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Halogenation of N-Substituted *p*-Quinone Imines and *p*-Quinone Oxime Esters: IV.* Chlorination and Bromination of *N*-Arylsulfonyl-2(3)-methyl(2-chloro)-1,4-benzoquinone Monoimines

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Abstract—The addition of halogens to *N*-arylsulfonyl-1,4-benzoquinone imines, which exist in a solution as *Z* and *E* isomers, is controlled by the steric factor. *Z*–*E* Isomerization strongly affects the stability of cyclohexene structures formed by halogenation of 1,4-benzoquinone imines. The halogenation of *N*-arylsulfonyl-1,4-benzoquinone imines was found to be accompanied by prototropic rearrangement.

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In the preceding communication [1] we have formulated general relations holding in reactions of *p*-benzoquinone oxime esters with halogens. *p*-Benzoquinone oxime esters possess a quinoid ring whose structure is similar to that in quinone imines. Like *p*-benzoquinone oxime esters, *N*-arylsulfonyl-1,4-benzoquinone imines having no substituent in the *ortho* position with respect to the imino group in solution exist as two isomers, *Z* and *E*. However, quinone monoimines are characterized by a lower barrier to inversion of the nitrogen atom; therefore, they readily undergo *Z*–*E* isomerization in solution [2]. Unlike *p*-benzoquinone oxime esters, *p*-quinone imines together with the corresponding aminophenols constitute a reversible redox system, which inevitably affects the halogenation process.

Halogenation of *N*-arylsulfonyl-1,4-benzoquinone monoimines having no substituents in the quinoid ring was studied in detail [3–11]; however, some problems still remain unresolved. For example, the mechanism of formation of chlorinated *N*-arylsulfonyl-1,4-benzoquinone monoimines containing one, two, or three chlorine atoms in the quinoid ring is not clear. *N*-Arylsulfonyl-1,4-benzoquinone monoimines with alkyl groups in the quinoid ring were not studied at all.

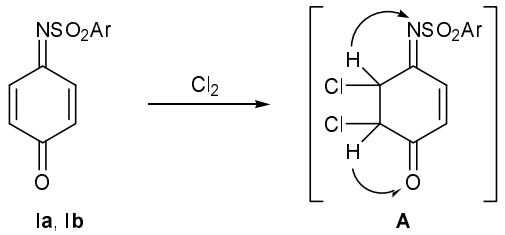
In order to elucidate general relations holding in reactions of *N*-arylsulfonyl-1,4-benzoquinone monoimines with halogens and compare the behaviors of *p*-benzoquinone oxime esters and the corresponding *p*-benzoquinone imines in these reactions, in the present work we examined halogenation of *N*-arylsulfonyl-2(3)-methyl(2-chloro)-1,4-benzoquinone monoimines. We previously believed [4, 5, 10] that halogenation of *N*-arylsulfonyl-1,4-benzoquinone imines **I** having no substituents in the quinoid ring involves initial addition of halogen molecule at the quinoid C=C bond, followed by dehydrohalogenation, addition of the second halogen molecule, dehydrohalogenation, etc. The bromination gave products of addition of one bromine molecule to the initial *p*-quinone imines, 4-arylsulfonylimino-5,6-dibromocyclohex-2-en-1-ones [6], while processes occurring in the initial chlorination stage, i.e., at a substrate-to-chlorine ratio of 1:1 or 1:2, were not studied. No rearrangements during the halogenation process were considered [10]. Therefore, we examined chlorination of compounds **I** with 1, 2, and 3 equiv of chlorine. The chlorination of quinone imines **Ia** and **Ib** was performed using gaseous chlorine in different solvents: chloroform, acetic acid, and a mixture of dimethylformamide with acetic acid at a ratio of 1:5.

We found that treatment of *N*-arylsulfonyl-1,4-benzoquinone imines **Ia** and **Ib** with 2 and 3 equiv of chlorine in all the above solvents afforded *N*-arylsulfonyl-2,3,6-trichloro-4-aminophenols **IIa** and **IIb** as

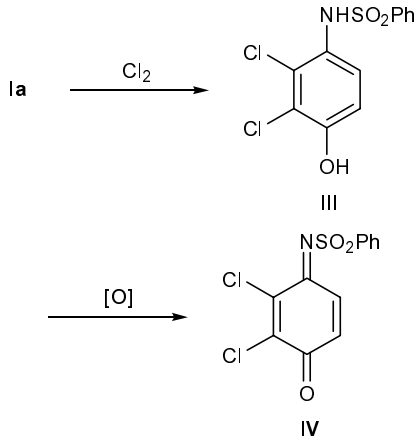
* For communication III, see [1].

the major products. At an equimolar ratio of the reactants, oily mixtures of products were obtained in most cases, and we failed to isolate individual compounds from these mixtures (e.g., as in the chlorination of **Ib**). In the reaction of quinone imine **Ia** with an equimolar amount of chlorine in acetic acid, we succeeded in isolating 2,3-dichloro-4-phenylsulfonylaminophenol (**III**) having two chlorine atoms in positions *2* and *3* of the quinoid ring (Scheme 1). Compound **III** was oxidized to 2,3-dichloro-4-phenylsulfonyliminocyclohexa-2,5-dienone (**IV**) with lead tetraacetate, and the structure of **IV** was established on the basis of its ^{1}H NMR spectrum and analytical data. The 5-H and 6-H signals in the ^{1}H NMR spectrum of **IV** appeared as two doublets with a characteristic *ortho*-coupling constant $^2J_{HH}$ of 10.4 Hz.

Scheme 1.



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

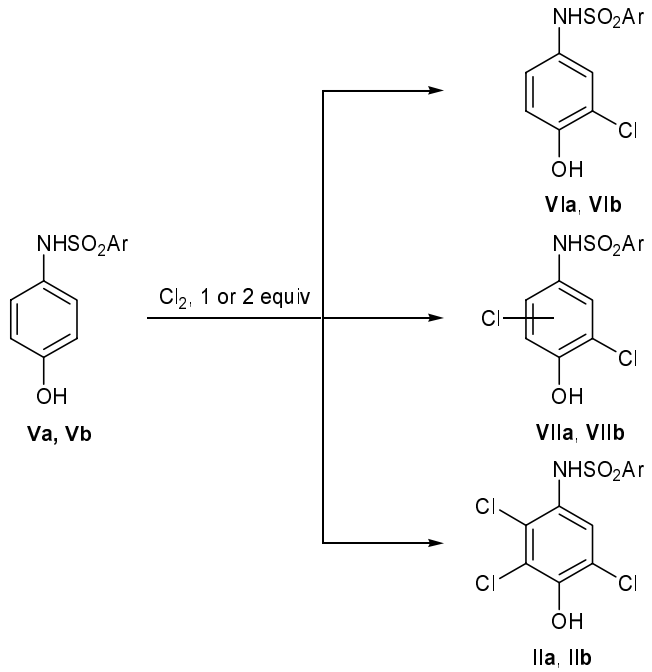


The formation of aminophenol **III** is possible only as follows. Addition of one chlorine molecule gives rise to cyclohexene (semiquinoid) intermediate **A** which undergoes prototropic rearrangement as shown in Scheme 1. Successive addition of chlorine, elimination of hydrogen chloride, and addition of HCl could not lead to formation of aminophenol **III**, for the product of this reaction sequence would contain chlorine atoms in positions *2* and *6*. The possibility for such rearrangement to occur in the halogenation of *N*-(*N*-arylsulfonylimidoyl)-1,4-benzoquinone monoimines was noted in [12]. An intermediate stage in the synthesis of polyhalogenated *N*-(*N*-arylsulfonylimidoyl)-1,4-benzoquinone monoimines is addition of halogen molecule at the unsubstituted C=C bond of the quinoid ring containing one halogen atom; the adduct thus formed is structurally related to intermediate **A**. It was isolated in the chlorination of *N*-(*N*-arylsulfonylimidoyl)-2-chloro-1,4-benzoquinone monoimines, but its spectral parameters were not determined because of fast prototropic rearrangement into the corresponding 4-amino-2,3,6-trichlorophenol [12].

Halogenation of *N*-arylsulfonyl-4-aminophenols **Va** and **Vb** with 1 or 2 equiv of chlorine led to formation of mixtures of products which were difficult to identify. We only found that these mixtures contained aminophenols having one (**VIa**, **VIb**), two (**VIIa**, **VIIb**), and three chlorine atoms (**IIa**, **IIb**) (Scheme 2). The position of chlorine atoms in aminophenols **VIIa** and **VIIb** was not determined, for the ^{1}H NMR spectra of the resulting mixtures were very difficult to interpret.

With a view to elucidate the chlorination patterns of quinone imines **I** and aminophenols **V** we performed chlorination of *N*-arylsulfonyl-2-chloro-1,4-benzoquinone monoimines **VIIIa** (Ar = Ph) and **VIIIb** (Ar = 4-MeC_6H_4) and *N*-arylsulfonyl-2-chloro-4-aminophenols **VIa** and **VIb** using 1, 2, and 3 equiv of

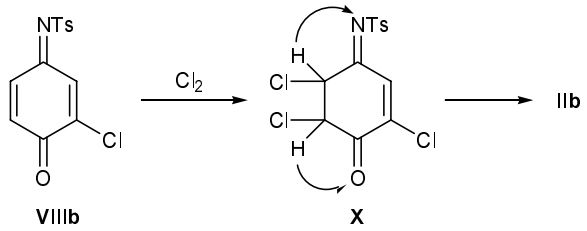
Scheme 2.



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

chlorine in different solvents ($CHCl_3$, AcOH, and 1:5 DMF–AcOH mixture). As in our previous studies [5, 10], the major chlorination products obtained from quinone imines **VIII** and aminophenols **VI** were *N*-arylsulfonyl-2,3,5-trichloro-4-aminophenols **IIa** and **IIb** and *N*-arylsulfonyl-2,3,5-trichloro-1,4-benzoquinone imines **IXa** and **IXb**. When the substrate-to-chlorine ratio was 1:1, a small amount of one more compound was detected in the product mixtures obtained in almost all experiments. We succeeded in isolating this compound in the chlorination of 2-chloro-*N*-*p*-tolylsulfonyl-1,4-benzoquinone imine (**VIIIb**) with 1 equiv of chlorine in acetic acid. It was identified as 2,5,6-trichloro-4-*p*-tolylsulfonyliminocyclohex-2-en-1-one (**X**). According to the ^{1}H NMR data, compound **X** in solution exists as a mixture of *Z* and *E* isomers (two similar sets of signals were observed in the spectrum). The 5-H and 6-H signals appeared as two doublets with a coupling constant J_{HH} of 3 Hz, which is typical of protons attached to two adjacent sp^3-hybridized carbon atoms. The 6-H signal of both isomers was located at δ 4.72–4.74 ppm, i.e., in the region typical of protons in the α-position with respect to carbonyl carbon atom. Compound **X** is unstable; it was converted into 2,5,6-trichloro-4-*p*-tolylsulfonylaminophenol (**IIb**) on storage for several weeks (Scheme 3). These findings may be regarded as a direct proof for the occurrence of prototropic rearrangement in the initial stage of chlorination of *p*-benzoquinone monoimines.

Scheme 3.



