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Halogenation of N-Substituted *p*-Quinone Monoimines and *p*-Quinone Monooxime Esters: VII.* Halogenation of 4-Aroyl(arylsulfonyl)imino- and 4-Aroyl(arylsulfonyl)-oxyimino-2,6-diisopropylcyclohexa-2,5-dien-1-ones

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Abstract—Halogenation of 4-aroyl(arylsulfonyl)imino-2,6-diisopropylcyclohexa-2,5-dien-1-ones gave 4-aroyl-(arylsulfonyl)imino-3-halo-2,6-diisopropylcyclohexa-2,5-dien-1-ones and 4-aroyl(arylsulfonyl)imino-3,5,6-trihalo-2,6-diisopropylcyclohex-2-en-1-ones. The latter were formed as mixtures of two stereoisomers, and the isopropyl group on the sp^3-hybridized carbon atom in one stereoisomer occupies axial position, which is untypical of such compounds. Halogenation of 4-aroyl(arylsulfonyl)oxyimino-2,6-diisopropylcyclohexa-2,5-dien-1-ones leads to the formation of the corresponding addition products with traditional *trans*-diaxial arrangement of the halogen atoms.

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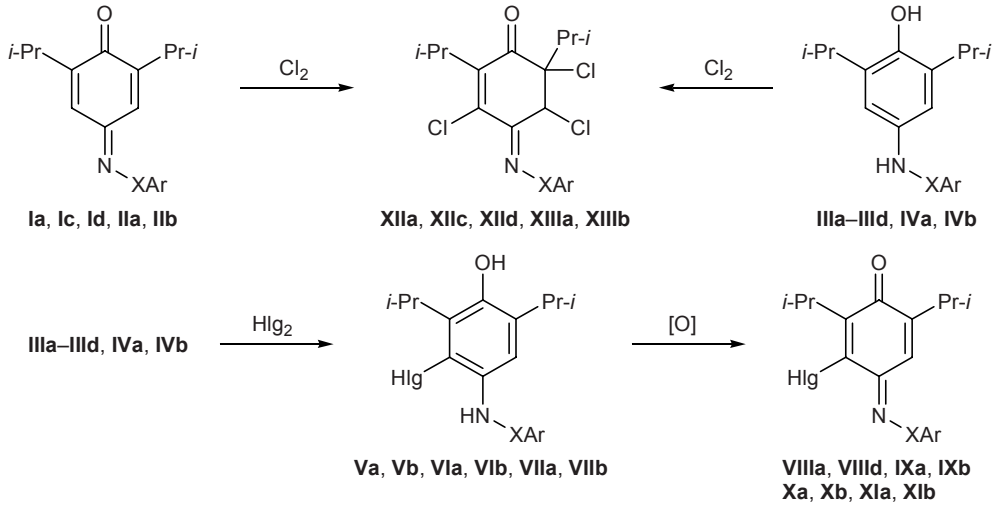
The present work continues our studies in the field of halogenation of N-substituted 1,4-benzoquinone monoimines [1] and 1,4-benzoquinone monooxime ethers [2]. On the basis of our experimental data and the results of semiempirical calculations we previously presumed that halogenation of 1,4-benzoquinone imines and 1,4-benzoquinone oxime ethers initially involves formation of intermediate halonium ion or carbocation [1–3]. According to semiempirical calculations, in the bromination of 1,4-benzoquinone oxime ethers, bromonium ion is more thermodynamically stable [2], so that the process is strictly stereoselective (only *trans*-addition is possible), and the products are characterized by *trans*-diaxial arrangement of the bromine atoms. In the halogenation of *N*-arylsulfonyl-1,4-benzoquinone imines, the corresponding carbocation is thermodynamically more stable [1], and the process is completely regioselective but not strictly stereoselective: the addition occurs at only one C=C bond in the quinoid ring, but both *trans*- and *cis*-addition is possible. The stereoisomer ratio depends on the steric structure of intermediate carbocation.

The results of our previous studies on the UV and ^{1}H NMR spectra (specifically, 2-H–3-H and 5-H–6-H coupling constants) of 5,6-dichlorocyclohex-2-ene-1,4-diones formed by addition of a halogen molecule to 1,4-benzoquinones led us to assign *trans*-diaxial orientation of chlorine atoms in their molecules [4, 5]. Our subsequent studies on halogenation of quinoid systems showed that addition of halogens across the quinoid C=C bonds gives products in which the halogen atoms at the sp^3-hybridized carbon atoms always occupy axial positions and are arranged *trans* while hydrogen atoms or alkyl groups occupy equatorial positions [2]. In most cases, the substrates were methyl-substituted benzoquinone derivatives. No halogenation products with axial orientation of alkyl substituents were detected.

Taking into account the data of [1, 2], we anticipated that the presence of bulky electron-donating groups in the quinoid ring and polar solvents should

* For communication VI, see [1].

Scheme 1.



Ia, **Ic**, **Id**, **IIa**, **IIb** — **XIIa**, **XIIc**, **XIId**, **XIIIa**, **XIIIb** — **IIIa–IIId**, **IVa**, **IVb**

IIIa–IIId, **IVa**, **IVb** — **Va**, **Vb**, **VIa**, **VIb**, **VIIa**, **VIIb** — **VIIIa**, **VIIId**, **IXa**, **IXb** **Xa**, **Xb**, **XIa**, **XIb**

Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-$MeOC_6H_4$ (**c**), 4-$O_2NC_6H_4$ (**d**); **I**, **III**, **V**, **VIII**, **IX**, **XII**, X = CO; **II**, **IV**, **VI**, **VII**, **X**, **XI**, **XIII**, X = SO_2; **VI**, **VIII**, **X**, Hlg = Cl; **V**, **VII**, **IX**, **XI**, Hlg = Br.

stabilize the corresponding carbocation and hence favor formation of halogen addition products having axially oriented alkyl groups [3, 6]. Thus the goal of the present work was to elucidate how bulky electron-donating isopropyl groups in positions *2* and *6* of the quinoid ring and solvent polarity affect halogenation of N-substituted 1,4-benzoquinone imines and 1,4-benzoquinone oxime ethers. For this purpose we examined halogenation of 4-aroyl(arylsulfonyl)imino-2,6-diisopropylcyclohexa-2,5-dien-1-ones **I** and **II** and their reduction products, the corresponding 4-aroyl(arylsulfonyl)amino-2,6-diisopropylphenols **III** and **IV** (Scheme 1).

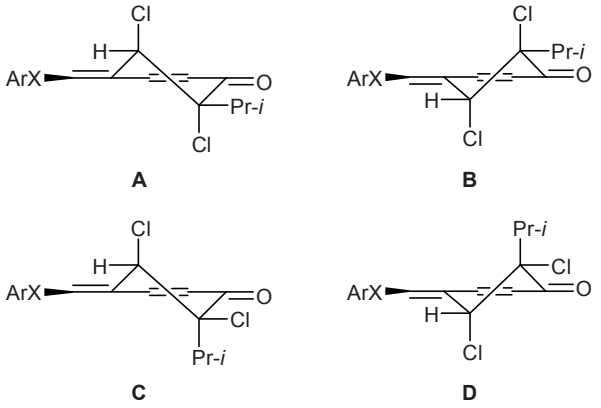
Compounds **I** and **II** were treated with gaseous chlorine or molecular bromine in different solvents ($CHCl_3$, AcOH, AcOH–DMF, 5:1) using various substrate-to-reagent ratios. The chlorination of benzoquinone imines **Ia**, **Ic**, **Id**, **IIa**, and **IIb** gave mainly the corresponding 4-aroyl(arylsulfonyl)imino-3,5,6-trichloro-2,6-diisopropylcyclohex-2-en-1-ones **XIIa**, **XIIc**, **XIId**, **XIIIa**, and **XIIIb**. We failed to isolate intermediate semiquinoid compounds, addition products of one chlorine molecule to quinone imines, presumably because of their instability. Such compounds, 4-aroyl(arylsulfonyl)imino-5,6-dichloro-2,6-diisopropylcyclohex-2-en-1-ones, are analogs of 4-arylsulfonylimino-5,6-dichloro-2,6-dimethylcyclohex-2-en-1-ones (products of addition of one chlorine molecule to *N*-arylsulfonyl-2,6-dimethyl-1,4-benzoquinone imines), which were obtained previously only as mixtures with the corresponding dehydrohalogenation products, quinone imines [7]. 4-Arylsulfonylimino-5,6-dichloro-2,6-dimethylcyclohex-2-en-1-ones were found to exist as two isomers. As we noted in [7], semiquinoid compounds capable of undergoing *Z*,*E* isomerization with respect to the C=N bond become highly reactive, for *cis*-arrangement of the substituent on the nitrogen atom relative to the C=C bond favors their dehydrohalogenation [7].

