 7.94. $C_{16}H_{18}N_2O_5S$. Calculated, %: N 7.99.

Characteristics of compounds **XXXIIIa, XXXIIIb, XXXIVa, XXXIVb, XLIVa, XLIVb, XLIXa**, and **XLIXb** were reported in [6].

Chlorination of quinone imines Ia–Ic–IIIa–IIIc, XXXIIIa, XXXIIIb, XXXIVa, XXXIVb, and aminophenols XIIa–XIIc–XIVa–XIVc, XLIVa, XLIVb, XLIXa, and XLIXb. Through a solution of 2 mmol of compounds under study in 3 ml of $CHCl_3$, AcOH, DMF or a mixture DMF–AcOH, 1:5, was passed a steam of dry chlorine at a rate 15–20 ml/min at 25–30°C. The ratio initial substance–chlorine was controlled by the weight gain, and it was varied in the range 1:1–1:3. In several hours the reaction products were filtered off. All compounds obtained were recrystallized from acetic acid.

3,6-Dimethyl-4-phenylsulfonylimino-5,6-dichloro-2-cyclohexen-1-one (IVa). Yield 79%, mp 114–115°C. ^{1}H NMR spectrum, δ, ppm: 6.52 q (1H, H^2), 6.24 s (1H, H^5), 2.07 d (3H, Me^3), 1.92 s [3H, Me^6, $J(H^2, Me^3)$ 1.5 Hz], 7.57–8.06 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 187.74 (C^1), 169.08 (C^4), 148.94 (C^5), 132.79 (C^6), 64.53 (C^2), 56.71 (C^3), 22.01 (Me^3), 18.48 (Me^6). Found, %: Cl 20.35, 20.40. $C_{14}H_{13}Cl_2NO_3S$. Calculated, %: Cl 20.48.

3,6-Dimethyl-4-tosylimino-5,6-dichloro-2-cyclohexen-1-one (IVb). Yield 82%, mp 108–109°C. ^{1}H NMR spectrum, δ, ppm: 6.51 q (1H, H^2), 6.26 s (1H, H^5), 2.06 d (3H, Me^3), 1.91 s [3H, Me^6, $J(H^2, Me^3)$ 1.2 Hz], 7.37–7.94 d.d (4H in Ts), 2.47C (3H, Me in Ts). Found, %: Cl 19.68, 19.75. $C_{15}H_{15}Cl_2NO_3S$. Calculated, %: Cl 19.68.

3,6-Dimethyl-4-(3-nitrophenylsulfonyl)imino-5,6-dichloro-2-cyclohexen-1-one (IVc). Yield 75%, mp 136–137°C. ^{1}H NMR spectrum, δ, ppm: 6.57 q (1H, H^2), 6.12 s (1H, H^5), 2.08 d (3H, Me^3), 1.94 s [3H, Me^6, $J(H^2, Me^3)$ 1.2 Hz], 7.81–8.91 m (4H in Ar). Found, %: Cl 18.20, 18.25. $C_{14}H_{12}Cl_2N_2O_5S$. Calculated, %: Cl 18.12.

6-Isopropyl-3-methyl-4-phenylsulfonylimino-5,6-dichloro-2-cyclohexen-1-one (VIa). Yield 65%, mp 120–121°C. ^{1}H NMR spectrum, δ, ppm: 6.59 q (1H, H^2), 6.34 s (1H, H^5), 2.20 m [1H, $(CH)^6$], 2.04 d (3H, Me^3), 0.90–1.33 d.d [6H, Me_2 in *i*-Pr, $J(H^2, Me^3)$ 1.5 Hz], 7.57–8.05 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 189.47 (C^1), 169.44 (C^4), 148.89 (C^3), 133.95 (C^2), 59.04 (C^5), 83.21 (C^6), 36.23 (C, CH in *i*-Pr), 18.75 (Me^3), 18.75 (Me in *i*-Pr), 17.59 (Me in *i*-Pr). Found, %: Cl 18.56, 18.65. $C_{16}H_{17}Cl_2NO_3S$. Calculated, %: Cl 18.94.

6-Isopropyl-3-methyl-4-(3-nitrophenylsulfonyl)imino-5,6-dichloro-2-cyclohexen-1-one (VIc). ^{1}H NMR spectrum, δ, ppm: 6.65 q (1H, H^2), 6.19 s (1H, H^5), 2.20 m [1H, $(CH)^6$], 2.05 d (3H, Me^3), 0.92–1.32 d.d [6H, Me_2 in *i*-Pr, $J(H^2, Me^3)$ 1.2 Hz], 7.81–8.87 m (4H in Ar).

2-Isopropyl-5-methyl-4-phenylsulfonylimino-5,6-dichloro-2-cyclohexen-1-one (VIIa). Yield 78%, mp 98–100°C. ^{1}H NMR spectrum, δ, ppm: 7.82 d (1H, H^3), 4.52 s (1H, H^6), 3.07 m [1H, $(CH)^2$], 1.86 s (3H, Me^5), 1.16–1.25 d.d {6H, Me_2 in *i*-Pr, $J[(CH)^2, H^3]$ 1.2 Hz}, 7.56–8.02 m (5H, Ph). Found, %: Cl 18.80, 18.85. $C_{16}H_{17}Cl_2NO_3S$. Calculated, %: Cl 18.94.

2-Isopropyl-5-methyl-4-tosylimino-5,6-dichloro-2-cyclohexen-1-one (VIIb). Yield 73%, mp 105–106°C. ^{1}H NMR spectrum, δ, ppm: 7.83 d (1H, H^3), 4.51 s (1H, H^6), 3.04 m [1H, $(CH)^2$], 1.85 s (3H, Me^5), 1.15–1.24 d.d {6H, Me_2 in *i*-Pr, $J[(CH)^2, H^3]$ 1.2 Hz}, 7.36–7.90 d.d (4H in Ts), 2.47s (3H, Me in Ts). Found, %: Cl 18.15, 18.20. $C_{17}H_{19}Cl_2NO_3S$. Calculated, %: Cl 18.26.

2-Isopropyl-5-methyl-4-(3-nitrophenylsulfonyl)-imino-5,6-dichloro-2-cyclohexen-1-one (VIIc). Yield 75%, mp 130–131°C. ^{1}H NMR spectrum, δ, ppm: 7.75 d (1H, H^3), 4.55 s (1H, H^6), 3.10 m [1H, $(CH)^2$], 1.86 s (3H, Me^5), 1.18–1.27 d.d {6H, Me_2 in *i*-Pr, $J[(CH)^2, H^3]$ 0.9 Hz}, 7.80–8.87m (4H in Ar). ^{13}C NMR spectrum, δ, ppm: 186.83 (C^1), 170.94 (C^4), 148.27 (C^6), 132.72 (C^5), 68.16 (C^3), 63.27 (C^2), 28.58 (C, CH in *i*-Pr), 24.36 (Me^3), 20.98 (Me in *i*-Pr), 20.31 (Me in *i*-Pr). Found, %: Cl 16.80, 16.85. $C_{16}H_{16}Cl_2N_2O_5S$. Calculated, %: Cl 16.91.

