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Halogenation of N-Substituted *p*-Quinone Monoimines and *p*-Quinone Monooxime Esters: X.* Halogenation of *N*-Aroyl-2,5(2,3)-dialkyl-1,4-benzoquinone Monoimines and Their Reduction Products

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Abstract—Introduction of a strong electron-withdrawing substituent to the nitrogen atom of 2,5(2,3)-dialkyl-1,4-benzoquinone imines makes their halogenation products, the corresponding cyclohexene derivatives, very unstable and favors halogenation of methyl groups in the quinoid ring. Bromination of 4-amino-*N*-aroyl-2,5-dialkyl-6-bromophenols gave 2,5-dialkyl-6-benzoyloxy-3,5-dibromocyclohex-2-ene-1,4-diones.

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We previously examined halogenation of *N*-arylsulfonyl-2,5-dialkyl-1,4-benzoquinone imines [2] and found that the main factors determining the direction of addition of halogen molecule are the size of substituents in the quinoid ring and the size of the halogen atom. The presence of a strong electron-withdrawing substituent on the nitrogen atom, in particular aroyl group, also considerably affects the halogenation process [1, 3, 4]. Halogenation of *N*-aroyl-2,5(2,3)-dialkyl-substituted 1,4-benzoquinone imines and their reduction products, *N*-aroyl-2,5(2,3)-dialkyl-4-aminophenols was not reported previously.

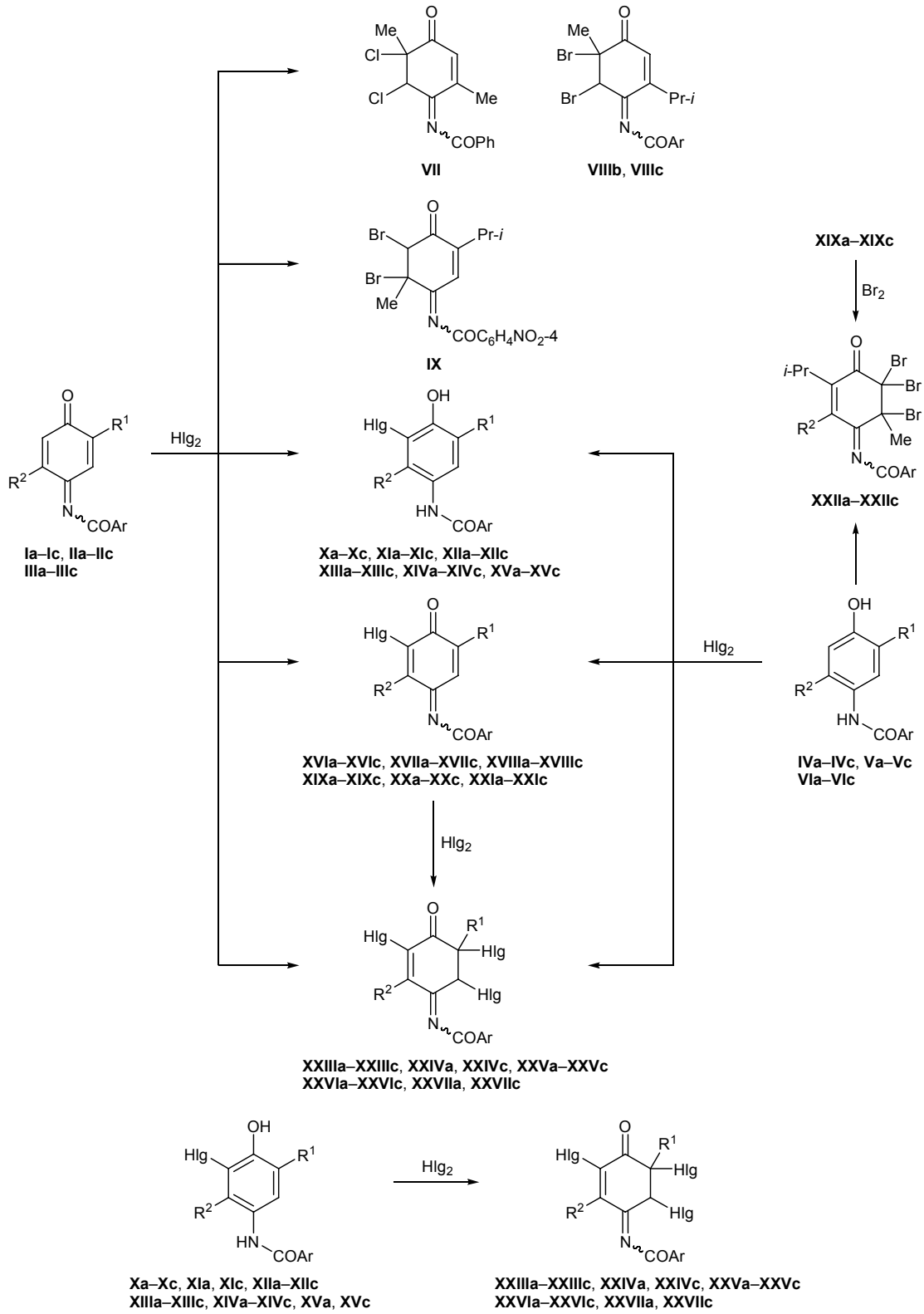
The goal of the present work was to study halogenation of *N*-aroyl-2,5(2,3)-dialkyl-1,4-benzoquinone imines, elucidate specific features of the halogenation process, and compare these reactions with halogenation of the corresponding *N*-arylsulfonyl derivatives. As substrates we used *N*-aroyl-1,4-benzoquinone imines which, like *N*-arylsulfonyl derivatives studied previously [2], contained different alkyl substituents (*i*-Pr, Me) in positions *2* and *5* of the quinoid ring: *N*-aroyl-2,5-dimethyl-, -2-isopropyl-5-methyl-, and -5-isopropyl-2-methyl-1,4-benzoquinone imines **Ia**–**Ic**, **IIa**–**IIc**, and **IIIa**–**IIIc**, and their reduction products, 4-amino-*N*-aroyl-2,5-dimethyl-, 2-isopropyl-5-methyl-, and -5-isopropyl-2-methylphenols **IVa**–**IVc**, **Va**–**Vc**, and **VIa**–**VIc**.