The bromination of quinone imines **Ia**, **Ic**, **Id**, **IIa**, and **IIb** led to the formation of noncrystallizable oily mixtures of products whose composition was not determined.

Depending on the solvent nature and reactant ratio, halogenation of 4-aroyl(arylsulfonyl)amino-2,6-diisopropylphenols **IIIa**–**IIId**, **IVa**, and **IVb** afforded 4-aroylamino-3-bromo-2,6-diisopropylphenols **Va** and **Vb**, 4-arylsulfonylamino-3-halo-2,6-diisopropylphenols **VIa**, **VIb**, **VIIa**, and **VIIb**, and semiquinoid compounds **XIIa**, **XIIc**, **XIId**, **XIIIa**, and **XIIIb**. *N*-Aroyl(arylsulfonyl)-3-bromo-2,6-diisopropyl-1,4-benzoquinone imines **IXa**, **IXb**, **XIa**, and **XIb** and *N*-arylsulfonyl-3-chloro-2,6-diisopropyl-1,4-benzoquinone imines **Xa** and **Xb** were obtained by oxidation of the corresponding aminophenols **Va**, **Vb**, **VIa**, **VIb**, **VIIa**, and **VIIb** with lead tetraacetate. We failed to isolate individual *N*-aroyl-3-chloro-2,6-diisopropyl-1,4-benzoquinone imines **VIIIa** and **VIIId** in the chlorination of quinone imines **Ia** and **Id** and aminophenols **IIIa** and **IIId**. Compounds **VIIIa** and **VIIId** were isolated as mixtures with semiquinoid derivatives **XIIIa** and **XIIId** in the chlorination of quinone imines **Ia** and **Id**.

The structure of the isolated compounds was proved by the IR and ^{1}H and ^{13}C NMR spectra and elemental analyses. The ^{1}H NMR spectra were recorded only for compounds having quinoid or semiquinoid structure. In the ^{1}H NMR spectra of quinone imines **X** and **XI**, the 5-H signal appeared as a broadened singlet at δ 7.92–7.94 ppm. The 5-H proton in the spectra of compounds **VIII** and **IX** resonated as a broadened singlet at δ 6.61–6.64 ppm. According to the ^{1}H and ^{13}C NMR data, compounds **XIIa**, **XIIc**, **XIId**, **XIIIa**, and **XIIIb** in solution exist as two isomers. By repeated recrystallization of compound **XIId** we succeeded in isolating its individual isomers which had different melting points.

Molecules of semiquinoid compounds **XIIa**, **XIIc**, **XIId**, **XIIIa**, and **XIIIb** possess two chiral centers (sp^3-hybridized carbon atoms); therefore, they can exist as four diastereoisomers or two couples of enantiomers **A**/**B** and **C**/**D**. While analyzing the steric structure of these compounds, we assumed that the substituent on the nitrogen atom is oriented *trans* with respect to the halogen atom at the C=C bond (the latter is characterized by a larger conformational volume than that attached to sp^3-hybridized carbon atom, C^5), i.e., compounds **XII** and **XIII** are *E* isomers.



Provided that the *E* configuration persists and that the cyclohexene ring inversion is slow on the NMR time scale, The ^{1}H NMR spectra should display four sets of signals belonging to eight possible conformers (enantiomer couples in achiral solvents give only one set of signals in ^{1}H and ^{13}C NMR spectra). X-Ray diffraction data for some structurally related compounds showed disorder of sp^3-hybridized carbon atoms with different populations for enantiomeric structures like **A** and **B** [8, 9], which may be responsible for their optical activity [10]. As we already noted, such differences in the steric structure of the compounds under study are not reflected in the ^{1}H and ^{13}C NMR spectra. Analysis of the ^{1}H and ^{13}C NMR spectra of **XIIa**, **XIIc**, **XIId**, **XIIIa**, and **XIIIb** showed that different chemical shifts of proton at the sp^3-carbon atom and protons in the isopropyl groups may result from different spatial orientations of the isopropyl group and chlorine atom with respect to each other; i.e., these compounds are diastereoisomers **B** and **D**.

Differences in the steric structure of diastereoisomers **B** and **D** are clearly observed in the ^{1}H NMR spectra where the 5-H protons and CH protons in the isopropyl groups have different chemical shifts. In the ^{1}H NMR spectrum of diastereoisomer **B**, the 5-H signal appears as a singlet at δ 5.00–5.03 (aroyl derivatives **XIIa**, **XIIc**, and **XIId**) or 6.37–6.40 ppm (sulfonyl derivatives **XIIIa** and **XIIIb**); the CH proton in the isopropyl group attached to C^6 (sp^3) resonates as a multiplet at δ 2.61–2.76 (**XII**) or 2.72–2.82 ppm (**XIII**). The other diastereoisomer **D** is characterized by 5-H signal at δ 5.14–5.17 (**XII**) or 6.34–6.36 ppm (**XIII**) and 6-CH signal at δ 2.31–2.44 (**XII**) or 2.25–2.36 ppm (**XIII**).

In the ^{13}C NMR spectra of diastereoisomers **B** and **D**, the largest difference in chemical shifts is observed for the sp^3-hybridized C^6 carbon atom bearing isopropyl group. The chemical shifts of C^5 and C^6 in diastereoisomer **B** of **XIId** are δ_C 55.8 and 74.4 ppm, respectively, and the chemical shifts of C^5 and C^6 in diastereoisomer **D** of **XIIa** and **XIId** are δ_C 60.1, 59.7 and 83.9, 83.5 ppm, respectively. The differences in the carbon chemical shifts ($\Delta\delta_C$) between diastereoisomers **B** and **D** are as follows, ppm: –8.98 (C^6), –3.89 (C^5), 0.29 (C^1), 0.61 (C^2), 0.52 (C^3), 0.95 (C^4), –6.40 (C^7), –0.48 and –1.85 (C^8, C^9), 0.01 (C^{10}), 0.13 and 0.21 (C^{11}, C^{12}), 0.13 (C^{13}), 0.33 (C^{14}), –0.15 (C^{15}, C^{19}), –0.04 (C^{16}, C^{18}), –0.03 (C^{17}); these values are very consistent with spatial arrangement of carbon atoms in structures **B** and **D**. In the ^{13}C NMR spectrum recorded without decoupling from protons, the C^5 signal of diastereoisomer **B** of **XIId** appeared as a doublet, and the C^6 atom resonated as a multiplet; the C^5 and C^6 signals of diastereoisomer **D** were a doublet of doublets and a multiplet, respectively. These spectral data may be useful for determination of the steric structure of halogen addition products at the C=C bond in the quinoid ring.

The structure of the isolated individual diastereoisomers of **XIId** was unambiguously proved by X-ray analysis. The isomer with lower melting point was shown to have structure **B** with equatorial orientation

of the isopropyl group on C^6 (Fig. 1). Correspondingly, the high-melting isomer of **XIId** has structure **D** with axial orientation of the isopropyl group on C^6 (Fig. 2). The semiquinoid ring in both stereoisomers has a conformation intermediate between *half-chair* and *sofa* with the following puckering parameters [11]: S = 0.75, Θ = 28.8°, Ψ = 8.1° (**B**); S = 0.71, Θ = 39.2°, Ψ = 12.9° (**D**). The deviations of the C^5 and C^6 atoms from the mean-square plane formed by the other ring carbon atoms were, respectively, –0.13 and 0.54 Å (**B**) and 0.16 and –0.55 Å (**D**).