3-Isopropyl-6-methyl-4-phenylsulfonylimino-5,6-dichloro-2-cyclohexen-1-one (IXa). Yield 67%, mp

123–124°C. ^{1}H NMR spectrum, δ, ppm: 6.43 s (1H, H^2), 6.27 s (1H, H^5), 3.03 m [1H, (CH)^3], 1.92 s (3H, Me^6), 1.02–1.13 d.d {6H, Me_2 in *i*-Pr, *J*[H^2, (CH)^3] 0.9 Hz}, 7.57–8.06 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 188.24 (C^1), 168.08 (C^4), 158.22 (C^3), 129.24 (C^2), 64.41 (C^6), 57.27 (C^5), 28.48 (C, CH in *i*-Pr), 22.01 (Me^6), 21.05 (Me in *i*-Pr), 20.38 (Me in *i*-Pr). Found, %: Cl 18.95, 18.98. $C_{16}H_{17}Cl_2NO_3S$. Calculated, %: Cl 18.94.

3-Isopropyl-6-methyl-4-tosylimino-5,6-dichloro-2-cyclohexen-1-one (IXb). Yield 74%, mp 106–107°C. ^{1}H NMR spectrum, δ, ppm: 6.41s (1H, H^2), 6.30s (1H, H^5), 3.01m [1H, (CH)^3], 1.91s (3H, Me^6), 1.02–1.13 d.d {6H, Me_2 in *i*-Pr, *J*[H^2, (CH)^3] 0.9 Hz}, 7.38–7.91 d.d (4H in Ts), 2.47s (3H, Me in Ts). Found, %: Cl 18.35, 18.40. $C_{17}H_{19}Cl_2NO_3S$. Calculated, %: Cl 18.26.

2,5-Dimethyl-4-phenylsulfonylamido-6-chlorophenol (XVa). Yield 83%, mp 204–205°C. Found, %: Cl 11.45, 11.56. $C_{14}H_{14}ClNO_3S$. Calculated, %: Cl 11.37.

2,5-Dimethyl-4-tosylamido-6-chlorophenol (XVb). Yield 86%, mp 170–171°C. Found, %: Cl 10.90, 10.99. $C_{15}H_{16}ClNO_3S$. Calculated, %: Cl 10.88.

2,5-Dimethyl-4-(3-nitrophenylsulfonyl)amido-6-chlorophenol (XVc). Yield 69%, mp 197–198°C. Found, %: Cl 10.00, 10.05. $C_{14}H_{13}ClN_2O_5S$. Calculated, %: Cl 9.94.

6-Isopropyl-3-methyl-4-phenylsulfonylamido-2-chlorophenol (XVIIa). Yield 65%, mp 177–178°C. Found, %: Cl 10.45, 10.56. $C_{16}H_{18}ClNO_3S$. Calculated, %: Cl 10.43.

6-Isopropyl-3-methyl-4-tosylamido-2-chlorophenol (XVIIb). Yield 69%, mp 175–176°C. Found, %: Cl 10.10, 10.15. $C_{17}H_{20}ClNO_3S$. Calculated, %: Cl 10.02.

6-Isopropyl-3-methyl-4-(3-nitrophenylsulfonyl)-amido-2-chlorophenol (XVIIc). Yield 71%, mp 166–167°C. Found, %: Cl 9.30, 9.35. $C_{16}H_{17}ClN_2O_5S$. Calculated, %: Cl 9.21.

5-Isopropyl-2-methyl-4-phenylsulfonylamido-6-chlorophenol (XIXa). Yield 71%, mp 196–197°C. Found, %: Cl 10.49, 10.54. $C_{16}H_{18}ClNO_3S$. Calculated, %: Cl 10.43.

5-Isopropyl-2-methyl-4-tosylamido-6-chlorophenol (XIXb). Yield 68%, mp 174–175°C. Found, %: Cl 10.10, 10.13. $C_{17}H_{20}ClNO_3S$. Calculated, %: Cl 10.02.

***N*-Phenylsulfonyl-2,5-dimethyl-6-chloro-1,4-benzoquinone monoimine (XXIa).** Yield 73%, mp 120–121°C. ^{1}H NMR spectrum, δ, ppm: 8.01 q (1H, H^3), 2.19 d (3H, Me^2), 2.19 s [3H, Me^5, *J*(Me^2, H^3) 1.2 Hz], 7.57–8.04 m (5H, Ph). Found, %: Cl 11.35, 11.40. $C_{14}H_{12}ClNO_3S$. Calculated, %: Cl 11.44.

***N*-Tosyl-2,5-dimethyl-6-chloro-1,4-benzoquinone monoimine (XXIb).** Yield 78%, mp 120–121°C. ^{1}H NMR spectrum, δ, ppm: 8.01 q (1H, H^3), 2.17 d (3H, Me^2), 2.18 s [3H, Me^5, *J*(Me^2, H^3) 1.5 Hz], 7.36–7.91 d.d (4H in Ts), 2.47s (3H, Me in Ts). Found, %: Cl 11.00, 11.10. $C_{15}H_{14}ClNO_3S$. Calculated, %: Cl 10.95.

***N*-(3-Nitrophenylsulfonyl)-2,5-dimethyl-6-chloro-1,4-benzoquinone monoimine (XXIc).** Yield 82%, mp 130–131°C. ^{1}H NMR spectrum, δ, ppm: 7.92 q (1H, H^3), 2.22 d (3H, Me^2), 2.19 s [3H, Me^5, *J*(Me^2, H^3) 1.5 Hz], 7.81–8.87 m (4H in Ar). Found, %: Cl 10.00, 10.10. $C_{14}H_{11}ClN_2O_5S$. Calculated, %: Cl 9.99.

***N*-Phenylsulfonyl-6-isopropyl-3-methyl-2-chloro-1,4-benzoquinone monoimine (XXIIIa).** Yield 80%, mp 120–121°C. ^{1}H NMR spectrum, δ, ppm: 7.94 d (1H, H^5), 3.14 m [1H, (CH)^6], 2.19 s (3H, Me^3), 1.21 d {6H, $(Me)_2$ in *i*-Pr, *J*[H^5, (CH)^6] 1.2 Hz}, 7.56–8.04 m (5H, Ph). Found, %: Cl 10.55, 10.60. $C_{16}H_{16}ClNO_3S$. Calculated, %: Cl 10.49.