Due to the presence of a methyl or isopropyl group in the *ortho* position with respect to the imino nitrogen atom, quinone imines **I**–**III** in solution exist as a single isomer, which is confirmed by the ^{1}H NMR data. In the ^{1}H NMR spectra of *N*-aroyl-2,5-dialkyl-1,4-benzoquinone imines, differences in the chemical shifts of protons in the quinoid ring were considerably smaller than those observed for analogous *N*-arylsulfonyl derivatives; therefore, assignment of signals in the spectra of compounds **I**–**III** was more difficult. The 3-H proton in **I**–**III** resonated in the ^{1}H NMR spectra in the region δ 6.58–6.66 ppm, while the 6-H signal was located at δ 6.44–6.59 ppm; the corresponding signals of *N*-arylsulfonyl derivatives appeared in the regions δ 7.89–7.96 and 6.50–6.64 ppm, respectively [2].

N-Aroyl-2,5-dialkyl-1,4-benzoquinone imines **I**–**III** were synthesized by oxidation of the corresponding aminophenols **IV**–**VI** with lead tetraacetate in acetic acid. The chlorination of quinone imines **I**–**III** and aminophenols **IV**–**VI** was performed using gaseous chlorine, and the bromination was carried out with molecular bromine in $CHCl_3$, AcOH, DMF, or DMF–AcOH (1 : 5) at different substrate-to-reagent ratios under different temperature conditions. The results are given in Scheme 1. Unlike *N*-arylsulfonyl-2,5-dialkyl-1,4-benzoquinone imines which took up one halogen molecule [2], the halogenation of *N*-aroyl-2,5-dialkyl-1,4-benzoquinone imines gave only several analogous cyclohexene compounds, namely *N*-(5,6-dichloro-2,5-

* For communication IX, see [1].

Scheme 1.