The isopropyl group on C^2 is turned in such a way that the C^{10}–H bond in both stereoisomers appears in a conformation close to *synperiplanar* [the torsion angle $C^3C^2C^{10}H^{10}$ is 23° in **B** and –7.6° in **D**). This conformation gives rise to steric repulsion between the substituents at the endocyclic double bond {shortened intramolecular contact $H^{10}\cdots Cl^1$ 2.60 (**B**), 2.51 Å (**D**); sum of van der Waals radii 3.06 Å [12]}. The chlorine atom on C^5 in both stereoisomers occupies equatorial position [torsion angle $C^3C^4C^5Cl^2$ –83.5(2)° (**B**), –87.4(3)° (**D**)]. Stereoisomers **B** and **D** differ by orientation of the substituents on C^6: the chlorine atom in **B** occupies axial position, and in **D**, equatorial [torsion angle $C^2C^1C^6Cl^3$ –60.1(2)° (**B**) and 167.1(2)° (**D**)]. Correspondingly, the isopropyl group on C^6 in **B** is equatorial, and in **D**, axial: its arrangement with respect to the C^1–C^6 bond is characterized by the following torsion angles: $C^2C^1C^6C^7$ 178.7(2)° (**B**), –70.7(4)° (**D**) and $C^1C^6C^7H^7$ –53.3° (**B**), 59.8° (**D**). The presence of fairly bulky substituents in the cyclohexene ring and their mutual arrangement produce an appreciable steric strain, as follows from the shortened intramolecular contacts $H^5\cdots C^8$ 2.62 Å (**B**, **D**; sum of van der Waals radii 2.87 Å); $H^5\cdots H^{8a}$ 2.21 (**B**), 2.07 Å (**D**) (2.34 Å); $H^7\cdots Cl^2$ 2.84 Å (**B**) (3.07 Å), $H^7\cdots C^3$ 2.79 Å (**D**) (2.87 Å); $H^7\cdots C^4$ 2.67 Å (**D**) (2.87 Å); $H^{8b}\cdots Cl^3$ 2.82 (**B**), 2.78 Å (**D**) (3.06 Å); $H^{8c}\cdots C^5$ 2.70 (**B**), 2.69 Å (**D**) (2.87 Å); $H^{9a}\cdots Cl^3$ 2.76 (**B**), 2.79 Å (**D**) (3.06 Å); $H^{9c}\cdots C^1$ 2.77 (**B**), 2.63 Å (**D**) (2.87 Å); $H^{12a}\cdots C^1$ 2.83 Å (**B**) (2.87 Å). Steric strain in isomer **B** with equatorial orientation of the 6-isopropyl group induces twisting of the endocyclic double bond [torsion angle $C^1C^2C^3C^4$ 7.2(3)°] and makes the endo- and exocyclic double bonds noncoplanar [torsion angles $O^1C^1C^2C^3$ 147.8(2)°, $C^2C^3C^4N^1$ 167.7(2)°]. Isomer **D** with axial orientation of the isopropyl group on C^6 is characterized by weaker steric strain, and only noncoplanarity of the C=C and C=O bonds is observed [torsion angle $O^1C^1C^2C^3$ 163.4(4)°].

The substituent on the nitrogen atom occupies *synperiplanar* position with respect to the C^4–C^5 bond and is almost orthogonal to the C^4–N^1 bond [torsion angles $C^{13}N^1C^4C^5$ –6.3(3)° (**B**), 3.4(5)° (**D**) and $C^4N^1C^{13}O^2$ –87.0(3)° (**B**), 84.1(5)° (**D**)], presumably due to appreciable repulsion between the H^5 and C^{13} atoms [shortened intramolecular contact $H^5\cdots C^{13}$ 2.52 (**B**), 2.55 Å (**D**) (2.87 Å)]. In addition, such orientation of the substituent on the nitrogen atom is stabilized by the attractive interaction $H^{15}\cdots N^1$ 2.58 (**B**), 2.53 Å (**D**) (sum of van der Waals radii 2.67 Å). The nitro group is almost coplanar to the aromatic ring plane [torsion angle $O^4N^2C^{17}C^{18}$ 14.3(3)° (**B**), 4.5(6)° (**D**)], which is

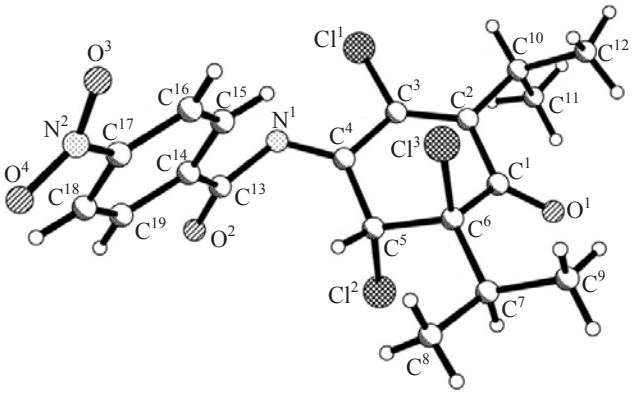


Fig. 1. Structure of the molecule of 3,5,6-trichloro-2,6-diisopropyl-4-(4-nitrobenzoylimino)cyclohex-2-en-1-one (**XIId**, diastereoisomer **B** with equatorial orientation of the isopropyl group on C^6) according to the X-ray diffraction data.

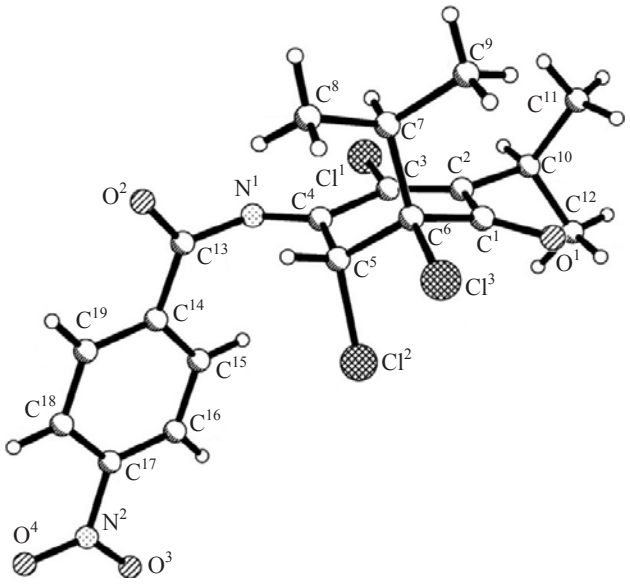


Fig. 2. Structure of the molecule of 3,5,6-trichloro-2,6-diisopropyl-4-(4-nitrobenzoylimino)cyclohex-2-en-1-one (**XIId**, diastereoisomer **G** with axial orientation of the isopropyl group on C^6) according to the X-ray diffraction data.

favored by the attractive interactions $H^{16}\cdots O^3$ 2.47 (**B**), 2.40 Å (**D**) and $H^{18}\cdots O^4$ 2.42 (**B**), 2.44 Å (**D**).

Thus the structure of cyclohexene structures **XIIa**, **XIIc**, **XIId**, **XIIIa**, and **XIIIb** suggests that the chlorination of benzoquinone imines **Ia**, **Ic**, **Id**, **IIa**, and **IIb** involves initial formation of the corresponding carbocation, followed by *trans*- or c*is*-addition of the second chlorine atom. The formation of carbocation is favored by the presence of a bulky electron-donating isopropyl group in the *ortho*-position with respect to the carbonyl carbon atom.

Preferential formation of intermediate carbocation and hence of stereoisomer **D** with axially oriented isopropyl group should also be favored by polar solvent. We performed chlorination of compounds **Id** and **IIb** in chloroform and acetic acid, and examined the product structure before recrystallization. When the reaction was carried out in chloroform, stereoisomer **B** prevailed among the products: the **B**:**D** isomer ratio was 84:16 for compound **XIId** and 60:40 for **XIIIb**. In going to acetic acid, stereoisomer **D** became the major product: the **B**:**D** isomer ratio was 22:78 for compound **XIId** and 15:85 for **XIIIb**. These data provide an additional support to the assumption that halogenation of quinoid systems involves formation of carbocationic species, which is favored by increased solvent polarity.