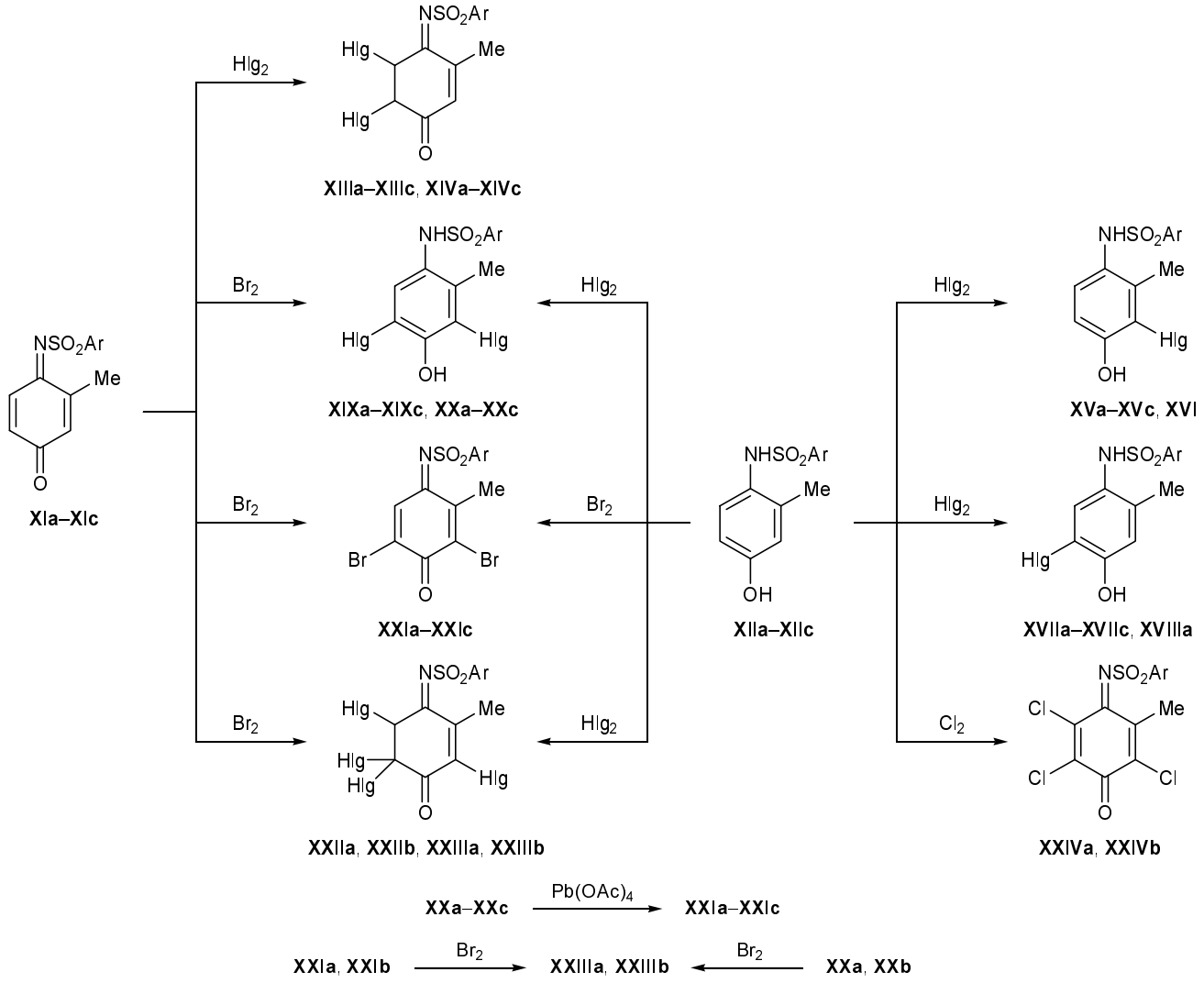
Thus the results of chlorination of quinone imines **I** and **VIII** and aminophenols **V** and **VI** showed that the process involves addition of chlorine molecule at the C=C bond of the quinoid ring, followed by prototropic rearrangements. In our previous studies [5, 10] we did not consider the possibility for some rearrangement to occur during the chlorination of *p*-quinone imines having no substituents in the quinoid ring.

N-Arylsulfonyl-3-methyl-1,4-benzoquinone monoimines **XIa**–**XIc** possess a methyl group in the *ortho* position with respect to the imino group. According to the ^{1}H NMR data, they exist in solution as *E* isomers (with respect to the 3-methyl group). Compounds **XIa**–**XIc** and *N*-arylsulfonyl-3-methyl-4-aminophenols **XIIa**–**XIIc** were subjected to chlorination and bromination in chloroform, acetic acid, dimethylformamide, and dimethylformamide–acetic acid (1:5) at different temperatures and reactant ratios.

The chorination of compounds **XIa**–**XIc** in all the above solvents at any reactant ratio afforded stable 4-arylsulfonylimino-5,6-dichloro-3-methylcyclohex-2-en-1-ones **XIIIa**–**XIIIc** having a semiquinoid structure (Scheme 4). Unlike chlorination, the effect of solvent on the bromination of quinone imines **XIa**–**XIc** was stronger. The corresponding 4-arylsulfonylimino-5,6-dibromo-3-methylcyclohex-2-en-1-ones **XIVa** and **XIVc** were obtained by bromination of *p*-quinone imines **XIa** and **XIc** only in DMF–AcOH (1:5). In the reactions of **XIa**–**XIc** with an equimolar amount of bromine in acetic acid or at any reactant ratio in chloroform we isolated only *N*-arylsulfonyl-2,6-dibromo-3-methyl-4-aminophenols **XXa**–**XXc**. In acetic acid at a substrate concentration of 0.2 M and reactant ratio **XI**:Br_2 = 1:8, the products were *N*-arylsulfonyl-2,6-dibromo-3-methyl-1,4-benzoquinone imines **XXIa**–**XXIc** and 4-arylsulfonylimino-2,5,6,6-tetrabromo-3-methylcyclohex-2-en-1-ones **XXIIIa**–**XXIIIc**. Individual quinone imines **XXI** were synthesized by oxidation of aminophenols **XX** with lead tetraacetate in acetic acid, and compounds **XXIII** were obtained by bromination of aminophenols **XX** and quinone imines **XXI** (Scheme 4). Thus the addition of the first halogen molecule to quinone imines **XIa**–**XIc** occurs only at the unsubstituted double bond of the quinoid ring (C^5=C^6), as in the halogenation of analogous *p*-quinone oxime esters [13], i.e., the process is regioselective.

The results of PM3 calculations showed that the unsubstituted *syn*-C^5=C^6 bond in quinone imine **XIa**, as well as in the corresponding *p*-benzoquinone oxime esters [1], is less polarized than the C^2=C^3 bond having a methyl group: $q(C^2)$ = –0.179, $q(C^3)$ = –0.0361, $q(C^5)$ = –0.139, $q(C^6)$ = –0,138; $|\Delta q(C^2{=}C^3)|$ = 0.143 > $|\Delta q(C^5{=}C^6)|$ = 0.001. This means that the C^5=C^6 bond in **XI** is more reactive toward halogens. As shown in [1], polarization of the quinoid C=C bonds may be used to determine the site of halogen addition to *p*-benzoquinone oxime esters. Moreover, the C^5=C^6 bond in molecule **XIa** is more spatially accessible. Thus both electronic and steric factors in the halogenation of quinone imines **XI** act in the same direction,

Scheme 4.



Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 3-$O_2NC_6H_4$ (**c**); **XVI**, Ar = Ph; **XIII**, **XV**, **XVII**, **XIX**, **XXII**, Hlg = Cl; **XIV**, **XVI**, **XVIII**, **XX**, **XXI**, **XXIII**, Hlg = Br.

and the addition of halogens is strictly regioselective (as might be expected).

By chlorination of aminophenols **XIIa**–**XIIc** with an equimolar amount of chlorine in chloroform and acetic acid at a substrate concentration of 1–1.5 M we obtained *N*-arylsulfonyl-2-chloro-3-methyl-4-aminophenols **XVa**–**XVc** (Scheme 4). When the concentration of aminophenols **XII** was reduced to 0.5–0.6 M, *N*-arylsulfonyl-6-chloro-3-methyl-4-aminophenols **XVIIa** and **XVIIc** and *N*-arylsulfonyl-2,6-dichloro-3-methyl-4-aminophenols **XIXa**–**XIXc** were formed. The chlorination in a 1:5 DMF–AcOH mixture (initial aminophenol concentration 1–1.5 M) afforded aminophenols **XIXa**–**XIXc** as the only product. Compounds **XVa**, **XVIIa**, **XVIIc**, and **XIXa**–**XIXc** were isolated as individual substances. Aminophenols **XVb** and **XVc** were obtained only as mixtures with aminophenols **XVIIb** or **XIXb** and **XVIIc** or **XIXc**. Raising the chlorine-to-substrate ratio to 2:1 and 3:1 resulted in formation of 4-arylsulfonylimino-2,5,6,6-tetrachloro-3-methylcyclohex-2-en-1-ones **XXIIa** and **XXIIb**. *N*-4-Tolylsulfonyl-2,5,6-trichloro-3-methyl-1,4-benzoquinone imine (**XXIVb**) was isolated as individual substance when the chlorination of aminophenol **XIIb** was carried out in DMF using 5 equiv of chlorine. The reaction mixtures were analyzed after oxidation of aminophenols to the corresponding quinone imines with lead tetraacetate, for the ^{1}H NMR spectra of quinone imines were more informative than the spectra of aminophenols.

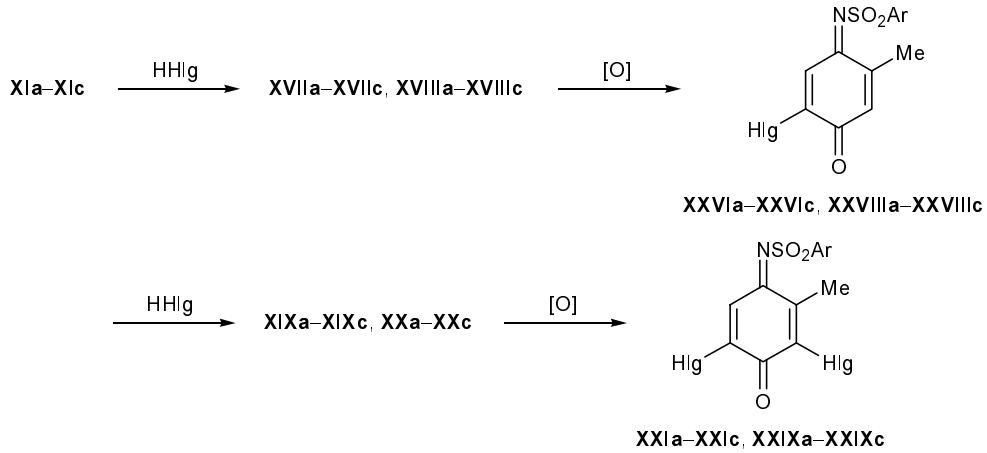
The bromination of aminophenols **XIIa**–**XIIc** (Scheme 4) gave the following products: *N*-phenylsulfonyl-2-bromo-3-methyl-4-aminophenol (**XVI**), *N*-phenylsulfonyl-6-bromo-3-methyl-4-aminophenol (**XVIIIa**), *N*-arylsulfonyl-2,6-dibromo-3-methyl-4-aminophenols **XXa**–**XXc**, *N*-arylsulfonyl-2,6-dibromo-3-methyl-1,4-benzoquinone imines **XXIa**–**XXIc**, and 4-arylsulfonylimino-2,5,6,6-tetrabromo-3-methylcyclohex-2-en-1-ones **XXIIIa** and **XXIIIb**. As individual substances we isolated compounds **XXa**–**XXc**, **XXIa**–**XXIc**, **XXIIIa**, and **XXIIIb**. Aminophenol **XVI** was obtained only as a mixture with aminophenols **XVIII** and **XXa**. The reaction mixtures were analyzed after oxidation to the corresponding quinone imine **XXIa**, *N*-phenylsulfonyl-2-bromo-3-methyl-1,4-benzoquinone imine (**XXVa**), and *N*-phenylsulfonyl-6-bromo-3-methyl-1,4-benzoquinone imine (**XXVIa**) (see above).