Ar =Ph (**a**), 4-MeC_6H_4 (**b**), 4-$O_2NC_6H_4$ (**c**); **I**, **IV**, **X**, **XI**, **XVI**, **XVII**, **XXIII**, **XXIV**, $R^1 = R^2 = Me$; **II**, **V**, **XII**, **XIII**, **XVIII**, **XIX**, **XXV**, R^1 = *i*-Pr, R^2 = Me; **III**, **VI**, **XIV**, **XV**, **XX**, **XXI**, **XXVI**, **XXVII**, R^1 = Me, R^2 = *i*-Pr; **X**, **XII**, **XIV**, **XVI**, **XVIII**, **XX**, **XXIII**, **XXV**, **XXVI**, Hlg = Cl; **XI**, **XIII**, **XV**, **XVII**, **XIX**, **XXI**, **XXIV**, **XXVII**, Hlg = Br.

dimethyl-4-oxocyclohex-2-en-1-ylidene)benzamide (**VII**), *N*-(5,6-dibromo-2-isopropyl-5-methyl-4-oxocyclohex-2-en-1-ylidene)benzamides **VIIIb** and **VIIIc**, and *N*-(5,6-dibromo-3-isopropyl-6-methyl-4-oxocyclohex-2-en-1-ylidene)-4-nitrobenzamide (**IX**). Obviously, the corresponding 4-aroyliminocylohex-2-en-1-one derivatives are unstable due to effect of a strong electron-withdrawing substituent on the nitrogen atom (aroyl group), and they readily undergo dehydrohalogenation.

Compounds **VII**, **VIIIb**, and **VIIIc** are products of addition of halogen molecule at the double C=C bond located *syn* with respect to the substituent on the nitrogen atom in quinone imines **Ia**, **IIIb**, and **IIIc**, respectively. Chlorine addition in the chlorination of quinone imine **Ia** strictly follows general relations found previously for the halogenation of *N*-arylsulfonyl-2,5-dimethyl-1,4-benzoquinone imines [2]. The bromination of compounds **IIIb** and **VIIIc** could occur at both double C=C bonds in the quinoid ring, but only isomer **VIII** was isolated. In the reaction with quinone imine **IIc**, as might be expected, bromine molecule adds at the more sterically accessible double C=C bond in the *trans* position with respect to the substituent on the nitrogen atom.

The structure of compounds **VII**, **VIIIb**, **VIIIc**, and **IX** was confirmed by the ^{1}H and ^{13}C NMR spectra. The 3-H signal appears in the ^{1}H NMR spectrum of *N*-(5,6-dichloro-2,5-dimethyl-4-oxocyclohex-2-en-1-ylidene)benzamide (**VII**) as a quartet at δ 6.52 ppm, which is consistent with *meta* position of that proton with respect to the C=N bond; the multiplicity of the 3-H signal results from coupling with protons in the neighboring methyl group (δ 2.30 ppm, d). The ^{1}H NMR spectrum of **VII** also contained a singlet from 6-H at δ 4.83 ppm, which is typical of a proton attached to an sp^3-hybridized carbon atom. The 3-H proton in *N*-(5,6-dibromo-2-isopropyl-5-methyl-4-oxocyclohex-2-en-1-ylidene)-4-methylbenzamide (**VIIIb**) gave s singlet at δ 6.40 ppm, and the 6-H signal was a singlet at δ 5.07 ppm. Compound **IX** in solution exists as *Z* isomer, and the substituent on the nitrogen atom is oriented *syn* with respect to the double C=C bond in the quinoid ring. The 6-H proton in **IX** resonates as a broadened singlet at δ 6.42 ppm; its position is typical of protons at the quinoid C=C double bond. The 3-H signal of **IX** was a singlet at δ 4.92 ppm; its position corresponds to a proton at an sp^3-hybridized carbon atom neighboring to a carbonyl group. Protons in the methyl group resonated in the spectrum as a singlet at δ 2.31 ppm. Compounds **VII** and **VIIIb** characteristically displayed in the ^{13}C NMR spectra two upfield signals from sp^3-hybridized carbon atoms at δ_C 64.99, 58.88 (**C**ClCH$_3$, CHCl) and 57.52, 49.37 ppm (**C**BrCH$_3$, **C**HBr), respectively.