***N*-Tosyl-6-isopropyl-3-methyl-2-chloro-1,4-benzoquinone monoimine (XXIIIb).** Yield 75%, mp 151–152°C. ^{1}H NMR spectrum, δ, ppm: 7.96 d (1H, H^5), 3.15 m [1H, (CH)^6], 2.19 s (3H, Me^3), 1.20 d {6H, Me_2 in *i*-Pr, *J*[H^5, (CH)^6] 1.2 Hz}, 7.36–7.91 d.d (4H in Ts), 2.47 s (3H, Me in Ts). Found, %: Cl 10.10, 10.15. $C_{17}H_{18}ClNO_3S$. Calculated, %: Cl 10.08.

***N*-Phenylsulfonyl-5-isopropyl-2-methyl-6-chloro-1,4-benzoquinone monoimine (XXVa).** Yield 76%, mp 105–106°C. ^{1}H NMR spectrum, δ, ppm: 7.97 q (1H, H^3), 3.52 m [1H, (CH)^5], 2.16 d (3H, Me^2), 1.19 d [6H, Me_2 in *i*-Pr, *J*(H^3, Me^2) 1.5 Hz], 7.58–8.02 m (5H, Ph). Found, %: Cl 10.50, 10.56. $C_{16}H_{16}ClNO_3S$. Calculated, %: Cl 10.49.

***N*-Tosyl-5-isopropyl-2-methyl-6-chloro-1,4-benzoquinone monoimine (XXVb).** Yield 69%, mp 138–139°C. ^{1}H, δ, ppm: 7.97 q (1H, H^3), 3.52 m [1H, (CH)^5], 2.16 d (3H, Me^2), 1.19 d [6H, Me_2 in *i*-Pr, *J*(H^3, Me^2) 1.5 Hz], 7.38–7.89 d.d (4H in Ts), 2.48 s (3H, Me in Ts). Found, %: Cl 10.15, 10.19. $C_{17}H_{18}ClNO_3S$. Calculated, %: Cl 10.08.

3,6-Dimethyl-4-phenylsulfonylimino-2,5,6-trichloro-2-cyclohexen-1-one (XXVIIa). Yield 85%, mp 126–127°C. ^{1}H NMR spectrum, δ, ppm: 6.27 s (1H, H^5), 2.23 s (3H, Me^3), 2.00 s (3H, Me^6), 7.58–8.06 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 181.34 (C^1), 167.40 (C^4), 145.19 (C^5), 139.49 (C^6), 64.38 (C^2), 56.59 (C^3),

22.66 (Me^6), 16.71 (Me^3). Found, %: Cl 28.05, 28.09. $C_{14}H_{12}Cl_3NO_3S$. Calculated, %: Cl 27.94.

3,6-Dimethyl-4-tosylimino-2,5,6-trichloro-2-cyclohexen-1-one (XXVIIb). Yield 88%, mp 162–163°C. ^{1}H NMR spectrum, δ, ppm: 6.30 s (1H, H^5), 2.22 s (3H, Me^3), 1.99 s (3H, Me^6), 7.38–7.94 d.d (4H in Ts), 2.48 s (3H, Me in Ts). Found, %: Cl 26.86, 26.90. $C_{15}H_{14}Cl_3NO_3S$. Calculated, %: Cl 26.95.

3,6-Dimethyl-4-(3-nitrophenylsulfonyl)imino-2,5,6-trichloro-2-cyclohexen-1-one (XXVIIc). Yield 93%, mp 128–129°C. ^{1}H NMR spectrum, δ, ppm: 6.16 s (1H, H^5), 2.23 s (3H, Me^3), 2.02 s (3H, Me^6), 7.83–8.90 m (4H in Ar). Found, %: Cl 25.10, 25.15. $C_{14}H_{11}Cl_3N_2O_5S$. Calculated, %: Cl 24.99.

6-Isopropyl-3-methyl-4-phenylsulfonylimino-2,5,6-trichloro-2-cyclohexen-1-one (XXIXa). Yield 65%, mp 144–145°C. ^{1}H NMR spectrum, δ, ppm: 6.36 s (1H, H^5), 2.24 m [1H, (CH)^6], 2.17 s (3H, Me^3), 0.89–1.33 d.d (6H, Me_2 in *i*-Pr), 7.56–8.04 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 183.17 (C^1), 167.54 (C^4), 144.98 (C^3), 141.12 (C^2), 82.96 (C^6), 58.75 (C^5), 36.48 (C, CH in *i*-Pr), 18.89 (Me^3), 17.60 (Me in *i*-Pr), 16.43 (Me in *i*-Pr). Found, %: Cl 26.08, 26.12. $C_{16}H_{16}Cl_3NO_3S$. Calculated, %: Cl 26.02.

6-Isopropyl-3-methyl-4-tosylimino-2,5,6-trichloro-2-cyclohexen-1-one (XXIXb). Yield 67%, mp 137–138°C. ^{1}H NMR spectrum, δ, ppm: 6.38 s (1H, H^5), 2.23 m [1H, (CH)^6], 2.19 s (3H, Me^3), 0.87–1.33 d.d (6H, Me_2 in *i*-Pr), 7.38–7.93 d.d (4H in Ts), 2.48 s (3H, Me in Ts). Found, %: Cl 25.25, 25.29. $C_{17}H_{18}Cl_3NO_3S$. Calculated, %: Cl 25.16.

3-Isopropyl-6-methyl-4-phenylsulfonylimino-2,5,6-trichloro-2-cyclohexen-1-one (XXXIa). Yield 73%, mp 98–100°C. ^{1}H NMR spectrum, δ, ppm: 6.25 s (1H, H^5), 3.47 m [1H, (CH)^3], 1.98 s (3H, Me^6), 1.11–1.22 d.d (6H, Me_2 in *i*-Pr), 7.58–8.02 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 181.65 (C^1), 166.27 (C^4), 152.28 (C^3), 138.04 (C^2), 64.12 (C^6), 57.33 (C^5), 32.06 (C, CH in *i*-Pr), 22.63 (Me^6), 19.78 (Me in *i*-Pr), 18.27 (Me in *i*-Pr). Found, %: Cl 26.10, 26.15. $C_{16}H_{16}Cl_3NO_3S$. Calculated, %: Cl 26.02.

3-Isopropyl-6-methyl-4-tosylimino-2,5,6-trichloro-2-cyclohexen-1-one (XXXIb). Yield 67%, mp 134–135°C. ^{1}H NMR spectrum, δ, ppm: 6.27 s (1H, H^5), 3.47 m [1H, (CH)^3], 1.97 s (3H, Me^6), 1.12–1.22 d.d (6H, Me_2 in *i*-Pr), 7.39–7.91 d.d (4H in Ts), 2.48 s (3H, Me in Ts). Found, %: Cl 25.20, 25.25. $C_{17}H_{18}Cl_3NO_3S$. Calculated, %: Cl 25.16.