The structure of the newly synthesized compounds was proved by their elemental analysis and IR and ^{1}H and ^{13}C NMR spectra. Semiquinoid derivatives **XIII**, **XIV**, **XXII**, and **XXIII** are characterized by IR absorption in the region 1688–1725 cm^{-1} due to stretching vibrations of the carbonyl group; the corresponding absorption band in the spectra of quinone imines **XXI**, **XXIV**, and **XXV**–**XXVII** is located at 1660–1683 cm^{-1}. The ^{1}H NMR spectra of *N*-phenylsulfonyl-2-bromo-3-methyl-1,4-benzoquinone imine (**XXVa**) and *N*-arylsulfonyl-2-chloro-3-methyl-1,4-benzoquinone imines **XXVIIa**–**XXVIIc** obtained by oxidation of aminophenols **XV** and **XVI** contained signals from the 5-H and 6-H protons (a doublet of doublets with an *ortho*-coupling constant $^3J_{HH}$ of 10.2 Hz). *N*-Arylsulfonyl-6-bromo-3-methyl-1,4-benzoquinone imines **XXVIa**–**XXVIc** and *N*-arylsulfonyl-6-chloro-3-methyl-1,4-benzoquinone imines **XXVIIIa**–**XXVIIIc** showed in the ^{1}H NMR spectra a singlet from 5-H and a quartet from 2-H. In the spectra of quinone imines **XXIa**–**XXIc** and **XXIXa**–**XXIXc**, a singlet at δ 8.35–8.72 ppm (5-H) was present. The ^{13}C NMR spectra of **XIIIa**, **XIVa**, **XXIIb**, and **XXIIIa** contained signals at δ_C 38–81 ppm due to sp^3-hybridized atoms in the semiquinoid ring (C^5 and C^6).

Thus the halogenation of quinone imines **XIa**–**XIc** and aminophenols **XIIa**–**XIIc** leads to different sets of products. Therefore, the formation of aminophenols **XV**–**XVIII** from *N*-arylsulfonyl-3-methyl-4-aminophenols **XIIa**–**XIIc** cannot be rationalized by the reaction sequence oxidation–halogen addition–elimination of hydrogen halide. Presumably, the sequence oxidation–addition of hydrogen halide is operative.

In order to verify the above assumption we examined hydrohalogenation of quinone imines **XIa**–**XIc**. Hydrochlorination was performed using gaseous hydrogen chloride in chloroform, and 46% aqueous HBr in acetic acid was used for hydrobromination. The addition of one hydrogen halide molecule to compounds **XIa**–**XIc** afforded aminophenols **XVIIa**–**XVIIc** and **XVIIIa**–**XVIIIc** as the major products (Scheme 5). The oxidation of aminophenols **XVIIa**–**XVIIc** and **XVIIIa**–**XVIIIc** with lead tetraacetate gave quinone imines **XXVIIIa**–**XXVIIIc** and **XXVIa**–**XXVIc**, respectively, and the subsequent addition of the second hydrogen halide molecule led to formation of aminophenols **XIXa**–**XIXc** and **XXa**–**XXc** having halogen atoms in positions *2* and *6*. Quinone imines **XXIXa**–**XXIXc** and **XXIa**–**XXIc** were obtained by oxidation of aminophenols **XIXa**–**XIXc** and **XXa**–

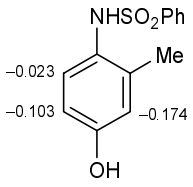
Scheme 5.



Ar = Ph (**a**), 4-MeC$_6$H$_4$ (**b**), 3-O$_2$NC$_6$H$_4$ (**c**); **XVII**, **XIX**, **XXVIII**, **XXIX**, Hlg = Cl; **XVIII**, **XX**, **XXI**, **XXVI**, Hlg = Br.

XXc, respectively. Thus the formation of aminophenols **XVII** and **XVIII** in the halogenation of compounds **XIIa**–**XIIc** involves the reaction sequence oxidation–addition of HHlg, while aminophenols **XIX** and **XX** are formed via oxidation–addition of Hlg_2 to give unstable semiquinoid structures–regioselective elimination of HHlg–addition of HHlg or oxidation–addition of HHlg to give aminophenols–oxidation–addition of HHlg.

However, the formation of *N*-arylsulfonyl-2-halo-3-methyl-4-aminophenols **XVa**–**XVc** and **XVI** from *N*-arylsulfonyl-3-methyl-4-aminophenols **XIIa**–**XIIc** cannot be rationalized in terms of the above schemes. Most probably, these compounds are formed as a result of electrophilic replacement of hydrogen atom in the 2-position by halogen, i.e., via substitution at the *meta* position with respect to the most electron-acceptor $ArSO_2NH$ group or at the *ortho* position with respect to the electron-donor methyl group; then, the C^2 atom should possess the maximal partial negative charge. This assumption is confirmed by the results of PM3 quantum-chemical calculations of molecule **XIIa**. The largest negative charge in this molecule is localized on the C^2 atom; therefore, the rate of electrophilic substitution at that position should be the maximal due to formation of more stable σ complex. We can conclude that halogenation of aminophenols **XIIa**–**XIIc** involves several transformation pathways: electrophilic substitution, oxidation–addition of HHlg, and oxidation–addition of Hlg_2–dehydrohalogenation. The contribution of one or another pathway depends on the reaction conditions (solvent nature, reactant ratio, substrate concentration, and temperature).



XIIa

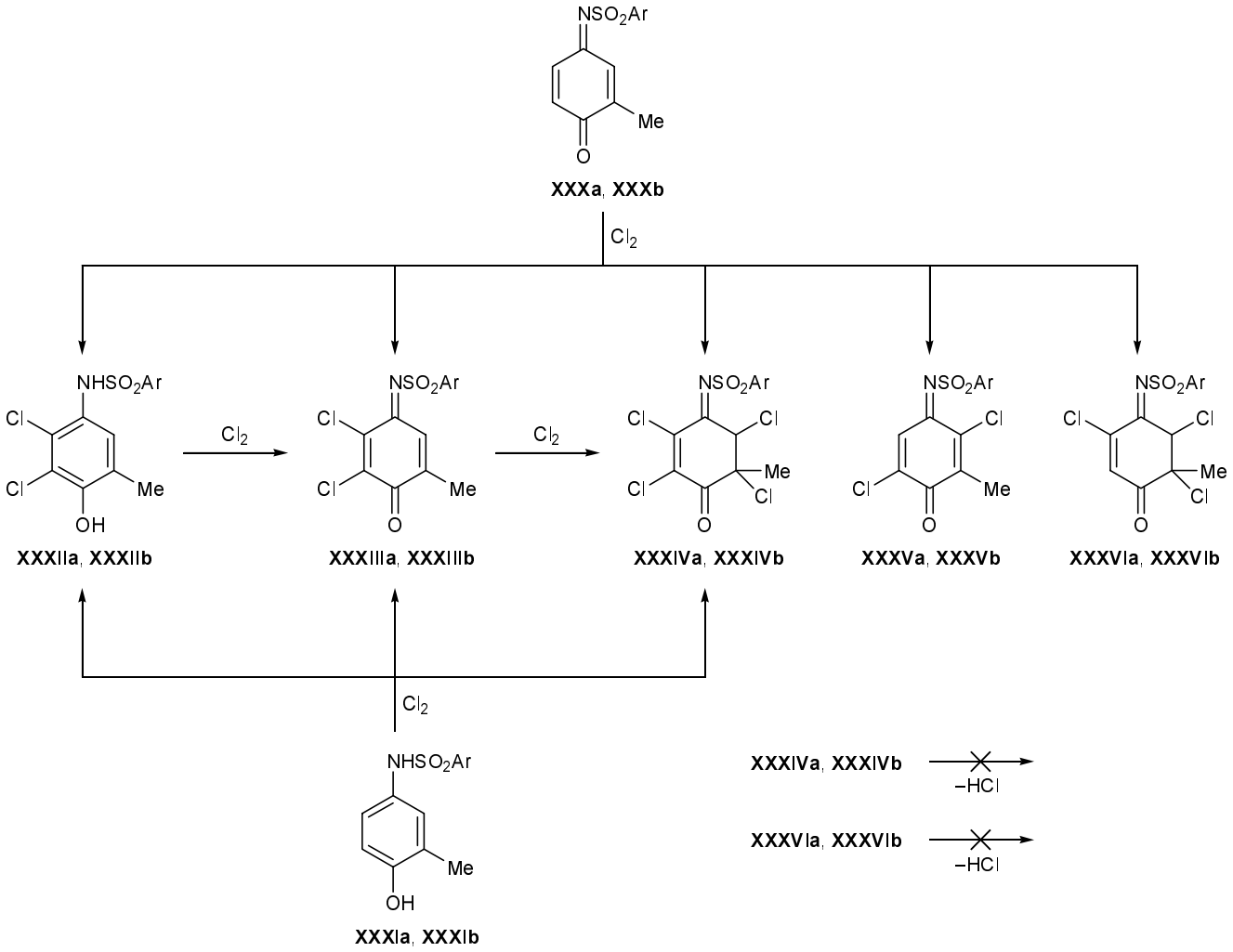
The effect of *Z*,*E* isomerization of initial quinone imine on the halogenation pattern can be revealed by comparing the behaviors of *p*-benzoquinone imines and the corresponding *p*-benzoquinone oxime esters in the halogenation process. For this purpose we examined halogenation of *N*-arylsulfonyl-2-methyl-1,4-benzoquinone imines **XXXa** and **XXXb** and the corresponding reduced forms, aminophenols **XXXIa** and **XXXIb**. Quinone imines **XXXa** and **XXXb** were subjected to chlorination in chloroform, acetic acid, dimethylformamide, and DMF–AcOH (1:5) at various reactant ratios. Depending on the conditions, compounds **XXXII**–**XXXVI** were obtained (Scheme 6). The chlorination process was found to be strongly influenced by the solvent nature. In DMF–AcOH (1:5), compounds **XXXII**–**XXXIV** were formed, depending on the amount of chlorine. The reactions in chloroform and acetic acid (substrate-to-chlorine ratio 1:1 or 1:2) gave only *N*-arylsulfonyl-5,6-dichloro-2-methyl-4-aminophenols **XXXIIa** and **XXXIIb**, while *N*-arylsulfonyl-3,6-dichloro-2-methyl-1,4-benzoquinone imines **XXXVa** and **XXXVb** and 4-arylsulfonylimino-3,5,6-trichloro-6-methylcyclohex-2-en-1-ones **XXXVIa** and **XXXVIb** were formed in the presence of a considerable excess of chlorine.