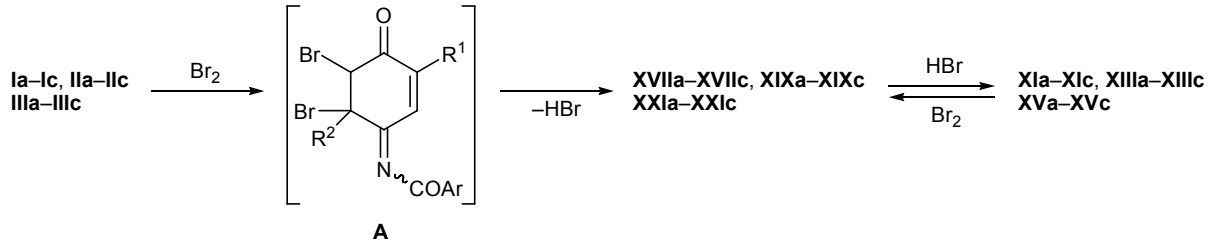
By chlorination of quinone imines **I**–**III** and aminophenols **IV**–**VI** we obtained *N*-(3-chloro-4-hydroxy-2,5-dimethylphenyl)benzamides **Xa**–**Xc**, *N*-(3-chloro-4-hydroxy-5-isopropyl-2-methylphenyl)benzamides **XIIa**–**XIIc**, *N*-(3-chloro-4-hydroxy-2-isopropyl-5-methylphenyl)benzamides **XIVa**–**XIVc**, *N*-(3-chloro-2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamides **XVIa**–**XVIc**, *N*-(3-chloro-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamides **XVIIIa**–**XVIIIc**, *N*-(3-chloro-2-isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamides **XXa**–**XXc**, *N*-(3,5,6-trichloro-2,5-dimethyl-4-oxocyclohex-2-en-1-ylidene)benzamides **XXIIIa**–**XXIIIc**, *N*-(3,5,6-trichloro-5-isopropyl-2-methyl-4-oxocyclohex-2-en-1-ylidene)benzamides **XXVa**–**XXVc**, and *N*-(3,5,6-trichloro-2-isopropyl-5-methyl-4-oxocyclohex-2-en-1-ylidene)benzamides **XXVIa**–**XXVIc**.

Compounds **XXIII**, **XXV**, and **XXVI** are the final stable chlorination products of the corresponding quinone imines **I**–**III**. The formation of aminophenols **X**, **XII**, and **XIV** in more than 50% yield from aminophenols **IV**–**VI** at a substrate-to-chlorine ratio of 1:1 indicates that the reaction occurs as electrophilic substitution of hydrogen in the benzene ring of aminophenol **IV**–**VI** by chlorine atom. Obviously, aminophenols **X**, **XII**, and **XIV** are then oxidized with chlorine to the corresponding quinone imines which take up one more chlorine molecule at the double C=C bond to give stable trichlorocyclohexene derivatives **XXIII**, **XXV**, and **XXVI**.

The bromination of quinone imines **I**–**III** afforded *N*-(3-bromo-4-hydroxy-2,5-dimethylphenyl)benzamides **XIa**–**XIc**, *N*-(3-bromo-4-hydroxy-5-isopropyl-2-methylphenyl)benzamides **XIIIa**–**XIIIc**, and *N*-(3-bromo-4-hydroxy-2-isopropyl-5-methylphenyl)-benzamides **XVa**–**XVc**. These compounds can be formed only as a result of reduction of quinone imines **XVII**, **XIX**, and **XXI**, respectively, with hydrogen bromide liberated in the dehydrohalogenation of intermediate cyclohexene derivatives **A** which cannot be isolated in most cases due to their instability (Scheme 2). Analogous cyclohexene compound **IX** was obtained only by bromination of quinone imine **IIc**.

The reduction of quinone imines **XVII**, **XIX**, and **XXI** is possible due to higher redox potential of *N*-aroyl-1,4-benzoquinone imines as compared to their

Scheme 2.