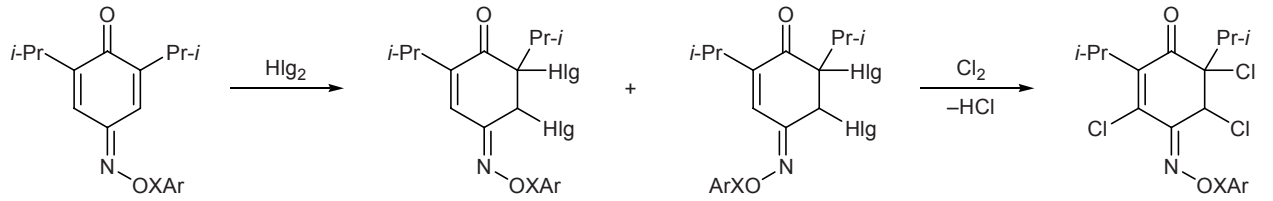
We previously reported [13] on the halogenation of 4-aroyl(arylsulfonyl)oxyimino-2,6-diisopropylcyclohexa-2,5-dien-1-ones which afforded only *E* isomers of the corresponding 4-aroyl(arylsulfonyl)oxyimino-5,6-dihalo-2,6-diisopropylcyclohex-2-en-1-ones with *trans* arrangement of the ArXO group and C=C bond in the cyclohexene ring with respect to the C=N bond. It was concluded that halogenation of quinone oxime ethers is strictly *syn*-regioselective. The products were analyzed by ^{1}H NMR spectroscopy after recrystallization. We failed to obtain products of more profound halogenation, for dehydrohalogenation of the dihalo derivatives was impossible [13]. In the present work we performed halogenation of 4-aroyloxyimino- and 4-arylsulfonyloxyimino-2,6-diisopropylcyclohexa-2,5-dien-1-ones **XIVa**, **XIVb**, **XVa**, and **XVb** and examined the product mixtures with a view to detect *Z* isomers and stereoisomers analogous to those formed in the halogenation of quinone imines **I** and **II**. The results are illustrated by Scheme 2.

Taking into account previously published data [2], we presumed that halogenation of 1,4-benzoquinone oxime ethers should give no stereoisomers with axially oriented alkyl group (in this case, intermediate formation of carbocation is energetically less favorable than the formation of halonium ion). The halogenation products contained no compounds that could be formed from intermediate carbocation [2].

The halogenation of **XIVa**, **XIVb**, **XVa**, and **XVb** was carried out under severe conditions, in DMF at elevated temperature, using a considerable excess of halogen. Both chlorination and bromination of compounds **XIVa**, **XIVb**, **XVa**, and **XVb** gave mixtures of the corresponding *E* and *Z* isomers, the former prevailing. The *E*/*Z* ratio for 4-(4-chlorobenzoyloxyimino)-5,6-dichloro-2,6-diisopropylcyclohex-2-en-1-one (**XVIb**) was 95:5, whereas 4-(4-methylbenzoyloxyimino)-5,6-dichloro-2,6-diisopropylcyclohex-2-en-1-one (**XVIa**) was isolated only as *E* isomer. In the halogenation of 4-arylsulfonyloxyimino-2,6-diisopropylcyclohexa-2,5-dien-1-ones **XVa** and **XVb** the ratios *E*-**XVIIIa**/*Z*-**XVIIIa**, *E*-**XIXa**/*Z*-**XIXa**, and *E*-**XIXb**/*Z*-**XIXb** were 92:8, 95:5, and 58:42, respectively. Only the bromination of 4-(4-chlorobenzoyloxyimino)cyclohexa-2,5-dien-1-one (**XIVb**) gave a mixture of isomers *E*-**XVIIb** and *Z*-**XVIIb** at a ratio of 32:68.

Thus we can state that halogenation of 1,4-benzoquinone oxime ethers having two isopropyl groups in positions *2* and *6* of the quinoid ring gives mainly the corresponding *syn*-addition products.

Scheme 2.



XIVa, **XIVb**, **XVa**, **XVb**

E-**XVIa**, *E*-**XVIb**, *E*-**XVIIb** *E*-**XVIIIa**, *E*-**XIXa**, *E*-**XIXb**

Z-**XVIb**, *Z*-**XVIIb**, *Z*-**XVIIIa** *Z*-**XIXa**, *Z*-**XIXb**

E-**XXa**, *E*-**XXb**, *E*-**XXIa**

Ar = 4-MeC_6H_4 (**a**), 4-ClC_6H_4 (**b**); **XIV**, **XVI**, **XVII**, **XX**, X = CO; **XV**, **XVIII**, **XIX**, **XXI**, X = SO_2; **XVI**, **XVIII**, Hlg = Cl; **XVII**, **XIX**, X = Br.

Analysis of the chemical shifts of protons in the cyclohexene ring and CH protons in the isopropyl groups at sp^3- and sp^2-carbon atoms in the ^{1}H NMR spectra of compounds **XVI**–**XXI**, as well as the position of signals from sp^3-hybridized carbon atoms in the ^{13}C NMR spectrum of *E*-**XVIb**, indicate that the halogen atoms in both *syn* and *anti* isomers of **XVI**–**XIX** occupy axial positions and are arranged *trans* with respect to each other. Correspondingly, the isopropyl group on C^6 is equatorial. In other words, the halogenation of benzoquinone oxime ethers gives only one stereoisomer like **B** with equatorial alkyl group. Unlike benzoquinone imines, the formation of halogenation products **XIVa**, **XIVb**, **XVa**, and **XVb** with only *trans*-diaxial orientation of the halogen atoms is consistent with the assumption that the process involves initial formation of halonium ion.

In the chlorination of benzoquinone oxime ethers **XIVa**, **XIVb**, and **XVa**, the products were mixtures of the corresponding 4-aroyl(arylsulfonyl)oxyimino-5,6-dichloro-2,6-diisopropylcyclohex-2-en-1-ones and 4-aroyl(arylsulfonyl)oxyimino-3,5,6-trichloro-2,6-diisopropylcyclohex-2-en-1-ones **XXa**, **XXb**, and **XXIa** (Scheme 2). In keeping with the ^{1}H NMR data, these compounds exist as *E* isomers. Insofar as quinone oximes are characterized by a high barrier to *Z*–*E* isomerization [14], compounds **XXa**, **XXb**, and **XXIa** could be formed only via dehydrochlorination of the *Z* isomers of **XVIa**, **XVIb**, and **XVIIIa** under severe reaction conditions and subsequent chlorination of intermediate 4-aroyl(arylsulfonyl)oxyimino-3-chloro-2,6-diisopropylcyclohexa-2,5-dien-1-ones at the *syn*-C=C bond.

We failed to effect dehydrohalogenation of 4-aroyl(arylsulfonyl)oxyimino-5,6-dichloro-2,6-diisopropylcyclohex-2-en-1-ones in diethyl ether or chloroform in the presence of triethylamine with a view to obtain 4-aroyl(arylsulfonyl)oxyimino-3-chloro-2,6-diisopropylcyclohexa-2,5-dien-1-ones and expose the latter to further halogenation.

Our results led us to conclude that halogen addition at the double C=C bond in the quinoid ring of N-substituted 1,4-benzoquinone imines can follow two different paths: (1) with intermediate formation of halonium ion and addition of the second halogen atom directly to the halonium ion; as a result, only *trans*-addition products with *trans*-diaxial arrangement of the halogen atoms are obtained; and (2) through intermediate carbocation with subsequent addition of the second halogen atom; in this case, the formation of both *trans*- and *cis*-addition products is possible. The relative contributions of these reaction paths are determined by the substrate structure and reaction conditions. The carbocationic path is favored by the presence of electron-donating groups in the substrate molecule and polar solvents. Halogenation of 1,4-benzoquinone oxime ethers follows only the path involving formation of halonium ion, and the addition products are only the corresponding isomers with *trans*-diaxial arrangement of the halogen atoms.