3,5-Dimethyl-4-phenylsulfonylimino-5,6-dichloro-2-cyclohexen-1-one (XXXVa). Yield 86%, mp 121–122°C. ^{1}H NMR spectrum, δ, ppm: 6.41 q (1H, H^2), 4.44 d (1H, H^6), 2.61 d (3H, Me^3), 1.78 s [3H, Me^5, *J*(H^2, Me^3) 1.5, *J*(H^2, H^6) 1.2 Hz], 7.55–7.99 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 186.73 (C^1), 170.18 (C^4), 149.03 (C^3), 132.46 (C^2), 62.88 (C^6), 50.92 (C^5), 25.22 (Me^3), 22.50 (Me^5). Found, %: Cl 20.50, 20.53. $C_{14}H_{13}Cl_2NO_3S$. Calculated, %: Cl 20.48.

3,5-Dimethyl-4-tosylimino-5,6-dichloro-2-cyclohexen-1-one (XXXVb). Yield 86%, mp 148–149°C. ^{1}H NMR spectrum, δ, ppm: 6.39 q (1H, H^2), 4.43 d (1H, H^6), 2.60 d (3H, Me^3), 1.78 s [3H, Me^5, *J*(H^2, Me^3) 1.5, *J*(H^2, H^6) 1.5 Hz], 7.36–7.85 d.d (4H in Ts), 2.47 s (3H, Me in Ts). Found, %: Cl 19.75, 19.83. $C_{15}H_{15}Cl_2NO_3S$. Calculated, %: Cl 19.68.

2,6-Dimethyl-4-phenylsulfonylimino-5,6-dichloro-2-cyclohexen-1-one (XXXVIIIa). ^{1}H NMR spectrum, δ, ppm: *Z*-isomer: 7.87 q (1H, H^3), 4.73 d (1H, H^5), 2.18 d (3H, Me^2), 1.89 s [3H, Me^6, *J*(Me^2, H^3) 1.2, *J*(H^3, H^5) 1.5 Hz], 7.56–8.07 m (5H, Ph); *E*-isomer: 6.70 q (1H, H^3), 6.20 d (1H, H^5), 2.10 d (3H, Me^2), 1.94 s [3H, Me^6, *J*(Me^2, H^3) 1.2, *J*(H^3, H^5) 2.1 Hz], 7.56–8.07 m (5H, Ph).

***N*-Phenylsulfonyl-2,6-dimethyl-3-chloro-1,4-benzoquinone monoimine (XLa).** Yield 62%, mp 162–163°C. ^{1}H NMR spectrum, δ, ppm: 8.01 q (1H, H^3), 2.23 s (3H, Me^6), 2.15 d [3H, Me^2, *J*(Me^2, H^3) 1.5 Hz], 7.56–8.07 m (5H, Ph). Found, %: Cl 11.45, 11.56. $C_{14}H_{12}ClNO_3S$. Calculated, %: Cl 11.44.

***N*-Tosyl-2,6-dimethyl-3-chloro-1,4-benzoquinone monoimine (XLb).** Yield 68%, mp 115–117°C. ^{1}H NMR spectrum, δ, ppm: 8.02 q (1H, H^5), 2.22 s (3H, Me^6), 2.15 d [3H, Me^2, *J*(Me^2, H^5) 2.1 Hz], 7.38–7.93 d.d (4H in Ts), 2.47 s (3H, Me in Ts). Found, %: Cl 11.45, 11.56. $C_{15}H_{14}ClNO_3S$. Calculated, %: Cl 10.95.

4-Phenylsulfonylimino-2,6-dimethyl-3,5,6-trichloro-2-cyclohexen-1-one (XLIIa). Yield 93%, mp 152–153°C. ^{1}H NMR spectrum, δ, ppm: 6.29 s (1H, H^5), 2.27 s (3H, Me^2), 1.96 s (3H, Me^6), 7.56–8.07 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 185.97 (C^1), 163.96 (C^4), 142.96 (C^2), 142.05 (C^3), 64.37 (C^6), 56.44 (C^5), 22.41 (Me^2), 15.62 (Me^6). Found, %: Cl 27.96, 28.03. $C_{14}H_{12}Cl_3NO_3S$. Calculated, %: Cl 27.94.

4-Tosylimino-2,6-dimethyl-3,5,6-trichloro-2-cyclohexen-1-one (XLIIb). Yield 88%, mp 115–116°C. ^{1}H NMR spectrum, δ, ppm: 6.31 s (1H, H^5), 2.26 s (3H, Me^2), 1.95 s (3H, Me^6), 7.38–7.94 d.d (4H in Ts), 2.47 s

(3H, Me in Ts). Found, %: Cl 27.05, 27.09. $C_{15}H_{14}Cl_3NO_3S$. Calculated, %: Cl 26.95.

4-Phenylsulfonylamido-3,5-dimethyl-2,6-dichlorophenol (XLVa). Yield 93%, mp 252–253°C. Found, %: Cl 20.53, 20.58. $C_{14}H_{13}Cl_2NO_3S$. Calculated, %: Cl 20.48.

***N*-Phenylsulfonyl-3,5-dimethyl-2,6-dichloro-1,4-benzoquinone monoimine (XLVIa).** Yield 89%, mp 162–163°C. ^{1}H NMR spectrum, δ, ppm: 2.44 C (6H, $Me^{3,5}$), 7.62–8.02 m (5H, Ph). Found, %: Cl 20.63, 20.70. $C_{14}H_{11}Cl_2NO_3S$. Calculated, %: Cl 20.60.

***N*-Tosyl-3,5-dimethyl-2,6-dichloro-1,4-benzoquinone monoimine (XLVIb).** Yield 85%, mp 177–178°C. ^{1}H NMR spectrum, δ, ppm: 2.46 s (6H, Me^3 and Me^5), 7.36–7.86 d.d (4H in Ts), 2.46 s (3H, Me in Ts). Found, %: Cl 19.65, 19.73. $C_{15}H_{13}Cl_2NO_3S$. Calculated, %: Cl 19.79.

4-Phenylsulfonylimino-3,5-dimethyl-2,5,6,6-tetrachloro-2-cyclohexen-1-one (XLVIIIa). Yield 67%, mp 111–113°C. ^{1}H NMR spectrum, δ, ppm: 2.70 s (3H, Me^3), 1.92 s (3H, Me^5), 7.56–7.97 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 175.12 (C^1), 167.91 (C^4), 146.29 (C^3), 136.47 (C^2), 88.51 (C^6), 77.13 (C^5), 22.86 (Me^3), 22.10 (Me^5). Found, %: Cl 34.05, 34.12. $C_{14}H_{11}Cl_4NO_3S$. Calculated, %: Cl 34.16.