N-arylsulfonyl analogs [5]; no reduction of the latter was observed previously [2]. By contrast, the bromination of *N*,*N*′-bis(arylsulfonyl)-1,4-benzoquinone diimines was accompanied by reduction process [6], for their redox potentials are considerably higher than those of the corresponding quinone monoimines [7].

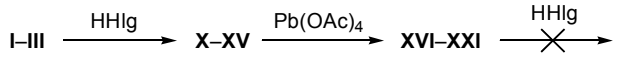
The bromination of aminophenol **Vb** in DMF with molecular bromine at a reactant ratio of 1:6.5 at 35°C gave 4-methyl-*N*-(5,5,6-tribromo-3-isopropyl-6-methyl-4-oxocyclohex-2-en-1-ylidene)benzamide (**XXIIb**). Compound **XXIIb** may be formed as a result of either electrophilic replacement of hydrogen in the *ortho*-position with respect to the hydroxy group in initial aminophenol **Vb**, followed by oxidation and addition of bromine molecule, or oxidation of aminophenol **Vb**, addition of bromine molecule at the sterically less hindered double C=C bond, dehydrobromination, and addition of the second bromine molecule at the same bond. Compound **XXIIb** was also synthesized by bromination of quinone imine **XIXb**. In the ^{1}H NMR spectrum of **XXIIb**, the 2-H signal appeared as a singlet at δ 6.58 ppm, and protons in the 6-methyl group resonated as a singlet at δ 2.08 ppm, in keeping with the assumed structure. The ^{13}C NMR spectrum of **XXIIb** contained signals from two sp^3-carbon atoms at δ_C 88.50 (CBr_2) and 70.47 ppm (fragment **C**$BrCH_3$).

By bromination of aminophenols **IV**–**VI** we obtained *o*-bromoaminophenols **XIa**–**XIc**, **XIIIa**–**XIIIc**, and **XVa**–**XVc**, *N*-(3-bromo-2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamides **XVIIa**–**XVIIc**, and *N*-(3,5,6-tribromo-2,5-dimethyl-4-oxocyclohex-2-en-1-ylidene)benzamides **XXIVa** and **XXIVc**. In these reactions, aminophenols **XI**, **XIII**, and **XV** are most likely to be formed via electrophilic replacement of hydrogen in initial aminophenols **IV**–**VI** by bromine. Taking into account high redox potential of *N*-aroyl derivatives, subsequent oxidation of aminophenols **XI**, **XIII**, and **XV** with bromine and addition of another bromine molecule seem to be improbable. Therefore, quinone imines **XVII**, **XIX**, and **XXI** were isolated mainly in the bromination of quinone imines **I**–**III**, while cyclohexene derivatives **XXIV** and **XXVII** were isolated in the bromination of quinone imines **I**–**III**, **XVII**, **XIX**, and **XXI**.

In the ^{1}H NMR spectra of cyclohexene compounds **XXIIIa**–**XXIIIc**, **XXIVa**, **XXIVc**, **XXVa**–**XXVc**, **XXVIa**–**XXVIc**, **XXVIIa**, and **XXVIIc**, the singlet in the region δ 4.78–5.10 ppm was assigned to 6-H attached to the sp^3-hybridized carbon atom in the *ortho* position with respect to the imino carbon atom. Methyl protons resonated as a singlet in the region δ 1.83–2.06 ppm. The ^{13}C NMR spectra of compounds **XXIIIa**, **XXIIIb**, **XXVIa**, and **XXVIb** contained two upfield signals belonging to sp^3-carbon atoms at δ_C 64.68–64.39 (**C**$ClCH_3$) and 59.19–58.05 ppm (CHCl). The corresponding signals of compound **XXIVa** are located in a stronger field relative to those of **XXIII** and **XXVI**: δ_C 56.40 (**C**$BrCH_3$) and 47.70 ppm (CHBr). The sp^3-carbon atoms in the cyclohexene ring of **XXVa** resonated at δ_C 82.86 (**C**ClPr-*i*) and 59.96 ppm (CHCl).