EXPERIMENTAL

The IR spectra were recorded in KBr on a UR-20 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured from solutions in $CDCl_3$ on a Varian VXR-300 instrument (300 MHz for ^{1}H); tetramethylsilane was used as reference. The reaction mixtures were analyzed by thin-layer chromatography on Silufol UV-254 plates; samples were applied from solutions in chloroform, benzene–hexane (10:1) was used as eluent, and spots were visualized under UV light.

X-Ray diffraction data for diastereoisomers of compound XIId. *Stereoisomer **B***. Monoclinic crystals, $C_{19}H_{19}Cl_3N_2O_4$. Unit cell parameters (20°C): a = 13.060(2), b = 7.148(1), c = 22.410(3) Å; β = 90.90(1)°, V = 2091.9(6) Å^3; M 445.71; Z = 4; space group $P2_1/c$; d_{calc} = 1.415 g/cm^3; μ(MoK_α) = 0.465 mm^{-1}; F(000) = 920. The unit cell parameters and intensities of 10205 reflections (4655 independent reflections with R_{int} = 0.03) were measured on an Xcalibur-3 diffractometer (MoK_α irradaition, CCD detector, graphite monochromator, ω-scanning, $2\theta_{max}$ = 55°). The structure was solved by the direct method using SHELXTL software package [15]. The positions of hydrogen atoms were determined by difference synthesis of electron density and were refined using *riding* model ($U_{iso} = n U_{eq.}$; n = 1.5 for methyl hydrogen atoms, n = 1.2 for the other hydrogen atoms). The structure was refined with respect to F^2 by full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms; wR_2 = 0.124 from 4612 reflections [R_1 = 0.044 from 3481 reflections with $F > 4\sigma(F)$, S = 1.125]. The coordinates of atoms and complete sets of bond lengths and bond angles were deposited to the Cambridge Crystallographic Data Center (entry no. CCDC 635555).

*Stereoisomer **D***. Monoclinic crystals, $C_{19}H_{19}Cl_3N_2O_4$. Unit cell parameters (20°C): a =

18.393(2), b = 9.217(1), c = 12.294(1) Å; β = 99.28(1)°; V = 2056.8(3) Å^3; M 445.71; Z = 4; space group $P2_1/c$; d_{calc} = 1.439 g/cm^3; μ(MoK_α) = 0.473 mm^{-1}; F(000) = 920. The unit cell parameters and intensities of 12978 reflections (3615 independent reflections with R_{int} = 0.112) were measured an Xcalibur-3 diffractometer (MoK_α irradaition, CCD detector, graphite monochromator, ω-scanning, $2\theta_{max}$ = 50°). The structure was solved by the direct method using SHELXTL software package [15]. The positions of hydrogen atoms were determined by difference synthesis of electron density and were refined using *riding* model ($U_{iso} = n U_{eq.}$; n = 1.5 for methyl hydrogen atoms, n = 1.2 for the other hydrogen atoms). The structure was refined with respect to F^2 by full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms; wR_2 = 0.226 from 3473 reflections [R_1 = 0.075 from 2686 reflections with $F > 4\sigma(F)$, S = 1.121]. The coordinates of atoms and complete sets of bond lengths and bond angles were deposited to the Cambridge Crystallographic Data Center (entry no. CCDC 635556).

4-Aroylamino-2,6-diisopropylphenols **IIIa**–**IIId** were synthesized by acylation of 4-amino-2,6-diisopropylphenol with the corresponding substituted benzoyl chlorides in DMF–AcOH (1:5) in the presence of sodium acetate according to the procedure described in [16]. 4-Aroylimino-2,6-diisopropylcyclohexa-2,5-dien-1-ones **Ia**, **Ic**, and **Id** were synthesized by oxidation of the corresponding 4-aroylamino-2,6-diisopropylphenols **IIIa**, **IIIc**, and **IIId** with lead tetraacetate in acetic acid as reported in [16]. The properties of quinone imines **Ia**, **Ic**, and **Id** and aminophenols **IIIa**–**IIId** were given in [17]. 4-Arylsulfonylamino-2,6-diisopropylphenols **IVa** and **IVb** were prepared by reaction of 4-amino-2,6-diisopropylphenol with the corresponding arenesulfonyl chlorides in water in the presence of sodium hydrogen carbonate according to the procedure described in [17]. 4-Arylsulfonylimino-2,6-diisopropylcyclohexa-2,5-dien-1-ones **IIa** and **IIb** were obtained by oxidation of 4-arylsulfonylamino-2,6-diisopropylphenols **IVa** and **IVb** with lead tetraacetate in acetic acid [17]. The properties of quinone imines **IIa** and **IIb** and aminophenols **IVa** and **IVb** were given in [16]. 4-Aroyl(arylsulfonyl)oxyimino-2,6-diisopropylcyclohexa-2,5-dien-1-ones **XIVa**, **XIVb**, **XVa**, and **XVb** were synthesized by acylation of 2,6-diisopropyl-4-iminocyclohexa-2,5-dien-1-one with the corresponding benzoyl and arenesulfonyl chlorides in diethyl ether in the presence of triethylamine according to the procedure described in [18]; their properties were given in [13].

4-(4-Chlorophenylsulfonyloxyimino)-2,6-diisopropylcyclohexa-2,5-dien-1-one (XVb). Yield 80%, mp 118–120°C. ^{1}H NMR spectrum, δ, ppm: 7.28 d (1H, 3-H), 6.78 d (1H, 5-H), 3.01–3.16 m [2H, C**H**(CH$_3$)$_2$], 1.10 d and 1.13 d (6H each, CH$_3$), 7.58–7.99 d.d (4H, H$_{arom}$). Found, %: N 3.55, 3.62. $C_{18}H_{20}ClNO_4S$. Calculated, %: N 3.67.

Chlorination of 4-aroyl(arylsulfonyl)-2,6-diisopropylcyclohexa-2,5-dien-1-ones Ia, Ic, Id, IIa, and IIb and 4-aroyl(arylsulfonyl)amino-2,6-diisopropylphenols IIIa–IIId, IVa, and IVb (*general procedure***).** A stream of dry chlorine was passed at a flow rate of 15–20 ml/min at 25–30°C through a solution of 2 mmol of quinone imine **Ia**, **Ic**, **Id**, **IIa**, or **IIb** or aminophenol **IIIa–IIId**, **IVa**, or **IVb** in 3 ml of chloroform, acetic acid, or DMF–AcOH (1:5). The substrate-to-reagent ratio was controlled by weight and was varied from 1:1 to 1:4. The mixture was left to stand for 24 h, and the precipitate was filtered off and recrystallized from acetic acid. The yields, melting points, and elemental analyses are given below only for those compounds which were isolated as individual substances.

***N*-(3-Chloro-4-hydroxy-3,5-diisopropylphenyl)-benzenesulfonamide (VIa).** Yield 65%, mp 121–122°C. Found, %: Cl 9.55, 9.78. $C_{18}H_{22}ClNO_3S$. Calculated, %: Cl 9.64.

***N*-(3-Chloro-4-hydroxy-3,5-diisopropylphenyl)-4-methylbenzenesulfonamide (VIb).** Yield 73%, mp 122–123°C. Found, %: Cl 9.35, 9.43. $C_{19}H_{24}ClNO_3S$. Calculated, %: Cl 9.28.

4-Benzoylimino-3-chloro-2,6-diisopropylcyclohexa-2,5-dien-1-one (VIIIa). ^{1}H NMR spectrum, δ, ppm: 6.61 d (1H, 5-H), 3.39–3.50 m (1H, 2-CH), 3.01–3.11 m (1H, 6-CH), 1.39 d [6H, 2-CH(C**H**$_3$)$_2$], 1.11 d [6H, 6-CH(C**H**$_3$)$_2$], 7.47–7.96 m (5H, H$_{arom}$).

3-Chloro-2,6-diisopropyl-4-(4-nitrobenzoylimino)cyclohexa-2,5-dien-1-one (VIIId). ^{1}H NMR spectrum, δ, ppm: 6.61 d (1H, 5-H), 3.52–3.62 m (1H, 2-CH), 3.00–3.08 m (1H, 6-CH), 1.35 d [6H, 2-CH(C**H**$_3$)$_2$], 1.07 d [6H, 6-CH(C**H**$_3$)$_2$], 8.13–8.38 d.d (4H, H$_{arom}$).