The structure of the chlorination products obtained from quinone imines **XXXa** and **XXXb** and the results of chlorination of *N*-*p*-tolylsulfonyl-2-chloro-1,4-benzoquinone imine (**VIIIb**) suggest that 4-arylsulfonylimino-5,6-dichloro-2-methylcyclohex-2-en-1-ones formed initially in DMF–AcOH (1:5), depending on the reactant ratio, undergo prototropic rearrangement into *N*-arylsulfonyl-5,6-dichloro-2-methyl-4-aminophenols **XXXIIa** and **XXXIIb**. Oxidation of the latter with chlorine gives rise to *N*-arylsulfonyl-5,6-dichloro-2-methyl-1,4-benzoquinone imines **XXXIIIa** and **XXXIIIb** which take up chlorine molecule to yield 4-arylsulfonylimino-2,3,5,6-tetrachloro-6-methylcyclohex-2-en-1-ones **XXXIVa** and **XXXIVb**; the latter are very stable compounds, and their dehydrochlorination does not occur.

Compounds **XXXVa**, **XXXVb**, **XXXVIa**, and **XXXVIb** can be formed from 4-arylsulfonylimino-5,6-dichloro-2-methylcyclohex-2-en-1-ones which are primary addition products; their dehydrochlorination gives two isomeric quinone imines: *N*-arylsulfonyl-6-chloro-2-methyl-1,4-benzoquinone imines **XXXVIIa** and **XXXVIIb** and *N*-arylsulfonyl-5-chloro-2-methyl-1,4-benzoquinone imines. The latter take up chlorine molecule to afford stable cyclohexene structure **XXXVIa** or **XXXVIb**, while addition of the second chlorine molecule to quinone imines **XXXVIIa** and **XXXVIIb**, followed by dehydrochlorination, yields compounds **XXXVa** and **XXXVb**.

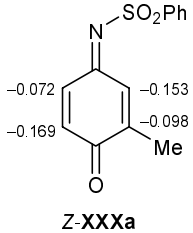
Thus the formation of a broad spectrum of products in the chlorination of quinone imines **XXX** may be rationalized by the following transformation sequence. The primary products formed by chlorine addition at the unsubstituted C=C bond in the quinoid ring have semiquinoid structure. Unlike structurally related

Scheme 6.



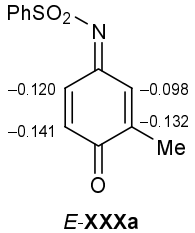
Ar = Ph (**a**), 4-MeC_6H_4 (**b**).

p-quinone oxime esters [1], the addition is regioselective. According to the PM3 calculations, the $C^2=C^3$ (*Z* isomer) or $C^5=C^6$ bond (*E* isomer) in **XXX** is less polarized; this means that orientation of substituent on the nitrogen atom in quinone imines **XXX** affects the electron density distribution in the quinoid ring to a stronger extent, as compared to *p*-quinone oxime esters [1]. Another difference is that quinone imines **XXX** in solution are characterized by a lower barrier to inversion of the nitrogen atom, which favors *Z*,*E* isomerization. Therefore, the different polarizations of the $C^2=C^3$ and $C^5=C^6$ bonds in quinone imines **XXX** could not affect the regioselectivity of halogenation to an appreciable extent, and steric factor should predominate (as observed experimentally). The addition of halogens occurs exclusively at the unsubstituted (i.e., spatially more accessible) $C^5=C^6$ bond.



Z-**XXXa**

$|\Delta q(C^2=C^3)| < \Delta q(C^5=C^6)$



E-**XXXa**

$|\Delta q(C^2=C^3)| > \Delta q(C^5=C^6)$

Thus our experiments showed that halogen addition at the quinoid C=C bond of *N*-arylsulfonyl-1,4-benzoquinone imines gives compounds having a cyclohexene structure. These compounds may be stable, e.g., as 4-arylsulfonylimino-5,6-dihalo-3-methylcyclohex-2-en-1-ones **XIII** and **XIV** formed by chlorination of *N*-arylsulfonyl-3-methyl-1,4-benzoquinone imines **XI** (in this case, they are the major reaction products),

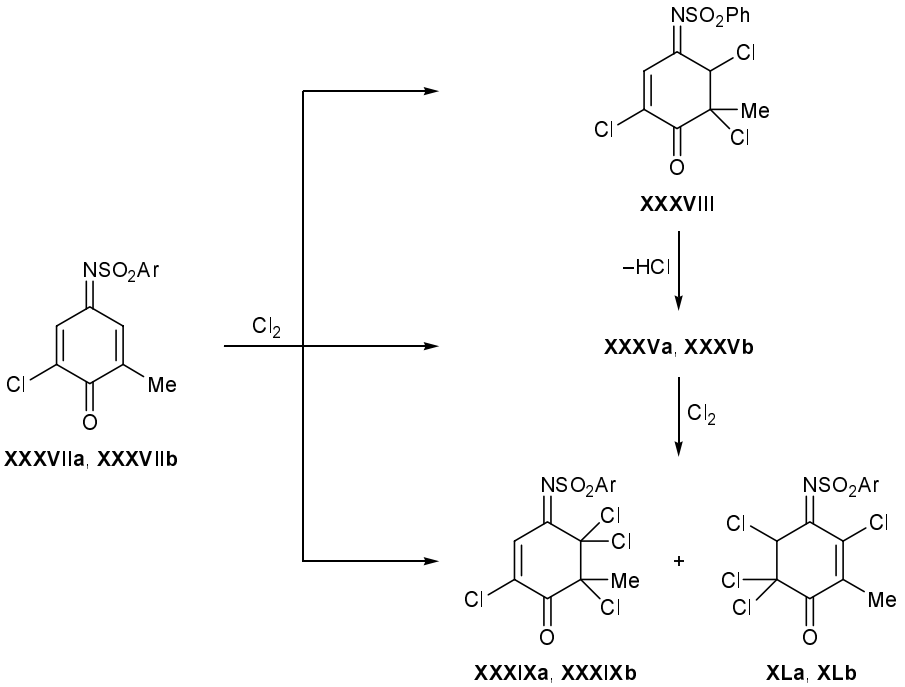
or unstable. In the latter case, the primary adducts undergo fast transformations, including prototropic rearrangement into the corresponding 4-aminophenols having two chlorine atoms in positions *2* and *3* (as in the chlorination of quinone imines **I** and **VIII**) or dehydrochlorination to afford quinone imines, e.g., **XXXVIIa** and **XXXVIIb**. Insofar as the dehydrochlorination process is regioselective, the resulting quinone imine may have chlorine atom in the *ortho* or *meta* position with respect to the carbonyl group. The most probable subsequent transformation of aminophenols is their oxidation to the corresponding quinone imines which in turn are capable of taking up another chlorine molecule, and the above reaction sequence is repeated.

The results of halogenation of quinone imines **I**, **XI**, and **XXX** led us to conclude that the stability of cyclohexene structures derived from *p*-quinone imines is strongly influenced by *Z*,*E*-isomerization. The probability of this process depends on the cyclohexene structure: the isomerization is possible if the *ortho* position with respect to the imino group is not substituted and hydrogen and chlorine atoms are attached to the sp^3-hybridized carbon atom.

We also performed chlorination of quinone imines **XXXVIIa** and **XXXVIIb** (Scheme 7) which are intermediate products in the chlorination of compounds **XXX** with a view to understand the halogenation paths in more detail. Quinone imines **XXXVIIa** and **XXXVIIb** were synthesized by oxidation with lead tetraacetate of the hydrochlorination products of compounds **XXXa** and **XXXb**, respectively. By chlorination of quinone imine **XXXVIIa** in acetic acid we obtained 2,5,6-trichloro-6-methyl-4-phenylsulfonyliminocyclohex-2-en-1-one (**XXXVIII**). After storage for several days, compound **XXXVIII** lost hydrogen chloride, thus being converted into quinone imine **XXXVa**; i.e., the cyclohexene structure of **XXXVIII** is not stable. According to the ^{1}H NMR data, compound **XXXVIII** in solution exists as a mixture of *Z* and *E* isomers; the spectrum contains two sets of signals. The 3-H signal appeared as a doublet at δ 7.08 and 8.31 ppm for the *E* and *Z* isomers, respectively; its position is typical of a proton located in the *ortho* position with respect to the imino group. Doublet signals at δ 6.23 and 4.76 ppm were assigned to proton at the sp^3-hybridized carbon atom (5-H) in the *E* and *Z* isomers, respectively.

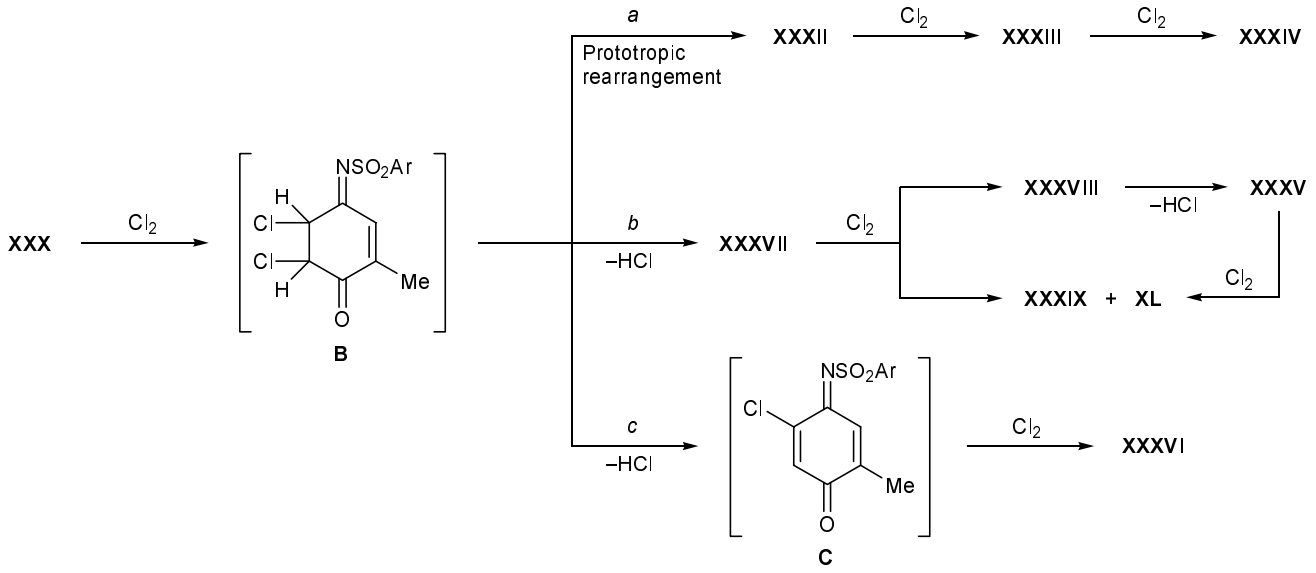
We failed to effect dehydrochlorination of compounds **XXXIVa**, **XXXIVb**, **XXXVIa**, and **XXXVIb** which possess an analogous ClHC–CClCH$_3$ fragment but exist in solution as a single *E* isomer. This result may be regarded as an additional evidence in favor of an appreciable effect of *Z*,*E* isomerization on the

Scheme 7.



Ar = Ph (**a**), 4-MeC$_6$H$_4$ (**b**).

Scheme 8.