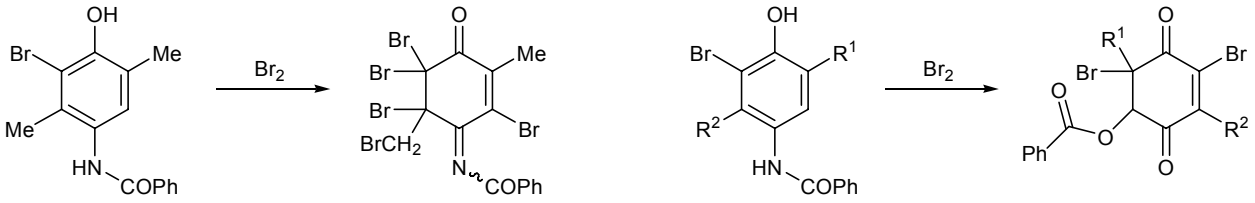
In order to identify aminophenols **X**–**XV**, these compounds were synthesized independently by hydrohalogenation of quinone imines **I**–**III** and were then oxidized to the corresponding quinone imines **XVI**–**XXI** with lead tetraacetate in acetic acid. Attempts to effect further hydrohalogenation of quinone imines **XVI**–**XXI** were unsuccessful, and the initial compounds were recovered from the reaction mixtures (Scheme 3).

Scheme 3.



The structure of quinone imines **XVI**–**XXI** was proved by the ^{1}H NMR data. The 6-H proton in **XVI**, **XVII**, **XX**, and **XXI** resonated in the ^{1}H NMR spectra as a quartet in the region δ 6.62–6.71 ppm, i.e., in the range corresponding to *ortho* position of that proton with respect to the quinone imine C=N fragment. The signal is split due to coupling with protons in the

Scheme 4.



XIa **XXVIII** **XIa**, **XIIIa** **XXIX**, **XXX**

XXIX, $R^1 = R^2 = Me$; **XXX**, $R^1 = i\text{-Pr}$, $R^2 = Me$.

methyl group on C^5; the 5-CH_3 signal appeared as a doublet at δ 1.98–2.02 ppm. The 6-H signal of quinone imines **XVIIIa**–**XVIIIc** and **XIXa**–**XIXc** was a doublet located in the region δ 6.59–6.61 ppm, while the 2-CH_3 group gave a singlet at δ 2.43–2.48 ppm.

The bromination of aminophenol **XIa** with 5 equiv of bromine in acetic acid at 70°C resulted in the formation of *N*-(2,5,5,6-tetrabromo-6-bromomethyl-3-methylcyclohex-2-en-1-ylidene)benzamide (**XXVIII**) (Scheme 4) whose structure was confirmed by ^1H and ^{13}C NMR and IR spectra and elemental analysis. In the ^1H NMR spectrum of **XXVIII** the CH_2Br signal is located at δ 4.36–4.43 ppm. Insofar as the CH_2Br group is attached to a chiral sp^3-hybridized carbon atom, protons therein are diastereotopic, and they appear in the spectrum as a doublet of doublets (J_1 = 3.3, J_2 = 9.0 Hz). The ^{13}C NMR spectrum of **XXVIII** contained signals from two sp^3-carbon atoms (C^5, C^6) at δ_C 66.93 and 87.51 ppm and a signal from the CH_2Br group at δ_C 25.60 ppm. In the IR spectrum of this compound we observed absorption band at 1720 cm^{-1} due to stretching vibrations of the carbonyl group.