4-Tosylimino-3,5-dimethyl-2,5,6,6-tetrachloro-2-cyclohexen-1-one (XLVIIIb). Yield 73%, mp 157–158°C. ^{1}H NMR spectrum, δ, ppm: 2.69 s (3H, Me^3), 1.92 s (3H, Me^5), 7.36–7.83 d.d (4H in Ts), 2.47 s (3H, Me in Ts). Found, %: Cl 33.10, 33.17. $C_{15}H_{13}Cl_4NO_3S$. Calculated, %: Cl 33.04.

4-Phenylsulfonylamido-2,6-dimethyl-3-chlorophenol (La). Yield 62%, mp 205–206°C. Found, %: Cl 11.40, 11.48. $C_{14}H_{14}ClNO_3S$. Calculated, %: Cl 11.37.

2,6-Dimethyl-4-tosylamido-3-chlorophenol (Lb). Yield 68%, mp 154–155°C. Found, %: Cl 10.95, 10.99. $C_{15}H_{16}ClNO_3S$. Calculated, %: Cl 10.88.

Bromination of quinone imines Ia–Ic–IIIa–IIIc, XXXIIIa, XXXIIIb, XXXIVa, XXXIVb, and aminophenols XIIa–XIIc–XIVa–XIVc, XLIVa, XLIVb, XLIXa, and XLIXb. To a solution of 2 mmol of compounds under study in 3 ml of $CHCl_3$, AcOH, DMF or a mixture DMF–AcOH, 1:5, was added dropwise at stirrng a bromine solution in an appropriate solvent to the desired ratio initial compound–bromine (1:1, 1:3, 1:5, 1:8). The reaction products obtained in several hours were filtered off, washed with acetic acid, and recrystallized from acetic acid.

5,6-Dibromo-2,5-dimethyl-4-phenylsulfonylimino-2-cyclohexen-1-one (Va). Yield 67%, mp 142–143°C. ^{1}H NMR spectrum, δ, ppm: 7.88 q (1H, H^3), 4.85 s (1H, H^6), 2.19 d (3H, Me^2), 2.06 s [3H, Me^5, $J(Me^2, H^3)$ 1.5 Hz], 7.56–8.03 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 187.70 (C^1), 169.60 (C^4), 144.61 (C^2), 128.41 (C^3), 60.51 (C^5), 53.53 (C^6), 27.70 (Me^2), 17.09 (Me^5). Found, %: Br 36.84, 36.95. $C_{14}H_{13}Br_2NO_3S$. Calculated, %: Br 36.73.

5,6-Dibromo-2,5-dimethyl-4-tosylimino-2-cyclohexen-1-one (Vb). Yield 70%, mp 123–124°C. ^{1}H NMR spectrum, δ, ppm: 7.89 q (1H, H^3), 4.84 s (1H, H^6), 2.18 d (3H, Me^2), 2.05 s [3H, Me^5, $J(Me^2, H^3)$ 1.5 Hz], 7.36–7.90 d.d (4H in Ts), 2.47s (3H, Me in Ts). Found, %: Br 35.40, 35.47. $C_{15}H_{15}Br_2NO_3S$. Calculated, %: Br 35.58.

5,6-Dibromo-2,5-dimethyl-4-(3-nitrophenylsulfonyl)imino-2-cyclohexen-1-one (Vc). Yield 63%, mp 129–130°C. ^{1}H NMR spectrum, δ, ppm: 7.80 q (1H, H^3), 4.87 s (1H, H^6), 2.22 d (3H, Me^2), 2.06 s [3H, Me^5, $J(Me^2, H^3)$ 1.5 Hz], 7.81–8.87 m (4H in Ar). Found, %: Br 33.35, 33.40. $C_{14}H_{12}Br_2N_2O_5S$. Calculated, %: Br 33.28.

5,6-Dibromo-2-isopropyl-5-methyl-4-phenylsulfonylimino-2-cyclohexen-1-one (VIIIa). Yield 78%, mp 80–82°C. ^{1}H NMR spectrum, δ, ppm: 7.77 d (1H, H^3), 4.83 s (1H, H^6), 3.08 m [1H, $(CH)^2$], 2.06 s (3H, Me^5), 1.17–1.24 d.d {6H, Me_2 in *i*-Pr, $J[(CH)^2, H^3]$ 1.2 Hz}, 7.56–8.02 m (5H, Ph). Found, %: Br 34.58, 34.63. $C_{16}H_{17}Br_2NO_3S$. Calculated, %: Br 34.50.

5,6-Dibromo-2-isopropyl-5-methyl-4-tosylimino-2-cyclohexen-1-one (VIIIb). Yield 67%, mp 127–128°C. ^{1}H NMR spectrum, δ, ppm: 7.79 d (1H, H^3), 4.82 s (1H, H^6), 3.07 m [1H, $(CH)^2$], 2.06 s (3H, Me^5), 1.16-1.23 d.d {6H, Me_2 in *i*-Pr, $J[(CH)^2, H^3]$ 1.2 Hz}, 7.36–7.88 d.d (4H in Ts), 2.46 s (3H, Me in Ts). Found, %: Br 33.40, 33.43. $C_{17}H_{19}Br_2NO_3S$. Calculated, %: Br 33.49.

5,6-Dibromo-2-isopropyl-5-methyl-4-(3-nitrophenylsulfonyl)imino-2-cyclohexen-1-one (VIIIc). Yield 66%, mp 131–132°C. ^{1}H NMR spectrum, δ, ppm: 7.71 d (1H, H^3), 4.85 s (1H, H^6), 3.11 m [1H, $(CH)^2$], 2.06 s (3H, Me^5), 1.20–1.26 d.d {6H, $(Me)_2$ in *i*-Pr, $J[(CH)^2, H^3]$ 0.9 Hz}, 7.80–8.86 m (4H in Ar). Found, %: Br 31.30, 31.38. $C_{16}H_{16}Br_2N_2O_5S$. Calculated, %: Br 31.45.

5,6-Dibromo-3-isopropyl-6-methyl-4-phenylsulfonylimino-2-cyclohexen-1-one (Xa). Yield 69%,

mp 136–137°C. ^{1}H NMR spectrum, δ, ppm: 6.51 s (1H, H^2), 6.38 s (1H, H^5), 3.02 m [1H, $(CH)^3$], 2.11 s (3H, Me^6), 1.02–1.13 d.d {6H, Me_2 in *i*-Pr, *J*[H^2, $(CH)^3$] 0.9 Hz}, 7.57–8.06 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 188.39 (C^1), 167.95 (C^4), 157.95 (C^3), 133.80 (C^2), 56.52 (C^6), 47.91 (C^5), 28.31 (C, CH in *i*-Pr), 24.61 (Me^6), 20.95 (Me in *i*-Pr), 20.30 (Me in *i*-Pr). Found, %: Br 34.60, 34.66. $C_{16}H_{17}Br_2NO_3S$. Calculated, %: Br 34.50.