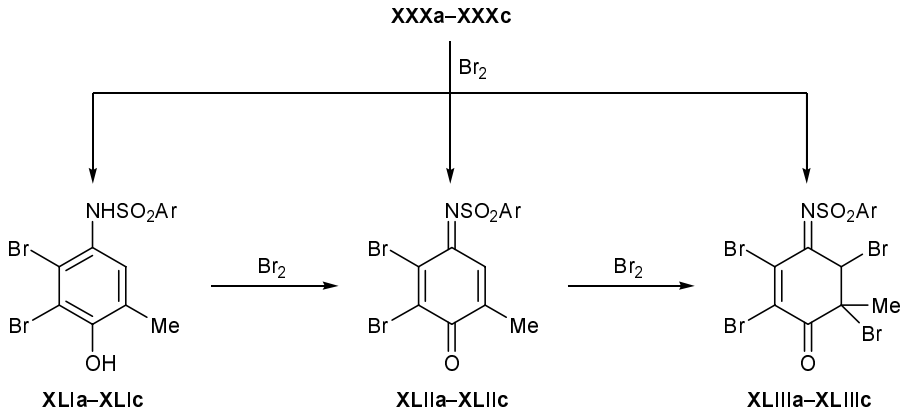


stability of cyclohexene structures and hence on the dehydrochlorination process. There are no steric hindrances to dehydrochlorination in the *Z* isomer of quinone imine **XXXVIII**.

The chlorination of quinone imines **XXXVIIa** and **XXXVIIb** gave mixtures of 4-arylsulfonylimino-2,5,5,6-tetrachloro-6-methylcyclohex-2-en-1-ones **XXXIXa** and **XXXIXb** and 4-arylsulfonylimino-3,5,6,6-tetrachloro-2-methylcyclohex-2-en-1-ones **XLa** and **XLb**; the same products were also obtained by chlorination of quinone imines **XXXVa** and **XXXVb** (Scheme 7). In the ^{1}H NMR spectra of the products we observed only one signal from proton in the cyclohexene ring at δ 8.40–8.41 (**XXXIX**) or 6.65–6.67 ppm (**XL**). Thus chlorine adds to quinone imines **XXXVa** and **XXXVb** at both ClC=CCH$_3$ and HC=CCl bonds.

The results of chlorination of quinone imines **XXXa** and **XXXb** may be illustrated in the general form by Scheme 8. In the first stage, addition of chlorine molecule at the unsubstituted C=C bond in the quinoid ring of **XXX** gives intermediate cyclohexene structure **B**. Taking into account the ^{1}H NMR spectra of compounds **Xb** and **XXXVIII** with an analogous substitution pattern (both substituents are located in the *ortho* positions with respect to the imino group), we presumed that compound **B** in solution should exist as a mixture of *Z* and *E* isomers due to isomerization. Insofar as the *Z*,*E*-isomerization process affects the stability of cyclohexene structures (see above), several transformation pathways of structure **B** are possible: (*a*) prototropic rearrangement and (*b*, *c*) regioselective dehydrohalogenation (Scheme 8). These pathways are likely to be responsible for the formation of a variety

Scheme 9.



Ar = Ph (**a**), 4-MeC$_6$H$_4$ (**b**), 3-O$_2$NC$_6$H$_4$ (**c**).

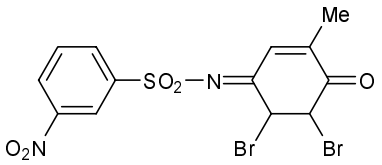
of products in the chlorination of quinone imines **XXX**. Unfortunately, we failed to isolate compounds having structure **B** or **C**.

We can state that the broad spectrum of products in the chlorination of *N*-arylsulfonyl-2-methyl-1,4-benzoquinone imines **XXX** arises from *Z*,*E* isomerization of both initial quinone imines and intermediate cyclohexene derivatives formed by addition of one chlorine molecule to the former and from their further transformations. Unlike 2-methyl-1,4-benzoquinone oxime esters [1], quinone imines **XXX** take up halogen molecule with high regioselectivity due to *Z*,*E* isomerization in solution.

The bromination of compounds **XXXa**–**XXXc** was performed in chloroform, acetic acid, dimethylformamide, and DMF–AcOH (1:5) with a solution of bromine in the same solvent. The reactions were carried out at different temperatures and reactant ratios. Depending on the conditions, compounds **XLIa**–**XLIc**, **XLIIa**–**XLIIc**, and **XLIIIa**–**XLIIIc** were obtained (Scheme 9).

The reaction in chloroform at a **XXX**-to-Br_2 ratio of 1:1 to 1:5 gave only *N*-arylsulfonyl-5,6-dibromo-2-methyl-4-aminophenols **XLIa**–**XLIc**. The same products were obtained in acetic acid using 1 or 2 equiv of bromine, while in the presence of 3 or 5 equiv of bromine the products were either individual *N*-arylsulfonyl-5,6-dibromo-2-methyl-1,4-benzoquinone imines **XLIIa**–**XLIIc** or their mixtures with 4-arylsulfonylimino-2,3,5,6-tetrabromo-6-methylcyclohex-2-en-1-ones **XLIIIa**–**XLIIIc**. The bromination of **XXX** in DMF led to formation of quinone imines **XLIIa**–**XLIIc** and cyclohexene derivatives **XLIIIa**–**XLIIIc**. Thus the depth of the bromination process clearly depends on the solvent nature.

By analogy with the chlorination process, the first reaction stage may be presumed to involve addition of bromine molecule at the unsubstituted C=C bond in the quinoid ring. This assumption is supported by the isolation of compound **XLIV** having a cyclohexene structure. According to the ^{1}H NMR data, compound **XLIV** in solution exists as a mixture of *Z* and *E* isomers. The spectrum contains two sets of signals, which included quartets at δ 6.70 (*E* isomer) and 7.82 ppm (*Z* isomer) from the 3-H proton, quartets at δ 4.95 and 6.28 ppm (5-H), and doublets at δ 4.78 and 4.81 ppm (6-H). The position of the 5-H and 6-H signals is typical of hydrogen atoms attached to sp^3-hybridized carbon atoms. These data provide a support to the assumption that intermediate structure **B** formed by halogenation of quinone imines **XXX** is a mixture of isomers. The structure of the bromination products indicates that further transformations of compound **XLIV**, in contrast to the chlorination process, include only prototropic rearrangement, followed by oxidation and addition of bromine molecule, i.e., semiquinoid structure **XLIV** does not undergo dehydrobromination.



XLIV

Depending on the conditions, the bromination of *N*-arylsulfonyl-2-methyl-4-aminophenols **XXXIa**–**XXXIc** led to formation of compounds **XLIa**–**XLIc**, **XLIIa**–**XLIIc**, and **XLVa**–**XLVc**. *N*-Arylsulfonyl-6-bromo-2-methyl-1,4-benzoquinone imines **XLVa**–**XLVc** were obtained only in DMF at a **XXXI**-to-Br_2 ratio of 1:1 or 1:2. Most probably, the reaction occurs as successive oxidation of the initial aminophenol with bromine, addition of bromine molecule, and regioselective dehydrobromination or oxidation, addition of hydrogen bromide, and oxidation. Also, electrophilic substitution of hydrogen in the benzene ring of the initial aminophenol with bromine, followed by oxidation, cannot be ruled out. No analogous quinone imines were formed in the chlorination of aminophenols **XXXIa**–**XXXIc** and *N*-arylsulfonyl-6-chloro-2-methyl-4-aminophenols **XLVIa** and **XLVIb**; in these reactions, the products were only compounds **XXXII**–**XXXIV**. The most probable reason is that initial aminophenols **XXXI** are readily oxidized with chlorine (which is a stronger oxidant than bromine) to give the corresponding quinone imines **XXX**, and the latter take up chlorine molecule. Further transformations include only prototropic rearrangement. It should be noted that no dehydrochlorination products were formed (in contrast to the chlorination of **XXX**).

We can conclude that the reactions of halogens with *N*-arylsulfonyl-1,4-benzoquinone imines existing in solution as mixtures of *Z* and *E* isomers reveal effect of only steric factor, for *Z*,*E* isomerization levels the difference in the electron density distribution over the C=C bonds in the quinoid ring. Cyclohexene structures arising from halogen addition at the quinoid C=C bond could undergo various transformations, depending on the reaction conditions; these transformations include

prototropic rearrangement or dehydrohalogenation, the latter process being not strictly regioselective, in contrast to *p*-benzoquinone oxime derivatives.

EXPERIMENTAL

The IR spectra were recorded in KBr on a UR-20 spectrometer. The ^{1}H NMR spectra were obtained on a Varian VXR-300 instrument at 300 MHz from solutions in $CDCl_3$; the chemical shifts were measured relative to tetramethylsilane. The ^{13}C NMR spectra were recorded on the same instrument at 75.4 MHz using $CDCl_3$ as solvent and TMS as reference. The reaction mixtures were analyzed by thin-layer chromatography on Silufol UV-254 plates using benzene–ethyl acetate (10:1, by volume) as eluent; spots were visualized under UV light.

Compounds **Ia**, **Ib**, **Va**, **Vb**, **XIa**–**XIc**, **XIIa**–**XIIc**, **XXXa**–**XXXc**, and **XXXIa**–**XXXIc** were synthesized by the procedures reported in [14] and were purified by recrystallization from acetic acid.

Compound **XIa**. Yield 90%, mp 141–142°C. ^{1}H NMR spectrum, δ, ppm: 2.07 d (3H, Me), 6.57 q (1H, 2-H), 6.61–6.65 d.d (1H, 6-H, $J_{2,6}$ = 2.4 Hz), 8.17 d (1H, 5-H, $J_{5,6}$ = 10.2 Hz), 7.57–8.04 m (5H, C_6H_5). Found, %: N 5.31. $C_{13}H_{11}NO_3S$. Calculated, %: N 5.36.

Compound **XIb**. Yield 88%, mp 154–155°C. ^{1}H NMR spectrum, δ, ppm: 2.06 d (3H, Me), 6.60–6.64 d.d (1H, 6-H), 6.57 q (1H, 2-H, $J_{2,6}$ = 2.1 Hz), 8.18 d (1H, 5-H, $J_{5,6}$ = 10.5 Hz), 7.38–7.90 d.d (4H, C_6H_4), 2.47 s (3H, **Me**C_6H_4). Found, %: N 4.93. $C_{14}H_{13}NO_3S$. Calculated, %: N 5.09.

Compound **XIc**. Yield 85%, mp 173–174°C. ^{1}H NMR spectrum, δ, ppm: 2.08 d (3H, Me), 6.61 q (1H, 2-H), 6.67–6.71 d.d (1H, 6-H, $J_{2,6}$ = 2.1 Hz), 8.10 d (1H, 5-H, $J_{5,6}$ = 10.5 Hz), 7.81–8.88 m (4H, C_6H_4). Found, %: N 9.20. $C_{13}H_{10}N_2O_5S$. Calculated, %: N 9.15.

Compound **XIIa**. Yield 93%, mp 133–134°C. Found, %: N 5.42. $C_{13}H_{13}NO_3S$. Calculated, %: N 5.34.

Compound **XIIb**. Yield 91%, mp 136–137°C. Found, %: N 5.29. $C_{14}H_{15}NO_3S$. Calculated, %: N 5.20.

Compound **XIIc**. Yield 85%, mp 148–149°C. Found, %: N 7.45. $C_{13}H_{12}N_2O_5S$. Calculated, %: N 7.38.