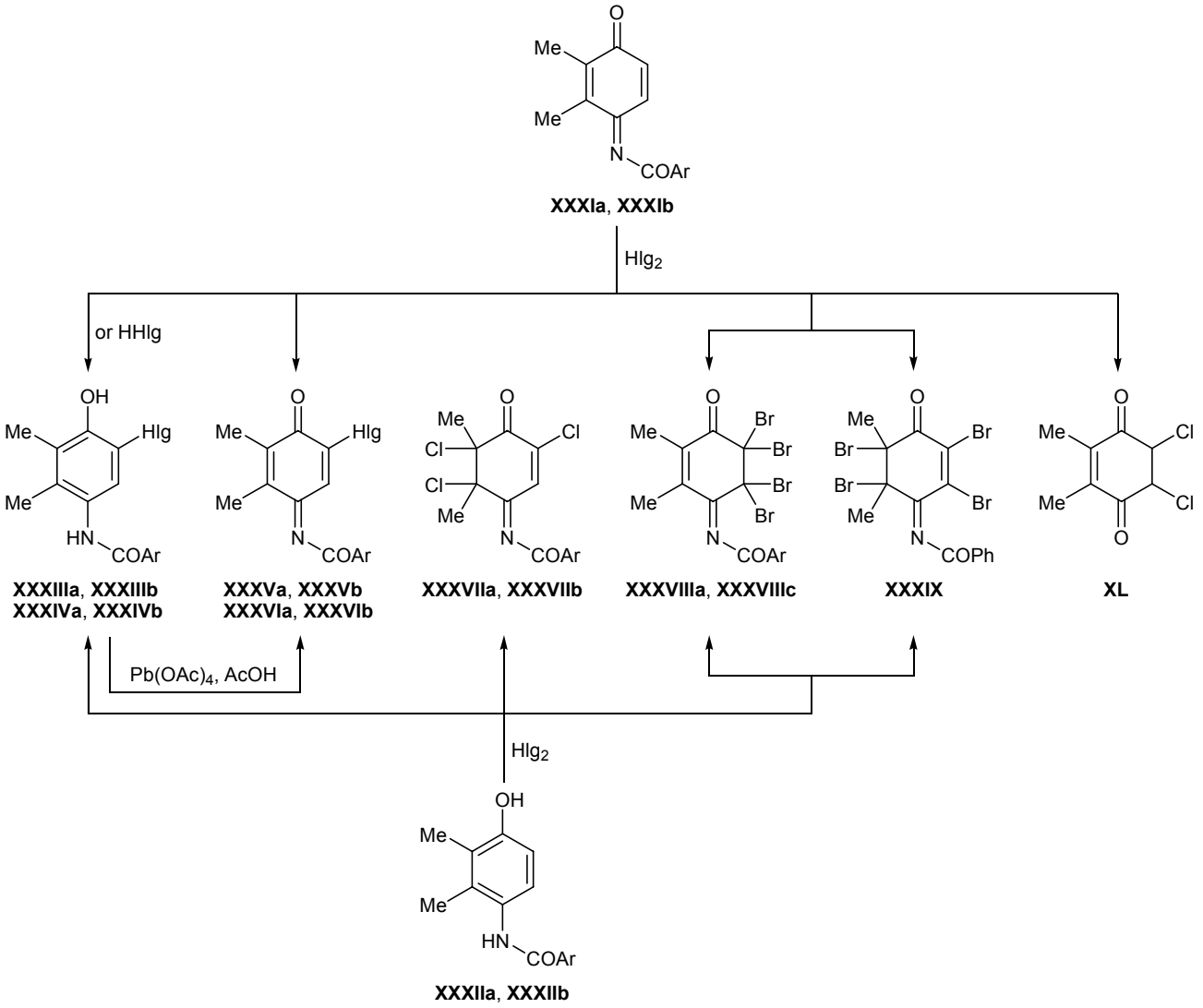
Bromination of the methyl group suggests the presence in the reaction mixture of radical species which may be formed as a result of oxidation of liberated hydrogen bromide with atmospheric oxygen. Halogenation of methyl group at the quinoid ring was observed by us previously only in the bromination of *N*-aroyl-2,6-dimethyl-1,4-benzoquinone imines and chlorination of *N*-aroyl-3,5-dimethyl-1,4-benzoquinone imines [1].