3-Chloro-2,6-diisopropyl-4-(phenylsulfonylimino)cyclohexa-2,5-dien-1-one (Xa). Yield 85%, mp 70–72°C. ^{1}H NMR spectrum, δ, ppm: 7.92 br.s (1H, 5-H), 3.47–3.56 m (1H, 2-CH), 3.04–3.13 m

(1H, 6-CH), 1.30 d [6H, 2-CH(C**H**$_3$)$_2$], 1.19 d [6H, 6-CH(C**H**$_3$)$_2$], 7.56–8.07 m (5H, H$_{arom}$). Found, %: Cl 9.55, 9.74. $C_{18}H_{20}ClNO_3S$. Calculated, %: Cl 9.69.

3-Chloro-2,6-diisopropyl-4-(4-methylphenylsulfonylimino)cyclohexa-2,5-dien-1-one (Xb). Yield 80%, mp 128–131°C. ^{1}H NMR spectrum, δ, ppm: 7.91 br.s (1H, 5-H), 3.46–3.54 m (1H, 2-CH), 3.05–3.14 m (1H, 6-CH), 1.29 d [6H, 2-CH(C**H**$_3$)$_2$], 1.18 d [6H, 6-CH(C**H**$_3$)$_2$], 7.37–7.93 d.d (4H, C_6H_4), 2.46 s (3H, C**H**$_3$C$_6$H$_4$). Found, %: Cl 9.25, 9.41. $C_{19}H_{22}ClNO_3S$. Calculated, %: Cl 9.33.

4-Benzoylimino-3,5,6-trichloro-2,6-diisopropylcyclohex-2-en-1-one (XIIa, isomer B). ^{1}H NMR spectrum, δ, ppm: 5.00 s (1H, 5-H), 3.36–3.48 m (1H, 2-CH), 2.61–2.74 m (1H, 6-CH), 1.26–1.39 d.d [6H, 2-CH(C**H**$_3$)$_2$], 0.92–1.11 d.d [6H, 6-CH(C**H**$_3$)$_2$], 7.43–7.98 m (5H, H$_{arom}$).

Isomer D. Yield 30%, mp 139–140°C. ^{1}H NMR spectrum, δ, ppm: 5.14 s (1H, 5-H), 3.45–3.59 m (1H, 2-CH), 2.31–2.44 m (1H, 6-CH), 1.27–1.40 d.d [6H, 2-CH(C**H**$_3$)$_2$], 0.89–1.13 d.d [6H, 6-CH(C**H**$_3$)$_2$], 7.48–7.96 m (5H, H$_{arom}$). ^{13}C NMR spectrum, δ$_C$, ppm: 187.53 (C^1); 177.70 (N**C**=O); 155.91 (C^4); 149.50 (C^2); 140.34 (C^3); 134.31 (C$^{4'}$); 131.20 (C$^{1'}$); 129.62 (C$^{2'}$); 128.84 (C$^{3'}$); 83.78 (C^6); 59.91 (C^5); 35.61, 31.92 (**C**HMe$_2$); 20.24, 18.75, 18.38, 17.12 (Me). Found, %: Cl 26.73, 26.84. $C_{19}H_{22}ClNO_3S$. Calculated, %: Cl 26.54.

3,5,6-Trichloro-2,6-diisopropyl-4-(4-methoxybenzoylimino)cyclohex-2-en-1-one (XIIc). ^{1}H NMR spectrum, δ, ppm: isomer **B**: 5.00 s (1H, 5-H), 3.40–3.50 m (1H, 2-CH), 2.64–2.76 m (1H, 6-CH), 1.23–1.40 d.d [6H, 2-CH(C**H**$_3$)$_2$], 0.89–1.12 d.d [6H, 6-CH(C**H**$_3$)$_2$], 3.88 s (3H, CH$_3$O), 7.91–8.09 d.d (4H, H$_{arom}$); isomer **D**: 5.15 s (1H, 5-H), 3.45–3.55 m (1H, 2-CH), 2.33–2.42 m (1H, 6-CH), 1.25–1.40 d.d [6H, 2-CH(C**H**$_3$)$_2$], 0.91–1.15 d.d [6H, 6-CH(C**H**$_3$)$_2$], 3.98 s (3H, CH$_3$O), 7.91–8.09 d.d (4H, H$_{arom}$).

3,5,6-Trichloro-2,6-diisopropyl-4-(4-nitrobenzoylimino)cyclohex-2-en-1-one (XIId, isomer B). Yield 82%, mp 121–123°C. ^{1}H NMR spectrum, δ, ppm: 5.03 s (1H, 5-H), 3.39–3.49 m (1H, 2-CH), 2.65–2.76 m (1H, 6-CH), 1.24–1.40 d.d [6H, 2-CH(C**H**$_3$)$_2$], 0.94–1.14 d.d [6H, 6-CH(C**H**$_3$)$_2$], 8.13–8.36 d.d (4H, H$_{arom}$). ^{13}C NMR spectrum, δ$_C$, ppm: 187.21 (C^1); 175.18 (N**C**=O); 156.21 (C^4); 151.40 (C^2); 150.83 (C$^{4'}$); 136.79 (C^3); 136.63 (C$^{1'}$); 130.48 (C$^{2'}$); 123.88 (C$^{3'}$); 74.38 (C^6); 55.85 (C^5); 32.03, 29.14 (**C**HMe$_2$); 20.32, 18.48, 18.16, 15.16 (Me). Found, %: Cl 23.40, 23.69. $C_{19}H_{19}Cl_3N_2O_4$. Calculated, %: Cl 23.86.

Isomer D. Yield 15%, mp 190–192°C. ^{1}H NMR spectrum, δ, ppm: 5.17 s (1H, 5-H), 3.47–3.56 m (1H, 2-CH), 2.35–2.44 m (1H, 6-CH), 1.27–1.41 d.d [6H, 2-CH(C**H**$_3$)$_2$], 0.92–1.20 d.d [6H, 6-CH(C**H**$_3$)$_2$], 8.12–8.37 d.d (4H, C_6H_4). ^{13}C NMR spectrum, δ$_C$, ppm: 187.23 (C^1); 175.51 (NC=O); 157.20 (C^4); 150.99 (C$^{4'}$); 150.49 (C^2); 139.41 (C^3); 136.09 (C$^{1'}$); 130.61 (C$^{2'}$); 123.97 (C$^{3'}$); 83.47 (C^6); 59.74 (C^5); 35.61, 32.09 (**C**HMe$_2$); 20.24, 18.67, 18,30, 17.05 (Me). Found, %: Cl 23.22, 23.47. $C_{19}H_{19}Cl_3N_2O_4$. Calculated, %: Cl 23.86.

3,5,6-Trichloro-2,6-diisopropyl-4-(phenylsulfonylimino)cyclohex-2-en-1-one (XIIIa, isomer B). ^{1}H NMR spectrum, δ, ppm: 6.37 s (1H, 5-H), 3.35–3.46 m (1H, 2-CH), 2.72–2.82 m (1H, 6-CH), 1.10–1.36 m (12H, CH$_3$), 7.56–8.08 m (5H, H$_{arom}$).

Isomer D. Yield 77%, mp 127–128°C. ^{1}H NMR spectrum, δ, ppm: 6.34 s (1H, 5-H), 3.41–3.55 m (1H, 2-CH), 2.25–2.36 m (1H, 6-CH), 0.90–1.37 m (12H, CH$_3$), 7.56–8.08 m (5H, H$_{arom}$). Found, %: Cl 23.95, 24.28. $C_{18}H_{20}Cl_3NO_3S$. Calculated, %: Cl 24.35.