Compound **XXXa**. Yield 89%, mp 109–111°C. ^{1}H NMR spectrum, δ, ppm: *E* isomer: 2.06 d (3H, Me), 6.67–6.70 d.d (1H, 6-H), 6.82 q (1H, 3-H), 8.14–8.17 d.d (1H, 5-H, $J_{5,6}$ = 10.2, $J_{3,5}$ = 2.4 Hz), 7.56–8.04 m (5H, C_6H_5); *Z* isomer: 2.15 d (3H, Me), 6.67–6.70 d.d (1H, 6-H), 6.90–6.93 d.d (1H, 5-H, $J_{5,6}$ = 10.2 Hz), 8.01 q (1H, 3-H, $J_{3,5}$ = 2.4 Hz), 7.56–8.04 m (5H, C_6H_5). Found, %: N 5.44. $C_{13}H_{11}NO_3S$. Calculated, %: N 5.36.

Compound **XXXb**. Yield 83%, mp 88–90°C. ^{1}H NMR spectrum, δ, ppm: *E* isomer: 2.06 d (3H, Me), 6.66–6.69 d.d (1H, 6-H), 6.81 q (1H, 3-H), 8.15–8.18 d.d (1H, 5-H, $J_{5,6}$ = 10.5, $J_{3,5}$ = 3 Hz), 7.38–7.89 d.d (4H, C_6H_4), 2.47 s (3H, **Me**C_6H_4); *Z* isomer: 2.14 d (3H, Me), 6.89–6.92 d.d (1H, 5-H), 6.66–6.69 d.d (1H, 6-H, $J_{5,6}$ = 10.5 Hz), 8.02 q (1H, 3-H, $J_{3,5}$ = 3 Hz), 7.38–7.89 d.d (4H, C_6H_4), 2.47 s (3H, **Me**C_6H_4). Found, %: N 5.15. $C_{14}H_{13}NO_3S$. Calculated, %: N 5.09.

Compound **XXXc**. Yield 82%, mp 143–144°C. ^{1}H NMR spectrum, δ, ppm: *E* isomer: 2.10 d (3H, Me), 6.72–6.75 d.d (1H, 6-H), 6.82 q (1H, 3-H), 8.06–8.08 d.d (1H, 5-H, $J_{5,6}$ = 10.5, $J_{3,5}$ = 3 Hz), 7.80–8.87 m (4H, C_6H_4); *Z* isomer: 2.18 d (3H, Me), 6.72–6.75 d.d (1H, 6-H), 6.91–6.93 d.d (1H, 5-H, $J_{5,6}$ = 10.5 Hz), 7.92 q (1H, 3-H, $J_{3,5}$ = 3 Hz), 7.38–7.89 m (4H, C_6H_4). Found, %: N 9.24. $C_{13}H_{10}N_2O_5S$. Calculated, %: N 9.15.

Compound **XXXIa**. Yield 88%, mp 198–199°C. Found, %: N 5.30. $C_{13}H_{13}NO_3S$. Calculated, %: N 5.34.

Compound **XXXIb**. Yield 86%, mp 181–182°C. Found, %: N 5.14. $C_{14}H_{15}NO_3S$. Calculated, %: N 5.20.

Compound **XXXIc**. Yield 82%, mp 178–179°C. Found, %: N 7.32. $C_{13}H_{12}N_2O_5S$. Calculated, %: N 7.38.

Chlorination of compounds Ia, Ib, Vb, VIa, VIb, VIIIa, VIIIb, XIa–XIc, XIIa–XIIc, XXa–XXc, XXXa, XXXb, XXXIa–XXXIc, XXXVIIa, and XXXVIIb (*general procedure***).** A stream of dry chlorine was passed at a flow rate of 15–20 ml/min through a solution of 2 mmol of the corresponding substrate in 3 ml of chloroform, acetic acid, dimethylformamide, or DMF–AcOH (1:5), maintained at 25–30°C. The amount of chlorine was controlled by the gain in weight; it was varied from 1 to 3 equiv. After 24 h, the precipitate was filtered off and recrystallized from acetic acid. The melting points and analytical data are given below only for products isolated as individual substances.

Compound **IV**. Yield 55%, mp 135–136°C. ^{1}H NMR spectrum, δ, ppm: 6.84 d (1H, 6-H), 8.31 d (1H, 5-H, *J* = 10.4 Hz), 7.59–8.32 m (5H, C_6H_5).

Found, %: Cl 22.10, 22.52. $C_{12}H_7Cl_2NO_3S$. Calculated, %: Cl 22.43.

Compound **Xb**. Yield 61%, mp 118–120°C. ^{1}H NMR spectrum, δ, ppm: *E* isomer: 4.74 d (1H, 6-H), 6.33 q (1H, 5-H, $J_{5,6}$ = 3 Hz), 7.11 d (1H, 3-H), 7.40–7.90 d.d (4H, C_6H_4), 2.48 s (3H, **Me**C_6H_4); *Z* isomer: 4.72 d (1H, 6-H), 4.81 q (1H, 5-H, $J_{5,6}$ = 3 Hz), 8.37 d (1H, 3-H), 7.40–7.90 d.d (4H, C_6H_4), 2.48 s (3H, **Me**C_6H_4). Found, %: Cl 27.98, 28.34. $C_{13}H_{10}Cl_3NO_3S$. Calculated, %: Cl 29.01.

Compound **XIIIa**. Yield 83%, mp 162–163°C. ^{1}H NMR spectrum, δ, ppm: 2.09 d (3H, 3-Me), 2.48 s (3H, Me), 4.54 q (1H, 6-H), 6.32 d (1H, 5-H, $J_{5,6}$ = 3 Hz), 6.52 q (1H, 2-H, $J_{2,6}$ = 1.8 Hz), 7.58–8.07 m (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 186.71 (C^1), 132.79 (C^2), 149.52 (C^3), 18.79 (3-Me), 167.84 (C^4), 55.46 (C^5), 50.75 (C^6). Found, %: Cl 21.15, 21.40. $C_{13}H_{11}Cl_2NO_3S$. Calculated, %: Cl 21.34.

Compound **XIIIb**. ^{1}H NMR spectrum, δ, ppm: 2.08 d (3H, Me), 4.52 q (1H, 6-H), 6.34 d (1H, 5-H, $J_{5,6}$ = 3.3 Hz), 6.50 q (1H, 2-H, $J_{2,6}$ = 1.8 Hz), 7.39–7.92 d.d (4H, C_6H_4), 2.47 s (3H, MeC_6H_4).

Compound **XIIIc**. Yield 79%, mp 138–139°C. ^{1}H NMR spectrum, δ, ppm: 2.10 d (3H, Me), 4.57 q (1H, 6-H), 6.20 d (1H, 5-H, $J_{5,6}$ = 3.3 Hz), 6.56 q (1H, 2-H, $J_{2,6}$ = 1.8 Hz), 7.82–8.91 m (4H, C_6H_4). Found, %: Cl 18.45, 18.64. $C_{13}H_{10}Cl_2N_2O_5S$. Calculated, %: Cl 18.8.

Compound **XVa**. Yield 68%, mp 183–184°C. Found, %: Cl 11.95, 12.15. $C_{13}H_{12}ClNO_3S$. Calculated, %: Cl 11.91.

Compound **XVIIa**. Yield 87%, mp 136–137°C. Found, %: Cl 11.85, 11.98. $C_{13}H_{12}ClNO_3S$. Calculated, %: Cl 11.91.

Compound **XVIIb**. Yield 88%, mp 161–62°C. Found, %: Cl 11.25, 11.34. $C_{14}H_{14}ClNO_3S$. Calculated, %: Cl 11.37.

Compound **XVIIc**. Yield 77%, mp 178–179°C. Found, %: Cl 10.28, 10.36. $C_{13}H_{11}ClN_2O_5S$. Calculated, %: Cl 10.34.

Compound **XIXa**. Yield 86%, mp 197–198°C. Found, %: Cl 21.30, 21.40. $C_{13}H_{11}Cl_2NO_3S$. Calculated, %: Cl 21.34.

Compound **XIXb**. Yield 92%, mp 182–183°C. Found, %: Cl 20.42, 20.53. $C_{14}H_{13}Cl_2NO_3S$. Calculated, %: Cl 20.48.

Compound **XIXc**. Yield 79%, mp 202–203°C. Found, %: Cl 18.78, 18.83. $C_{13}H_{10}Cl_2N_2O_5S$. Calculated, %: Cl 18.8.

Compound **XXIIa**. Yield 85%, mp 124–126°C. ^{1}H NMR spectrum, δ, ppm: 2.25 s (3H, Me), 6.64 s (1H, 5-H), 7.59–8.06 m (5H, C_6H_5). Found, %: Cl 35.30, 35.40. $C_{13}H_9Cl_4NO_3S$. Calculated, %: Cl 35.36.

Compound **XXIIb**. Yield 91%, mp 142–143°C. ^{1}H NMR spectrum, δ, ppm: 2.24 s (3H, Me), 6.66 s (1H, 5-H), 7.39–7.94 d.d (4H, C_6H_4), 2.49 s (3H, **Me**C_6H_4). ^{13}C NMR spectrum, δ_C, ppm: 174.83 (C^1), 135.83 (C^2), 146.46 (C^3), 17.02 (3-Me), 164.68 (C^4), 58.64 (C^5), 81.63 (C^6). Found, %: Cl 34.05, 34.15. $C_{14}H_{11}Cl_4NO_3S$. Calculated, %: Cl 34.16.

Compound **XXIVb**. Yield 61%, mp 189–190°C. ^{1}H NMR spectrum, δ, ppm: 2.52 s (3H, Me), 7.35–7.90 d.d (4H, C_6H_4), 2.47 s (3H, **Me**C_6H_4). ^{13}C NMR spectrum, δ_C, ppm: 170.39 (C^1), 138.91 (C^2), 143.39 (C^3), 18.94 (3-Me), 155.76 (C^4), 140.81 (C^5), 139.34 (C^6). Found, %: Cl 28.13, 28.19. $C_{14}H_{10}Cl_3NO_3S$. Calculated, %: Cl 28.09.

Compound **XXXIIc**. Yield 95%, mp 210–212°C. Found, %: Cl 18.50, 18.65. $C_{13}H_{10}Cl_2N_2O_5S$. Calculated, %: Cl 18.80.

Compound **XXXIIIc**. Yield 89%, mp 179–180°C. Found, %: Cl 18.95, 19.10. $C_{13}H_8Cl_2N_2O_5S$. Calculated, %: Cl 18.90.

Compound **XXXIVa**. Yield 93%, mp 131–132°C. ^{1}H NMR spectrum, δ, ppm: 2.02 s (3H, Me), 6.33 s (1H, 3-H), 7.59–8.08 m (5H, C_6H_5). Found, %: Cl 34.21, 33.89. $C_{13}H_9Cl_4NO_3S$. Calculated, %: Cl 35.36.

Compound **XXXIVb**. Yield 88%, mp 125–126°C. ^{1}H NMR spectrum, δ, ppm: 2.02 s (3H, Me), 6.35 s (1H, 3-H), 7.39–7.96 d.d (4H, C_6H_4), 2.48 s (3H, **Me**C_6H_4). Found, %: Cl 35.86, 35.97. $C_{14}H_{11}Cl_4NO_3S$. Calculated, %: Cl 34.16.

Compound **XXXIVc**. Yield 84%, mp 122–123°C. ^{13}C NMR spectrum, δ_C, ppm: 179.49 (C^1), 140.96 (C^2), 142.30 (C^3), 164.16 (C^4), 56.67 (C^5), 64.34 (C^6), 22.39 (6-Me). Found, %: Cl 31.85, 31.90. $C_{13}H_8Cl_4N_2O_5S$. Calculated, %: Cl 31.79.