5,6-Dibromo-3-isopropyl-6-methyl-4-tosylimino-2-cyclohexen-1-one (Xb). ^{1}H NMR spectrum, δ, ppm: 6.54 s (1H, H^2), 6.36 s (1H, H^5), 3.02 m [1H, $(CH)^3$], 2.10 s (3H, Me^6), 1.02–1.13 d.d {6H, Me_2 in *i*-Pr, *J*[H^2, $(CH)^3$] 0.9 Hz}, 7.38–7.91 d.d (4H in Ts), 2.47 C (3H, Me in Ts).

5,6-Dibromo-5-isopropyl-2-methyl-4-phenylsulfonylimino-2-cyclohexen-1-one (XIa). ^{1}H NMR spectrum, δ, ppm: 7.85 q (1H, H^3), 4.85 s (1H, H^6), 2.36 m [1H, $(CH)^5$], 2.15 d (3H, Me^2), 1.01–1.08 d.d [6H, Me_2 in *i*-Pr, *J*(Me^2, H^3) 1.2 Hz], 7.57–8.06 m (5H, Ph).

5,6-Dibromo-5-isopropyl-2-methyl-4-tosylimino-2-cyclohexen-1-one (XIb). ^{1}H NMR spectrum, δ, ppm: 7.86 q (1H, H^3), 4.84 s (1H, H^6), 2.38 m [1H, $(CH)^5$], 2.15 d (3H, Me^2), 1.01–1.08 d.d [6H, Me_2 in *i*-Pr, *J*(Me^2, H^3) 1.2 Hz], 7.38–7.91 d.d (4H in Ts), 2.47 s (3H, Me in Ts).

6-Bromo-2,5-dimethyl-4-phenylsulfonylamidophenol (XVIa). Yield 89%, mp 206–207°C. Found, %: Br 22.35, 22.42. $C_{14}H_{14}BrNO_3S$. Calculated, %: Br 22.43.

6-Bromo-2,5-dimethyl-4-tosylamidophenol (XVIb). Yield 93%, mp 162–163°C. Found, %: Br 21.68, 21.72. $C_{15}H_{16}BrNO_3S$. Calculated, %: Br 21.58.

6-Bromo-2,5-dimethyl-4-(3-nitrophenylsulfonyl)-amidophenol (XVIc). Yield 89%, mp 172–173°C. Found, %: Br 19.80, 19.89. $C_{14}H_{13}BrN_2O_5S$. Calculated, %: Br 19.91.

2-Bromo-6-isopropyl-3-methyl-4-phenylsulfonyl-amidophenol (XVIIIa). Yield 91%, mp 156–157°C. Found, %: Br 20.65, 20.70. $C_{16}H_{18}BrNO_3S$. Calculated, %: Br 20.79.

2-Bromo-6-isopropyl-3-methyl-4-tosylamidophenol (XVIIIb). Yield 88%, mp 165–166°C. Found, %: Br 19.85, 19.95. $C_{17}H_{20}BrNO_3S$. Calculated, %: Br 20.06.

6-Bromo-5-isopropyl-2-methyl-4-phenylsulfonyl-amidophenol (XXa). Yield 85%, mp 198–199°C. Found, %: Br 20.75, 20.82. $C_{16}H_{18}BrNO_3S$. Calculated, %: Br 20.79.

6-Bromo-5-isopropyl-2-methyl-4-tosylamidophenol (XXb). Yield 87%, mp 178–179°C. Found, %: Br 20.10, 20.15. $C_{17}H_{20}BrNO_3S$. Calculated, %: Br 20.06.

6-Bromo-5-isopropyl-2-methyl-4-(3-nitrophenylsulfonyl)amidophenol (XXc). Yield 78%, mp 145–146°C. Found, %: Br 18.55, 18.60. $C_{16}H_{17}BrN_2O_5S$. Calculated, %: Br 18.61.

***N*-Phenylsulfonyl-6-bromo-2,5-dimethyl-1,4-benzoquinone monoimine (XXIIa).** Yield 76%, mp 156–157°C. ^{1}H NMR spectrum, δ, ppm: 8.00 q (1H, H^3), 2.24 s (3H, Me^5), 2.19 d [3H, Me^2, *J*(Me^2, H^3) 1.5 Hz], 7.57–8.03 m (5H, Ph). Found, %: Br 22.48, 22.58. $C_{14}H_{12}BrNO_3S$. Calculated, %: Br 22.56.

***N*-Tosyl-6-bromo-2,5-dimethyl-1,4-benzoquinone monoimine (XXIIb).** Yield 81%, mp 133–134°C. ^{1}H NMR spectrum, δ, ppm: 8.01 q (1H, H^3), 2.23 s (3H, Me^5), 2.19 d [3H, Me^2, *J*(Me^2, H^3) 1.5 Hz], 7.37–7.91 d.d (4H in Ts), 2.47 s (3H, Me in Ts). Found, %: Br 21.60, 21.67. $C_{15}H_{14}BrNO_3S$. Calculated, %: Br 21.70.

***N*-(3-Nitrophenylsulfonyl)-6-bromo-2,5-dimethyl-1,4-benzoquinone monoimine (XXIIc).** Yield 72%, mp 155–156°C. ^{1}H NMR spectrum, δ, ppm: 7.91 q (1H, H^3), 2.23 s (3H, Me^5), 2.22 d [3H, Me^2, *J*(Me^2, H^3) 1.5 Hz], 7.81–8.87 m (4H in Ar). Found, %: Br 20.09, 20.16. $C_{14}H_{11}BrN_2O_5S$. Calculated, %: Br 20.01.

***N*-Phenylsulfonyl-2-bromo-6-isopropyl-3-methyl-1,4-benzoquinone monoimine (XXIVa).** Yield 74%, mp 132–133°C. ^{1}H NMR spectrum, δ, ppm: 7.93 d (1H, H^5), 3.15 m [1H, $(CH)^6$], 2.24 s (3H, Me^3), 1.20 d {6H, Me_2 in *i*-Pr, *J*[H^5, $(CH)^6$] 1.2 Hz}, 7.57–8.03 m (5H, Ph). Found, %: Br 20.96, 20.99. $C_{16}H_{16}BrNO_3S$. Calculated, %: Br 20.90.

***N*-Tosyl-2-bromo-6-isopropyl-3-methyl-1,4-benzoquinone monoimine (XXIVb).** Yield 71%, mp 146–147°C. ^{1}H NMR spectrum, δ, ppm: 7.94 d (1H, H^5), 3.14 m [1H, $(CH)^6$], 2.23 s (3H, Me^3), 1.20 d {6H, Me_2 in *i*-Pr, *J*[H^5, $(CH)^6$] 1.2 Hz}, 7.38–7.89 d.d (4H in Ts), 2.47 s (3H, Me in Ts). Found, %: Br 20.26, 20.30. $C_{17}H_{18}BrNO_3S$. Calculated, %: Br 20.16.