3,5,6-Trichloro-2,6-diisopropyl-4-(4-methylphenylsulfonylimino)cyclohex-2-en-1-one (XIIIb). ^{1}H NMR spectrum, δ, ppm: isomer **B**: 6.40 s (1H, 5-H), 3.36–3.45 m (1H, 2-CH), 2.73–2.81 m (1H, 6-CH), 1.10–1.35 m [12H, CH(C**H**$_3$)$_2$], 7.36–7.95 d.d (4H, C_6H_4), 2.46 s (3H, C**H**$_3$C$_6$H$_4$); isomer **D**: 6.36 s (1H, 5-H), 3.43–3.53 m (1H, 2-CH), 2.25–2.34 m (1H, 6-CH), 0.89–1.35 m [12H, CH(C**H**$_3$)$_2$], 7.38–7.95 d.d (4H, C_6H_4), 2.47 s (3H, C**H**$_3$C$_6$H$_4$).

The IR spectra of semiquinoid compounds **XIIa**, **XIIc**, **XIId**, **XIIIa**, and **XIIIb** contained absorption bands in the regions 1720–1700 (C^1=O), 1630–1610 (C=N), and 1678–1660 cm^{-1} (NC=O, **XII**).

Bromination of 4-aroyl(arylsulfonyl)amino-2,6-diisopropylphenols IIIa, IIIb, IVa, and IVb (*general procedure***).** Aminophenol **IIIa**, **IIIb**, **IVa**, or **IVb**, 2 mmol, was dissolved in 3 ml of chloroform, acetic acid, DMF, or DMF–AcOH (1:5), and a solution of bromine in the same solvent was added dropwise to attain a substrate-to-bromine ratio of 1:1, 1:3, or 1:5. We succeeded in isolating products when the reaction was performed in chloroform with an equimolar amount of bromine. In the other cases, noncrystallizable oily materials were formed, which contained several components (according to the TLC data). The product was filtered off, washed with acetic acid and recrystallized from acetic acid. The structure of compounds **Va**, **Vb**, **VIIa**, and **VIIb** was proved by the

^{1}H NMR data for the corresponding quinone imines **IXa**, **IXb**, **XIa**, and **XIb** and elemental analyses.

4-Benzoylamino-3-bromo-2,6-diisopropylphenol (Va). Yield 68%, mp 158–160°C. Found, %: Br 20.86, 21.02. $C_{19}H_{22}BrNO_2$. Calculated, %: Br 21.23.

3-Bromo-2,6-diisopropyl-4-(4-methylbenzoylamino)phenol (Vb). Yield 87%, mp 175–176°C. Found, %: Br 21.10, 21.17. $C_{20}H_{24}BrNO_2$. Calculated, %: Br 20.47.

3-Bromo-2,6-diisopropyl-4-(phenylsulfonylamino)phenol (VIIa). Yield 90%, mp 160–164°C. Found, %: Br 19.05, 19.17. $C_{18}H_{22}BrNO_3S$. Calculated, %: Br 19.38.

3-Bromo-2,6-diisopropyl-4-(4-methylphenylsulfonylamino)phenol (VIIb). Yield 89%, mp 136–138°C. Found, %: Br 18.30, 18.64. $C_{19}H_{24}BrNO_3S$. Calculated, %: Br 18.74.

4-Aroyl(arylsulfonyl)imino-3-bromo-2,6-diisopropylcyclohexa-2,5-dien-1-ones IXa, IXb, XIa, and XIb (*general procedure*). Lead tetraacetate, 0.88 mmol, was added at room temperature to a mixture of 0.8 mmol of aminophenol **Va**, **Vb**, **VIIa**, or **VIIb** in 3 ml of acetic acid, and the mixture was stirred. Initial aminophenols dissolved, the solution warmed up and turned yellow, and a solid separated. The mixture was cooled, 2–3 drops of ethylene glycol were added under stirring, and the yellow precipitate was filtered off, washed with acetic acid, and recrystallized from acetic acid.

4-Benzoylimino-3-bromo-2,6-diisopropylcyclohexa-2,5-dien-1-one (IXa). Yield 78%, mp 95–96°C. ^{1}H NMR spectrum, δ, ppm: 6.64 d (1H, 5-H), 3.53–3.62 m (1H, 2-CH), 2.95–3.04 m (1H, 6-CH), 1.35 d [6H, 2-CH(C**H**$_3$)$_2$], 1.02 d [6H, 6-CH(C**H**$_3$)$_2$], 7.47–7.96 m (5H, H_{arom}). Found, %: Br 20.95, 21.32. $C_{19}H_{20}BrNO_2$. Calculated, %: Br 21.35.

3-Bromo-2,6-diisopropyl-4-(4-methylbenzoylimino)cyclohexa-2,5-dien-1-one (IXb). Yield 90%, mp 104–106°C. ^{1}H NMR spectrum, δ, ppm: 6.63 d (1H, 5-H), 3.53–3.62 m (1H, 2-CH), 2.95–3.04 m (1H, 6-CH), 1.35 d [6H, 2-CH(C**H**$_3$)$_2$], 1.01 d [6H, 6-CH(C**H**$_3$)$_2$], 7.28–7.84 d.d (4H, C_6H_4), 2.44 s (3H, C**H**$_3$C$_6$H$_4$). Found, %: Br 20.65, 20.98. $C_{20}H_{22}BrNO_2$. Calculated, %: Br 20.58.

3-Bromo-2,6-diisopropyl-4-(phenylsulfonylimino)cyclohexa-2,5-dien-1-one (XIa). Yield 76%, mp 104–106°C. ^{1}H NMR spectrum, δ, ppm: 7.96 br.s (1H, 5-H), 3.47–3.57 m (1H, 2-CH), 3.04–3.13 m (1H, 6-CH), 1.30 d [6H, 2-CH(C**H**$_3$)$_2$], 1.19 d [6H, 6-CH(C**H**$_3$)$_2$], 7.56–8.07 m (5H, H_{arom}). Found, %: Br 19.10, 19.52. $C_{18}H_{20}BrNO_3S$. Calculated, %: Br 19.47.

3-Bromo-2,6-diisopropyl-4-(4-methylphenylsulfonylimino)cyclohexa-2,5-dien-1-one (XIb). Yield 83%, mp 136–138°C. ^{1}H NMR spectrum, δ, ppm: 7.94 br.s (1H, 5-H), 3.46–3.56 m (1H, 2-CH), 3.05–3.14 m (1H, 6-CH), 1.29 d [6H, 2-CH(C**H**$_3$)$_2$], 1.18 d [6H, 6-CH(C**H**$_3$)$_2$], 7.37–7.94 d.d (4H, C_6H_4), 2.46 s (3H, C**H**$_3$C$_6$H$_4$). Found, %: Br 18.73, 18.99. $C_{19}H_{22}BrNO_3S$. Calculated, %: Br 18.83.

The IR spectra of quinone imines **IXa**, **IXb**, **XIa**, and **XIb** contained absorption bands in the regions 1660–1645 (C^1=O), 1620–1605 (C=N), and 1690–1670 cm^{-1} (NC=O, **IX**).

Chlorination of 4-aroyl(arylsulfonyl)oxyimino-2,6-diisopropylcyclohexa-2,5-dien-1-ones XIVa, XIVb, XVa, and XVb (*general procedure*). Quinone oxime ether **XIVa**, **XIVb**, **XVa**, or **XVb**, 2 mmol, was dissolved in dimethylformamide, and a stream of dry chlorine was passed through the solution at a flow rate of 15–20 ml/min until complete saturation. The mixture was diluted with 10–15 ml of water, and the precipitate was filtered off and recrystallized from acetic acid.

Cyclohexene derivatives *E*-**XVIa**, *E*-**XVIb**, and *E*-**XVIIIa** were identical to those reported in [11].

(*Z*)-5,6-Dichloro-2,6-diisopropyl-4-(4-methylbenzoyloxyimino)cyclohex-2-en-1-one (*Z*-XVIa). ^{1}H NMR spectrum, δ, ppm: 7.20 q (1H, 3-H), 5.31 d (1H, 5-H, $J_{3,5}$ = 2.1 Hz), 3.01–3.11 m (1H, 2-CH), 2.74–2.88 m (1H, 6-CH), 1.16–1.22 d.d [6H, 2-CH(C**H**$_3$)$_2$], 1.08–1.14 d.d [6H, 6-CH(C**H**$_3$)$_2$], 7.32–8.00 d.d (4H, C_6H_4), 2.46 s (3H, C**H**$_3$C$_6$H$_4$).