Compound **XXXVa**. Yield 72%, mp 146–147°C. ^{1}H NMR spectrum, δ, ppm: 2.29 s (3H, Me), 8.44 s (1H, 5-H), 7.59–8.07 m (5H, C_6H_5). Found, %: Cl 20.15, 20.86. $C_{13}H_9Cl_2NO_3S$. Calculated, %: Cl 21.47.

Compound **XXXVb**. Yield 67%, mp 158–159°C. ^{1}H NMR spectrum, δ, ppm: 2.29 s (3H, Me), 8.46 s

(1H, 5-H), 7.39–7.93 d.d (4H, C_6H_4), 2.48 s (3H, **Me**C_6H_4). Found, %: Cl 21.48, 21.87. $C_{14}H_{11}Cl_2NO_3S$. Calculated, %: Cl 20.6.

Compound **XXXVIa**. Yield 63%, mp 148–149°C. ^{1}H NMR spectrum, δ, ppm: 1.94 s (3H, Me), 6.29 s (1H, 5-H), 6.91 s (1H, 2-H), 7.59–8.08 m (5H, C_6H_5). Found, %: Cl 30.05, 30.87. $C_{13}H_{10}Cl_3NO_3S$. Calculated, %: Cl 29.01.

Compound **XXXVIb**. Yield 69%, mp 136–137°C. ^{1}H NMR spectrum, δ, ppm: 1.93 s (3H, Me), 6.31 s (1H, 5-H), 6.90 s (1H, 2-H), 7.40–7.95 d.d (4H, C_6H_4), 2.48 s (3H, **Me**C_6H_4). Found, %: Cl 29.01, 28.65. $C_{14}H_{12}Cl_3NO_3S$. Calculated, %: Cl 27.94.

Compound **XXXVIIIa**. Yield 63%, mp 90–92°C. ^{1}H NMR spectrum, δ, ppm: *E* isomer: 2.00 s (3H, Me), 6.23 d (1H, 5-H), 7.08 d (1H, 3-H, $J_{3,5}$ = 2.7 Hz), 7.56–8.05 m (5H, C_6H_5); *Z* isomer: 1.95 s (3H, Me), 4.76 d (1H, 5-H), 8.31 d (1H, 3-H, $J_{3,5}$ = 3.0 Hz), 7.56–8.05 m (5H, C_6H_5). Found, %: Cl 27.56, 28.05. $C_{13}H_{10}Cl_3NO_3S$. Calculated, %: Cl 29.01.

The melting points and elemental analyses of compounds **XXXIIa**, **XXXIIb**, **XXXIIIa**, and **XXXIIIb** were reported in [15].

Compound **XXXIXa**. ^{1}H NMR spectrum, δ, ppm: 2.15 s (3H, Me), 8.40 s (1H, 3-H), 7.59–8.09 m (5H, C_6H_5).

Compound **XXXIXb**. ^{1}H NMR spectrum, δ, ppm: 2.15 s (3H, Me), 8.41 s (1H, 3-H), 7.40–7.93 d.d (4H, C_6H_4), 2.48 s (3H, **Me**C_6H_4).

Compound **XLa**. ^{1}H NMR spectrum, δ, ppm: 2.34 s (3H, Me), 6.65 s (1H, 5-H), 7.95–8.09 m (5H, C_6H_5).

Compound **XLb**. ^{1}H NMR spectrum, δ, ppm: 2.33 s (3H, Me), 6.67 s (1H, 5-H), 7.40–7.95 d.d (4H, C_6H_4), 2.48 s (3H, **Me**C_6H_4).

Bromination of compounds XIa–XIc, XIIa–XIIc, XXa–XXc, XXIa–XXIc, XXXa–XXXc, and XXXIa–XXXIc (*general procedure***).** To a solution of 2 mmol of the corresponding substrate in 3 ml of chloroform, acetic acid, or DMF–AcOH (1:5) we added dropwise under vigorous stirring a solution of bromine in the same solvent to attain a required substrate-to-bromine molar ratio (1:1, 1:3, 1:5, or 1:8). The products were purified by recrystallization from acetic acid. The melting points and analytical data are given below only for products isolated as individual substances.

Compound **XIVa**. Yield 64%, mp 152–153°C. ^{1}H NMR spectrum, δ, ppm: 2.09 d (3H, Me), 4.72 q (1H, 6-H), 6.43 d (1H, 5-H, $J_{5,6}$ = 3 Hz), 6.46 q (1H, 2-H, $J_{2,6}$ = 1.5 Hz), 7.58–8.07 m (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 186.94 (C^1), 132.28 (C^2), 149.24 (C^3), 18.87 (3-Me), 168.10 (C^4), 38.68 (C^5), 43.81 (C^6). Found, %: Br 37.86, 37.94. $C_{13}H_{11}Br_2NO_3S$. Calculated, %: Br 37.95.

Compound **XIVc**. Yield 67%, mp 120–121°C. ^{1}H NMR spectrum, δ, ppm: 2.10 d (3H, Me), 4.74 q (1H, 6-H), 6.32 d (1H, 5-H, $J_{5,6}$ = 3 Hz), 6.50 q (1H, 2-H, $J_{2,6}$ = 1.8 Hz), 7.82–8.91 m (4H, C_6H_4). Found, %: Br 34.01, 34.20. $C_{13}H_{10}Br_2N_2O_5S$. Calculated, %: Br 34.29.

Compound **XVIIIa**. Yield 70%, mp 180–181°C. Found, %: Br 23.20, 23.30. $C_{13}H_{12}BrNO_3S$. Calculated, %: Br 23.35.

Compound **XXa**. Yield 78%, mp 201–202°C. Found, %: Br 37.80, 37.85. $C_{13}H_{11}Br_2NO_3S$. Calculated, %: Br 37.95.

Compound **XXb**. Yield 72%, mp 153–154°C. Found, %: Br 36.69, 36.78. $C_{14}H_{13}Br_2NO_3S$. Calculated, %: Br 36.73.

Compound **XXc**. Yield 73%, mp 174–175°C. Found, %: Br 34.25, 34.29. $C_{13}H_{10}Br_2N_2O_5S$. Calculated, %: Br 34.29.

Compound **XXIIIa**. Yield 85%, mp 144–145°C. ^{1}H NMR spectrum, δ, ppm: 2.29 s (3H, Me), 6.80 s (1H, 5-H), 7.59–8.07 m (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 175.11 (C^1), 130.15 (C^2), 149.33 (C^3), 20.45 (3-Me), 165.31 (C^4), 49.79 (C^5), 56.59 (C^6). Found, %: Br 55.15, 55.23. $C_{13}H_9Br_4NO_3S$. Calculated, %: Br 55.21.

Compound **XXIIIb**. Yield 79%, mp 150–151°C. ^{1}H NMR spectrum, δ, ppm: 2.28 s (3H, Me^3), 6.83 s (1H, 5-H), 7.38–7.94 d.d (4H, C_6H_4), 2.48 s (3H, **Me**C_6H_4). Found, %: Br 53.86, 53.96. $C_{14}H_{11}Br_4NO_3S$. Calculated, %: Br 53.90.

Compound **XLIa**. Yield 95%, mp 210–211°C. Found, %: Br 37.35, 37.45. $C_{13}H_{11}Br_2NO_3S$. Calculated, %: Br 37.95.

Compound **XLIb**. Yield 91%, mp 160–161°C. Found, %: Br 36.78, 36.84. $C_{14}H_{13}Br_2NO_3S$. Calculated, %: Br 36.73.

Compound **XLIc**. Yield 88%, mp 184–185°C. Found, %: Br 34.42, 34.56. $C_{13}H_{10}Br_2N_2O_5S$. Calculated, %: Br 34.29.

Compound **XLIIa**. Yield 74%, mp 204–205°C. ^{1}H NMR spectrum, δ, ppm: 2.22 d (3H, Me), 8.13 q

(1H, 3-H, $J_{3,2\text{-Me}}$ = 1.8 Hz), 7.58–8.07 m (5H, C_6H_5). Found, %: Br 38.01, 38.12. $C_{13}H_9Br_2NO_3S$. Calculated, %: Br 38.13.

Compound **XLIIb**. Yield 69%, mp 189–190°C. ^{1}H NMR spectrum, δ, ppm: 2.22 d (3H, Me), 8.14 q (1H, 3-H, $J_{3,2\text{-Me}}$ = 1.5 Hz), 7.39–7.93 d.d (4H, C_6H_4), 2.48 s (3H, **Me**C_6H_4). Found, %: Br 36.59, 36.67. $C_{14}H_{11}Br_2NO_3S$. Calculated, %: Br 36.90.

Compound **XLIIc**. Yield 83%, mp 173–174°C. ^{1}H NMR spectrum, δ, ppm: 2.26 d (3H, Me), 8.04 q (1H, 3-H, $J_{3,Me}$ = 1.5 Hz), 7.82–8.92 m (4H, C_6H_4). Found, %: Br 34.26, 34.38. $C_{13}H_8Br_2N_2O_5S$. Calculated, %: Br 34.43.

Compound **XLIIIa**. Yield 89%, mp 142–143°C. ^{1}H NMR spectrum, δ, ppm: 2.20 s (3H, Me), 6.54 s (1H, 5-H), 7.58–8.08 m (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 179.71 (C^1), 138.03 (C^2), 140.53 (C^3), 163.35 (C^4), 45.70 (C^5), 55.23 (C^6), 25.27 (6-Me). Found, %: Br 55.36, 55.48. $C_{13}H_9Br_4NO_3S$. Calculated, %: Br 55.21.

Compound **XLIIIb**. Yield 92%, mp 148–149°C. ^{1}H NMR spectrum, δ, ppm: 2.20 s (3H, Me), 6.56 s (1H, 5-H), 7.40–7.95 d.d (4H, C_6H_4), 2.48 s (3H, **Me**C_6H_4). ^{13}C NMR spectrum, δ_C, ppm: 179.77 (C^1), 136.13 (C^2), 140.68 (C^3), 162.90 (C^4), 45.57 (C^5), 55.59 (C^6), 25.29 (6-Me). Found, %: Br 53.69, 53.73. $C_{14}H_{11}Br_4NO_3S$. Calculated, %: Br 53.90.

Compound **XLIIIc**. Yield 86%, mp 160–161°C. ^{1}H NMR spectrum, δ, ppm: 2.22 s (3H, Me), 6.41 s (1H, 5-H), 7.83–8.93 m (4H, C_6H_4). Found, %: Br 51.31, 51.42. $C_{13}H_8Br_4N_2O_5S$. Calculated, %: Br 51.23.

Compound **XLIVc**. Yield 70%, mp 131–132°C. ^{1}H NMR spectrum, δ, ppm: *Z* isomer: 2.22 d (3H, Me), 4.81 d (1H, 6-H), 4.95 q (1H, 5-H, $J_{5,6}$ = 3 Hz), 7.82 q (1H, 3-H, $J_{3,5}$ = 2.4, $J_{3,2\text{-Me}}$ = 1.5 Hz), 7.80–8.88 m (4H, C_6H_4); *E* isomer: 2.15 d (3H, Me), 4.78 d (1H, 6-H), 6.28 q (1H, 5-H, $J_{5,6}$ = 2.7 Hz), 6.70 q (1H, 3-H, $J_{3,5}$ = 2.4, $J_{3,2\text{-Me}}$ = 1.5 Hz), 7.80–8.88 m (4H, C_6H_4). Found, %: Br 34.35, 34.42. $C_{13}H_{10}Br_2N_2O_5S$. Calculated, %: Br 34.29.