***N*-(3-Nitrophenylsulfonyl)-2-bromo-6-isopropyl-3-methyl-1,4-benzoquinone monoimine (XXIVc).** Yield 77%, mp 106–108°C. Found, %: Br 18.74, 18.77. $C_{16}H_{15}BrN_2O_5S$. Calculated, %: Br 18.70.

***N*-Phenylsulfonyl-6-bromo-5-isopropyl-2-methyl-1,4-benzoquinone monoimine (XXVIa).** Yield 82%,

mp 114–115°C. ^{1}H NMR spectrum, δ, ppm: 7.95 q (1H, H^3), 3.53 m [1H, $(CH)^5$], 2.17 d (3H, Me^2), 1.18 d [6H, Me_2 in *i*-Pr, $J(H^3, Me^2)$ 1.5 Hz], 7.58–8.02 m (5H, Ph). Found, %: Br 20.80, 20.88. $C_{16}H_{16}BrNO_3S$. Calculated, %: Br 20.90.

***N*-Tosyl-6-bromo-5-isopropyl-2-methyl-1,4-benzoquinone monoimine (XXVIb).** Yield 86%, mp 123–124°C. Found, %: Br 20.10, 20.17. $C_{17}H_{18}BrNO_3S$. Calculated, %: Br 20.16.

***N*-(3-Nitrophenylsulfonyl)-6-bromo-5-isopropyl-2-methyl-1,4-benzoquinone monoimine (XXVIc).** Yield 80%, mp 124–125°C. Found, %: Br 18.65, 18.70. $C_{16}H_{15}BrN_2O_5S$. Calculated, %: Br 18.70.

2,5,6-Tribromo-3,6-dimethyl-4-phenylsulfonylimino-2-cyclohexen-1-one (XXVIIIa). Yield 78%, mp 155–156°C. ^{1}H NMR spectrum, δ, ppm: 6.48 s (1H, H^5), 2.28 s (3H, Me^3), 2.19 s (3H, Me^6), 7.58–8.06 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 181.51 (C^1), 167.08 (C^4), 148.23 (C^5), 133.95 (C^6), 55.58 (C^2), 46.59 (C^3), 25.48 (Me^3), 20.12 (Me^6). Found, %: Br 46.40, 46.45. $C_{14}H_{12}Br_3NO_3S$. Calculated, %: Br 46.63.

2,5,6-Tribromo-3,6-dimethyl-4-tosylimino-2-cyclohexen-1-one (XXVIIIb). Yield 84%, mp 152–153°C. ^{1}H NMR spectrum, δ, ppm: 6.50 s (1H, H^5), 2.28 s (3H, Me^3), 2.18 s (3H, Me^6), 7.37–7.94 d.d (4H in Ts), 2.48 s (3H, Me in Ts). Found, %: Br 45.15, 45.20. $C_{15}H_{14}Br_3NO_3S$. Calculated, %: Br 45.39.

2,5,6-Tribromo-3,6-dimethyl-4-(3-nitrophenylsulfonyl)imino-2-cyclohexen-1-one (XXVIIIc). Yield 80%, mp 142–143°C. ^{1}H NMR spectrum, δ, ppm: 6.35 s (1H, H^5), 2.28 s (3H, Me^3), 2.21 s (3H, Me^6), 7.82–8.91 m (4H in Ar). Found, %: Br 43.05, 43.12. $C_{14}H_{11}Br_3N_2O_5S$. Calculated, %: Br 42.88.

2,5,6-Tribromo-6-isopropyl-3-methyl-4-(3-nitrophenylsulfonyl)imino-2-cyclohexen-1-one (XXXs). Yield 68%, mp 110–111°C. ^{1}H NMR spectrum, δ, ppm: 6.43 s (1H, H^5), 2.49 m [1H, $(CH)^6$], 2.25 s (3H, Me^3), 1.14–1.30 d.d (6H, Me_2 in *i*-Pr), 7.81–8.89 m (4H in Ar). Found, %: Br 40.56, 40.68. $C_{16}H_{15}Br_3N_2O_5S$. Calculated, %: Br 40.83.

2,5,6-Tribromo-3-isopropyl-6-methyl-4-phenylsulfonylimino-2-cyclohexen-1-one (XXXIIa). Yield 71%, mp 116–117°C. ^{1}H NMR spectrum, δ, ppm: 6.44 s (1H, H^5), 3.49 m [1H, $(CH)^3$], 2.17 s (3H, Me^6), 1.10–1.21 d.d (6H, Me_2 in *i*-Pr), 7.58–8.02 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 181.81 (C^1), 165.51 (C^4), 155.11 (C^3), 133.90 (C^2), 55.55 (C^6), 47.77 (C^5), 35.90 (C, CH in *i*-Pr), 25.47 (Me^6), 19.96 (Me in *i*-Pr), 18.16 (Me in *i*-Pr). Found, %: Br 44.10, 44.20. $C_{16}H_{16}Br_3NO_3S$. Calculated, %: Br 44.22.

2,5,6-Tribromo-3-isopropyl-6-methyl-4-tosylimino-2-cyclohexen-1-one (XXXIIb). Yield 73%, mp 127–128°C. ^{1}H NMR spectrum, δ, ppm: 6.46 s (1H, H^5), 3.49 m [1H, $(CH)^3$], 2.16 s (3H, Me^6), 1.11–1.22 d.d (6H, Me_2 in *i*-Pr), 7.39–7.91 d.d (4H in Ts), 2.48 s (3H, Me in Ts). Found, %: Br 43.15, 43.20. $C_{17}H_{18}Br_3NO_3S$. Calculated, %: Br 43.10.

5,6-Dibromo-3,5-dimethyl-4-phenylsulfonylimino-2-cyclohexen-1-one (XXXVIa). Yield 86%, mp 152–153°C. ^{1}H NMR spectrum, δ, ppm: 6.35 q (1H, H^2), 4.74 d (1H, H^6), 2.58 d (3H, Me^3), 2.00 s [3H, Me^5, $J(H^2, Me^3)$ 1.5, $J(H^2, H^6)$ 1.5 Hz], 7.56–8.01 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 186.92 (C^1), 170.41 (C^4), 148.66 (C^2), 132.18 (C^3), 62.62 (C^5), 53.89 (C^6), 28.34 (Me^3), 22.51 (Me^5). Found, %: Br 36.90, 36.98. $C_{14}H_{13}Br_2NO_3S$. Calculated, %: Br 36.73.

5,6-Dibromo-3,5-dimethyl-4-tosylimino-2-cyclohexen-1-one (XXXVIb). Yield 79%, mp 140–141°C. ^{1}H NMR spectrum, δ, ppm: 6.34 q (1H, H^2), 4.73 d (1H, H^6), 2.57 d (3H, Me^3), 2.00 s [3H, Me^5, $J(H^2, Me^3)$ 1.2, $J(H^2, H^6)$ 1.5 Hz], 7.36–7.86 d.d (4H in Ts), 2.46 s (3H, Me in Ts). Found, %: Br 35.68, 35.76. $C_{15}H_{15}Br_2NO_3S$. Calculated, %: Br 35.58.