5,6-Dichloro-4-(4-chlorobenzoyloxyimino)-2,6-diisopropylcyclohex-2-en-1-one (XVIb, *E* isomer). ^{13}C NMR spectrum, δ_C, ppm: 190.13 (C^1); 187.95 (NC=O); 157.23 (C^4); 151.44 (C^2); 140.64 (C$^{4'}$); 131.09, 129.26 (C$^{2'}$, C$^{3'}$); 126.33 (C$^{1'}$); 126.23 (C^3); 72.70 (C^6); 51.55 (C^5); 29.38, 28.21 (**C**HMe$_2$); 21.07, 20.29, 18.92, 15.67 (Me).

***Z* Isomer.** ^{1}H NMR spectrum, δ, ppm: 7.21 q (1H, 3-H), 5.30 d (1H, 5-H, $J_{3,5}$ = 2.1 Hz), 3.00–3.13 m (1H, 2-CH), 2.74–2.88 m (1H, 6-CH), 1.17–1.23 d.d [6H, 2-CH(C**H**$_3$)$_2$], 1.09–1.15 d.d [6H, 6-CH(C**H**$_3$)$_2$], 7.50–8.06 d.d (4H, C_6H_4).

5,6-Dichloro-2,6-diisopropyl-4-(4-methylphenylsulfonyloxyimino)cyclohex-2-en-1-one (XVIIIa, *E* isomer). ^{13}C NMR spectrum, δ_C, ppm: 189.93 (C^1); 157.34 (C^4); 151.42 (C^2); 145.77 ($C^{4'}$); 131.69 ($C^{1'}$); 129.81, 128.91 ($C^{2'}$, $C^{3'}$); 125.16 (C^3); 72.59 (C^6); 50.92 (C^5); 29.36, 28.16 (**C**HMe$_2$); 21.70, 20.99, 20.17, 18.95, 15.77 (Me).

***Z* Isomer.** ^{1}H NMR spectrum, δ, ppm: 7.02 q (1H, 3-H), 4.93 d (1H, 5-H, $J_{3,5}$ = 1.8 Hz), 2.94–3.02 m (1H, 2-CH), 2.66–2.75 m (1H, 6-CH), 1.11–1.16 d.d [6H, 2-CH(C**H**$_3$)$_2$], 1.01–1.09 d.d [6H, 6-CH(C**H**$_3$)$_2$], 7.36–7.91 d.d (4H, C_6H_4), 2.46 s (3H, C**H**$_3$C$_6$H$_4$).

(*E*)-3,5,6-Trichloro-2,6-diisopropyl-4-(4-methylbenzoyloxyimino)cyclohex-2-en-1-one (*E*-XXa). Yield 83%, mp 136–138°C. ^{1}H NMR spectrum, δ, ppm: 5.65 s (1H, 5-H), 3.42–3.52 m (1H, 2-CH), 2.76–2.84 m (1H, 6-CH), 1.21–1.38 d.d [6H, 2-CH(C**H**$_3$)$_2$], 1.09–1.18 d.d [6H, 6-CH(C**H**$_3$)$_2$], 7.32–8.00 d.d (4H, C_6H_4), 2.46 s (3H, $CH_3C_6H_4$). Found, %: Cl 24.40, 24.61. $C_{20}H_{22}Cl_3NO_3$. Calculated, %: Cl 24.69.

(*E*)-3,5,6-Trichloro-4-(4-chlorobenzoyloxyimino)-2,6-diisopropylcyclohex-2-en-1-one (*E*-XXb). ^{1}H NMR spectrum, δ, ppm: 5.61 s (1H, 5-H), 3.42–3.52 m (1H, 2-CH), 2.74–2.87 m (1H, 6-CH), 1.23–1.38 d.d [6H, 2-CH(C**H**$_3$)$_2$], 1.09–1.17 d.d [6H, 6-CH(C**H**$_3$)$_2$], 7.51–8.06 d.d (4H, C_6H_4).

(*E*)-3,5,6-Trichloro-2,6-diisopropyl-4-(4-methylphenylsulfonyloxyimino)cyclohex-2-en-1-one (*E*-XXIa). ^{1}H NMR spectrum, δ, ppm: 5.44 s (1H, 5-H), 3.41–3.52 m (1H, 2-CH), 2.66–2.75 m (1H, 6-CH), 1.18–1.25 d.d [6H, 2-CH(C**H**$_3$)$_2$], 1.05–1.10 d.d [6H, 6-CH(C**H**$_3$)$_2$], 7.36–7.99 d.d (4H, C_6H_4), 2.46 s (3H, C**H**$_3$C$_6$H$_4$).

Bromination of 4-aroyl(arylsulfonyl)oxyimino-2,6-diisopropylcyclohexa-2,5-dien-1-ones XIVb, XVa, and XVb (*general procedure*). A solution of bromine in DMF was added dropwise under stirring to a solution of 2 mmol of quinone oxime ether **XIVb**, **XVa**, or **XVb** in 3 ml of DMF until a substrate-to-bromine ratio of 1:5 or 1:8 was attained. The mixture was diluted with 10–15 ml of water, and the crystalline product was filtered off and analyzed without additional purification.

The properties of compounds *E*-**XVIIb** and *E*-**XIXa** were consistent with the data reported in [11].

(*Z*)-5,6-Dibromo-4-(4-chlorobenzoyloxyimino)-2,6-diisopropylcyclohex-2-en-1-one (*Z*-XVIIb). ^{1}H NMR spectrum, δ, ppm: 7.17 q (1H, 3-H), 5.51 d (1H, 5-H, $J_{3,5}$ = 1.8 Hz), 3.05–3.19 m (1H, 2-CH), 2.45–2.55 m (1H, 6-CH), 1.15–1.20 d.d [6H, 2-CH(C**H**$_3$)$_2$], 1.09–1.12 d.d [6H, 6-CH(C**H**$_3$)$_2$], 7.51–8.07 d.d (4H, C_6H_4).

(*Z*)-5,6-Dibromo-2,6-diisopropyl-4-(4-methylphenylsulfonyloxyimino)cyclohex-2-en-1-one (*Z*-XIXa). ^{1}H NMR spectrum, δ, ppm: 6.96 q (1H, 3-H), 5.13 d (1H, 5-H, $J_{3,5}$ = 1.5 Hz), 2.95–3.06 m (1H, 2-CH), 2.35–2.44 m (1H, 6-CH), 1.11–1.20 d.d [6H, 2-CH(C**H**$_3$)$_2$], 1.02–1.07 d.d [6H, 6-CH(C**H**$_3$)$_2$], 7.36–7.92 d.d (4H, C_6H_4), 2.46 s (3H, C**H**$_3$C$_6$H$_4$).

(*E*)-5,6-Dibromo-4-(4-chlorophenylsulfonyloxyimino)-2,6-diisopropylcyclohex-2-en-1-one (*E*-XIXb). ^{1}H NMR spectrum, δ, ppm: 6.47 q (1H, 3-H), 5.56 d (1H, 5-H, $J_{3,5}$ = 1.8 Hz), 2.96–3.06 m (1H, 2-CH), 2.36–2.46 m (1H, 6-CH), 1.13–1.19 d.d [6H, 2-CH(C**H**$_3$)$_2$], 1.02–1.08 d.d [6H, 6-CH(C**H**$_3$)$_2$], 7.54–7.98 d.d (4H, C_6H_4).

(*Z*)-5,6-Dibromo-4-(4-chlorophenylsulfonyloxyimino)-2,6-diisopropylcyclohex-2-en-1-one (*Z*-XIXb). ^{1}H NMR spectrum, δ, ppm: 6.98 q (1H, 3-H), 5.12 d (1H, 5-H, $J_{3,5}$ = 1.8 Hz), 3.05–3.19 m (1H, 2-CH), 2.45–2.55 m (1H, 6-CH), 1.15–1.20 d.d [6H, 2-CH(C**H**$_3$)$_2$], 1.02–1.06 d.d [6H, 6-CH(C**H**$_3$)$_2$], 7.51–8.07 d.d (4H, C_6H_4).

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