Compound **XLVa**. Yield 63%, mp 143–144°C. Found, %: Br 23.48, 23.58. $C_{13}H_{10}BrNO_3S$. Calculated, %: Br 23.49.

Hydrochlorination of *N*-arylsulfonyl-3-methyl-1,4-benzoquinone imines XIa–XIc, *N*-arylsulfonyl-6-chloro-3-methyl-1,4-benzoquinone imines XXVIIIa–XXVIIIc, and *N*-arylsulfonyl-2-methyl-1,4-benzoquinone imines XXXa and XXXb (*general procedure***).** A stream of dry hydrogen chloride was passed over a period of 15–20 min through a solution of 0.01 mol of quinone imine **XIa**–**XIc**, **XXVIIIa**–**XXVIIIc**, **XXXa**, or **XXXb** in 5 ml of anhydrous chloroform. The reaction solution turned lighter, and a white solid separated. The precipitate was filtered off and recrystallized from acetic acid to isolate aminophenol **XVIIa**–**XVIIc**, **XIXa**–**XIXc**, **XLVIa**, or **XLVIb**. Oxidation of the products with lead tetraacetate according to the procedure described in [16] gave quinone imines **XXVIIIa**–**XXVIIIc**, **XXIXa**–**XXIXc**, **XXXVIIa**, and **XXXVIIb**.

Compound **XXVIIIa**. Yield 83%, mp 141–142°C. ^{1}H NMR spectrum, δ, ppm: 2.08 d (3H, Me), 6.69 q (1H, 2-H, $J_{2,3\text{-Me}}$ = 1.2 Hz), 8.40 s (1H, 5-H), 7.58–8.04 m (5H, C_6H_5). Found, %: Cl 11.94, 12.05. $C_{13}H_{10}ClNO_3S$. Calculated, %: Cl 11.99.

Compound **XXVIIIb**. Yield 92%, mp 130–132°C. ^{1}H NMR spectrum, δ, ppm: 2.07 d (3H, Me), 6.68 q (1H, 2-H, $J_{2,3\text{-Me}}$ = 1.2 Hz), 8.41 s (1H, 5-H), 7.37–7.91 d.d (4H, C_6H_4), 2.47 s (3H, **Me**C_6H_4). Found, %: Cl 11.37, 11.45. $C_{14}H_{12}ClNO_3S$. Calculated, %: Cl 11.44.

Compound **XXVIIIc**. Yield 86%, mp 212–213°C. ^{1}H NMR spectrum, δ, ppm: 2.09 d (3H, Me), 6.73 q (1H, 2-H, $J_{2,3\text{-Me}}$ = 1.2 Hz), 8.31 s (1H, 5-H), 7.82–8.88 m (4H, C_6H_4). Found, %: Cl 10.45, 10.50. $C_{13}H_9ClN_2O_5S$. Calculated, %: Cl 10.4.

Compound **XXIXa**. Yield 82%, mp 138–139°C. ^{1}H NMR spectrum, δ, ppm: 2.23 s (3H, Me), 8.45 s (1H, 5-H), 7.59–8.04 m (5H, C_6H_5). Found, %: Cl 21.38, 21.45. $C_{13}H_9Cl_2NO_3S$. Calculated, %: Cl 21.47.

Compound **XXIXb**. Yield 82%, mp 127–129°C. ^{1}H NMR spectrum, δ, ppm: 2.22 s (3H, Me), 8.46 s (1H, 5-H), 7.39–7.90 d.d (4H, C_6H_4), 2.48 s (3H, **Me**C_6H_4). Found, %: Cl 20.54, 20.60. $C_{14}H_{11}Cl_2NO_3S$. Calculated, %: Cl 20.6.

Compound **XXIXc**. Yield 83%, mp 142–143°C. ^{1}H NMR spectrum, δ, ppm: 2.23 s (3H, Me), 8.35 s (1H, 5-H), 7.83–8.87 m (4H, C_6H_4). Found, %: Cl 18.85, 18.95. $C_{13}H_8Cl_2N_2O_5S$. Calculated, %: Cl 18.9.

Compound **XXXVIIa**. Yield 86%, mp 132–133°C. ^{1}H NMR spectrum, δ, ppm: *E* isomer: 2.20 d (3H, Me), 7.12 d (1H, 5-H), 8.02 q (1H, 3-H, $J_{3,5}$ = 2.4 Hz), 7.59–8.08 m (5H, C_6H_5); *Z* isomer: 2.12 d (3H, Me), 6.82 q (1H, 3-H), 8.39 d (1H, 5-H, $J_{3,5}$ = 2.4 Hz),

7.59–8.08 m (5H, C_6H_5). Found, %: Cl 11.08, 11.17. $C_{13}H_{10}ClNO_3S$. Calculated, %: Cl 11.99.

Compound **XXXVIIb**. Yield 84%, mp 120–121°C. ^{1}H NMR spectrum, δ, ppm: *E* isomer: 2.20 d (3H, Me), 7.11 d (1H, 5-H), 8.04 q (1H, 3-H, $J_{3,5}$ = 2.1 Hz), 7.38–7.89 d.d (4H, C_6H_4), 2.47 s (3H, **Me**C_6H_4); *Z* isomer: 2.12 d (3H, Me), 6.82 q (1H, 3-H), 8.40 d (1H, 5-H, $J_{3,5}$ = 2.1 Hz), 7.38–7.89 d.d (4H, C_6H_4), 2.47 s (3H, **Me**C_6H_4). Found, %: Cl 11.69, 11.78. $C_{14}H_{12}ClNO_3S$. Calculated, %: Cl 11.44.

Compound **XLVIa**. Yield 96%, mp 159–160°C. Found, %: Cl 11.85, 11.95. $C_{13}H_{12}ClNO_3S$. Calculated, %: Cl 11.91.

Compound **XLVIb**. Yield 93%, mp 140–141°C. Found, %: Cl 11.28, 11.34. $C_{14}H_{14}ClNO_3S$. Calculated, %: Cl 11.37.

Hydrobromination of *N*-arylsulfonyl-3-methyl-1,4-benzoquinone imines XIa–XIc and *N*-arylsulfonyl-6-bromo-3-methyl-1,4-benzoquinone imines XXVIa–XXVIc (*general procedure***).** Quinone imine **XIa**–**XIc** or **XXVIa**–**XXVIc**, 0.01 mol, was dissolved in 10 ml of acetic acid, and 2 ml of 46% hydrobromic acid was added in portions under stirring. The solution turned lighter. After addition of water, a colorless solid separated and was filtered off and recrystallized from acetic acid. We thus obtained compounds **XVIIIa**–**XVIIIc** and **XXa**–**XXc** which were identical to the corresponding bromination products. Compounds **XVIIIa**–**XVIIIc** were oxidized to quinone imines **XXVIa**–**XXVIc** with lead tetraacetate according to the procedure described in [16].

Compound **XXIa**. Yield 75%, mp 166–167°C. ^{1}H NMR spectrum, δ, ppm: 2.26 s (3H, Me), 8.71 s (1H, 5-H), 7.59–8.04 m (5H, C_6H_5). Found, %: Br 38.05, 38.20. $C_{13}H_9Br_2NO_3S$. Calculated, %: Br 38.13.

Compound **XXIb**. Yield 71%, mp 146–147°C. ^{1}H NMR spectrum, δ, ppm: 2.25 s (3H, Me), 8.72 s (1H, 5-H), 7.38–7.91 d.d (4H, C_6H_4), 2.48 s (3H, **Me**C_6H_4). Found, %: Br 36.75, 36.86. $C_{14}H_{11}Br_2NO_3S$. Calculated, %: Br 36.90.

Compound **XXIc**. Yield 78%, mp 160–161°C. ^{1}H NMR spectrum, δ, ppm: 2.26 s (3H, Me), 8.62 s (1H, 5-H), 7.83-8.87 m (4H, C_6H_4). Found, %: Br 34.49, 34.54. $C_{13}H_8Br_2N_2O_5S$. Calculated, %: Br 34.43.

Compound **XXVIa**. Yield 85%, mp 148–149°C. ^{1}H NMR spectrum, δ, ppm: 2.07 d (3H, Me), 6.74 q (1H, 2-H, $J_{2,3\text{-Me}}$ = 1.2 Hz), 8.67 s (1H, 5-H), 7.57–8.04 m (5H, C_6H_5). Found, %: Br 23.40, 23.49. $C_{13}H_{10}BrNO_3S$. Calculated, %: Br 23.49.

Compound **XXVIb**. Yield 95%, mp 137–139°C. ^{1}H NMR spectrum, δ, ppm: 2.07 d (3H, Me), 6.72 q (1H, 2-H, $J_{2,3\text{-Me}}$ = 1.5 Hz), 8.69 s (1H, 5-H), 7.37–7.91 d.d (4H, C_6H_4), 2.47 s (3H, **Me**C_6H_4). Found, %: Br 22.54, 22.63. $C_{14}H_{12}BrNO_3S$. Calculated, %: Br 22.56.

Compound **XXVIc**. Yield 89%, mp 216–217°C. ^{1}H NMR spectrum, δ, ppm: 2.08 d (3H, Me), 6.78 q (1H, 2-H, $J_{2,3\text{-Me}}$ = 1.5 Hz), 8.58 s (1H, 5-H), 7.82–8.88 m (4H, C_6H_4). Found, %: Br 20.70, 20.79. $C_{13}H_9BrN_2O_5S$. Calculated, %: Br 20.74.

Compound **XLVa**. ^{1}H NMR spectrum, δ, ppm: *Z* isomer: 2.22 d (3H, Me), 7.40 d (1H, 5-H), 8.00 q (1H, 3-H, $J_{3,5}$ = 2.4, $J_{3,\text{Me}}$ = 1.5 Hz), 7.58–8.02 m (5H, C_6H_5); *E* isomer: 2.13 d (3H, Me), 6.83 q (1H, 3-H, $J_{3,2\text{-Me}}$ = 1.5 Hz), 8.67 d (1H, 5-H, $J_{3,5}$ = 2.4 Hz), 7.58–8.02 m (5H, C_6H_5).

Compound **XLVb**. ^{1}H NMR spectrum, δ, ppm: *Z* isomer: 2.21 d (3H, Me), 7.39 d (1H, 5-H), 8.03 q (1H, 3-H, $J_{3,5}$ = 2.4, $J_{3,2\text{-Me}}$ = 1.5 Hz), 7.38–7.88 d.d (4H, C_6H_4), 2.47 s (3H, **Me**C_6H_4); *E* isomer: 2.12 d (3H, Me), 6.81 q (1H, 3-H, $J_{3,2\text{-Me}}$ = 1.2 Hz), 8.68 d (1H, 5-H, $J_{3,5}$ = 2.4 Hz), 7.38–7.88 d.d (4H, C_6H_4), 2.47 s (3H, **Me**C_6H_4).

Compound **XLVc**. ^{1}H NMR spectrum, δ, ppm: *Z* isomer: 2.25 d (3H, Me), 7.41 d (1H, 5-H), 7.94 q (1H, 3-H, $J_{3,5}$ = 2.4, $J_{3,2\text{-Me}}$ = 1.5 Hz), 7.80–8.88 m (4H, C_6H_4); *E* isomer: 2.17 d (3H, Me), 6.84 q (1H, 3-H, $J_{3,2\text{-Me}}$ = 1.5 Hz), 8.54 d (1H, 5-H, $J_{3,5}$ = 2.4 Hz), 7.80–8.88 m (4H, C_6H_4).

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