4-Phenylsulfonylamido-2,6-dibromo-3,5-dimethylphenol (XXXVIIa). Yield 92%, mp 260–262°C. Found, %: Br 36.86, 36.95. $C_{14}H_{13}Br_2NO_3S$. Calculated, %: Br 36.73.

5,6-Dibromo-2,6-dimethyl-4-phenylsulfonylimino-2-cyclohexen-1-one (XXXIXa). ^{1}H NMR spectrum, δ, ppm: *Z*-isomer: 7.82 q (1H, H^3), 5.02 d (1H, H^5), 2.18 d (3H, Me^2), 2.09 s [3H, Me^6, $J(Me^2, H^3)$ 1.5, $J(H^3, H^5)$ 1.5 Hz], 7.56–8.07 m (5H, Ph); *E*-isomer: 6.64 q (1H, H^3), 6.45 d (1H, H^5), 2.13 s (3H, Me^6), 2.11 d [3H, Me^2, $J(Me^2, H^3)$ 1.2, $J(H^3, H^5)$ 2.4 Hz], 7.56–8.07 m (5H, Ph).

***N*-Phenylsulfonyl-5-bromo-2,6-dimethyl-1,4-benzoquinone monoimine (XLIa).** Yield 74%, mp 165–166°C. ^{1}H NMR spectrum, δ, ppm: 8.05 q (1H, H^3), 2.27 s (3H, Me^6), 2.15 d [3H, Me^2, $J(Me^2, H^3)$ 1.5 Hz], 7.56–8.07 m (5H, Ph). Found, %: Br 22.78, 22.85. $C_{14}H_{12}BrNO_3S$. Calculated, %: Br 22.56.

***N*-Tosyl-5-bromo-2,6-dimethyl-1,4-benzoquinone monoimine (XLIb).** Yield 69%, mp 146–147°C. ^{1}H NMR spectrum, δ, ppm: 8.06 q (1H, H^3), 2.27 s (3H, Me^6), 2.15 d [3H, Me^2, $J(Me^2, H^3)$ 1.8 Hz], 7.37–7.93 d.d (4H in Ts), 2.47 s (3H, Me in Ts). Found, %: Br 21.85, 21.92. $C_{15}H_{14}BrNO_3S$. Calculated, %: Br 21.70.

3,5,6-Tribromo-2,6-dimethyl-4-phenylsulfonylimino-2-cyclohexen-1-one (XLIIIa). Yield 84%, mp 150–151°C. ^{1}H NMR spectrum, δ, ppm: 6.52 s (1H, H^5), 2.33 s (3H, Me^2), 2.15 s (3H, Me^6), 7.56–8.07 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 185.26 (C^1), 164.67 (C^4), 145.86 (C^2), 136.46 (C^3), 56.05 (C^6), 46.20 (C^5), 24.98 (Me^2), 24.55 (Me^6). Found, %: Br 46.75, 46.86. $C_{14}H_{12}Br_3NO_3S$. Calculated, %: Br 46.63.

3,5,6-Tribromo-2,6-dimethyl-4-tosylimino-2-cyclohexen-1-one (XLIIIb). ^{1}H NMR spectrum, δ, ppm: 6.55 s (1H, H^5), 2.32 s (3H, Me^2), 2.14 s (3H, Me^6), 7.38–7.96 d.d (4H in Ts), 2.47 s (3H, Me in Ts).

***N*-Phenylsulfonyl-2,6-dibromo-3,5-dimethyl-1,4-benzoquinone monoimine (XLVIIa).** Yield 78%, mp 144–145°C. ^{1}H NMR spectrum, δ, ppm: 2.50 s (6H, Me^3 and Me^5), 7.56–8.00 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 171.54 (C^1), 162.07 (C^4), 147.59 (C^{3,5}), 132.86 (C^{2,6}), 21.93 (Me^3 and Me^5). Found, %: Br 36.72, 36.85. $C_{14}H_{11}Br_2NO_3S$. Calculated, %: Br 36.90.

***N*-Tosyl-2,6-dibromo-3,5-dimethyl-1,4-benzoquinone monoimine (XLVIIb).** Yield 72%, mp 200–201°C. ^{1}H NMR spectrum, δ, ppm: 2.50 s (6H, Me^3 and Me^5), 7.35–7.85 d.d (4H in Ts), 2.46 s (3H, Me in Ts). Found, %: Br 35.50, 35.62. $C_{15}H_{13}Br_2NO_3S$. Calculated, %: Br 35.74.

3-Bromo-2,6-dimethyl-4-phenylsulfonylamidophenol (LIa). Yield 61%, mp 210–211°C. Found, %: Br 22.20, 22.35. $C_{14}H_{14}BrNO_3S$. Calculated, %: Br 22.43.

3-Bromo-2,6-dimethyl-4-tosylamidophenol (LIb). Yield 65%, mp 154–155°C. Found, %: Br 21.69, 21.78. $C_{15}H_{16}BrNO_3S$. Calculated, %: Br 21.58.

Hydrochlorination of *N*-arylsulfonyl-2,5-dialkyl-1,4-benzoquinone imines Ia–Ic–IIIa–IIIc. Through a solution of 0.01 mol of quinone imines **Ia–Ic–IIIa–IIIc** in 5 ml of dry chloroform was passed a flow of dry gaseous hydrogen chloride for 15–20 min. The color of the reaction mixture got lighter, a colorless precipitate formed that was filtered off and recrystallized from acetic acid. Thus were obtained compounds **XVa–XVc, XVIIa–XVIIc, XIXa**, and **XIXb** identical to the corresponding chlorination products. Their oxidation with lead tetraacetate by procedure [8] afforded quinone imines **XXIa–XXIc, XXIIIa, XXIIIb, XXVa**, and **XXVb** identical to the corresponding chlorination products.

Hydrobromination of *N*-arylsulfonyl-2,5-dialkyl-1,4-benzoquinone iminoin Ia–Ic–IIIa–IIIc. To a solution of 0.01 mol of quinone imines **Ia–Ic–IIIa–IIIc** in 10 ml of acetic acids was added by portions while stirring 2 ml of 46% hydrobromic acid. The color of the reaction mixture got lighter. On adding water a colorless compound precipitated, it was filtered off and recrystallized from acetic acid. Thus were obtained compounds **XVIa–XVIb, XVIIIa, XVIIIb**, and **XXa–XXc** identical to the corresponding bromination products. Their oxidation with lead tetraacetate by procedure [8] afforded quinone imines **XXIIa–XXIc**, **XXIVa, XXIVb**, and **XXVIa–XXVIc** identical to the corresponding bromination products.

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