3,6-Dialkyl-4,6-dibromo-2,5-dioxocyclohex-2-en-1-yl benzoates **XXIX** and **XXX** were synthesized by bromination of aminophenols **XIa** and **XIIIa**, respectively, with 2 equiv of molecular bromine in DMF at 60°C (Scheme 4). Compound **XXX** was formed only in a mixture with cyclohexene derivative **XXIIa**. Analogous dioxocyclohexenes were obtained previously in the bromination of *N*-aroyl-2,6-dimethyl-1,4-benzoquinone imines, and their structure was proved by X-ray analysis [1]. The IR spectrum of **XXIX** contained carbonyl absorption bands at 1710, 1735, and 1590 cm^{-1}; the latter was assigned to the ester carbonyl. In the ^{13}C NMR spectrum of **XXIX**, carbonyl carbon atoms in the cyclohexene ring resonated at δ_C 186.35 and 183.66 ppm, and two upfield signals (δ_C 78.73 and 58.09 ppm) were assigned to the sp^3-hybridized carbon atoms. Compounds **XXIX** and **XXX** displayed in the ^1H NMR spectra singlets from the 1-H proton at δ 6.07–6.17 ppm and from the methyl group on C^6 at δ 2.00–2.27 ppm.

We then examined halogenation of *N*-aroyl-2,3-dimethyl-1,4-benzoquinone imines **XXXIa** and **XXXIb** which exist in solution as a single isomer where both methyl groups are located at the double C=C bond in the *anti* position with respect to the *N*-aroyl group, thus creating considerable steric hindrances to halogen addition at that double bond. Therefore, addition of the first halogen molecule should be strictly regioselective and should occur at the unsubstituted C=C bond in the quinoid ring. Quinone imines **XXXIa** and **XXXIb** were synthesized by oxidation of the corresponding *N*-aroyl-4-amino-2,3-dimethylphenols **XXXIIa** and **XXXIIb** with lead tetraacetate in acetic acid. Compounds **XXXIIa** and **XXXIIb** were prepared in turn by acylation of 4-amino-2,3-dimethylphenol with benzoyl and 4-methylbenzoyl chlorides, respectively.

The chlorination and bromination of benzoquinone imines **XXXIa** and **XXXIb** and aminophenols **XXXIIa** and **XXXIIb** were carried out according to the procedures described above for the halogenation of 2,5-dialkyl-substituted derivatives. The results are given in Scheme 5. As expected, we isolated no products of addition of one halogen molecule at the unsubstituted double bond of quinone imines **XXXIa** and **XXXIb** because of their very low stability. Obviously, the primary adducts underwent dehydrohalogenation with formation of *N*-(5-halo-2,3-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamides **XXXVa**, **XXXVb**, **XXXVIa**, and **XXXVIb**. At a lower sub-

Scheme 5.



Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 3-Br-4-MeC_6H_3 (**c**); **XXXIII**, **XXXV**, Hlg = Cl; **XXXIV**, **XXXVI**, Hlg = Br.

strate-to-halogen ratio we also isolated *N*-(5-halo-4-hydroxy-2,3-dimethylphenyl)benzamides **XXXIIIa**, **XXXIIIb**, **XXXIVa**, and **XXXIVb**. Quinone imines **XXXV** and **XXXVI** were also synthesized by oxidation of aminophenols **XXXIII** and **XXXIV** with lead tetraacetate (Scheme 5). Further chlorination of compounds **XXXVa** and **XXXVb** resulted in chlorine addition only at the methyl-substituted double C=C bond to give stable *N*-(3,5,6-trichloro-5,6-dimethyl-4-oxocyclohex-2-en-1-ylidene)benzamides **XXXVIIa** and **XXXVIIb**.

Likewise, we failed to isolate the corresponding *N*-(5,5,6-tribromo-2,3-dimethyl-4-oxocyclohex-2-en-1-ylidene)benzamides which should be formed as a result of bromine addition to quinone imines **XXXVIa** and **XXXVIb**. These intermediates were unstable, and they readily lose hydrogen bromide with subsequent addition of one more bromine molecule. In this case, the second bromine molecule added at both dimethyl-substituted double C=C bond, yielding *N*-(5,5,6,6-tetrabromo-2,3-dimethylcyclohex-2-en-1-ylidene)-benzamide (**XXXVIIIa**), and the other C=C bond (CH=CBr) to give *N*-(2,3,5,6-tetrabromo-5,6-dimethyl-cyclohex-2-en-1-ylidene)benzamide (**XXXIX**); compound **XXXVIIIa** was formed as the major product.

The chlorination of quinone imines **XXXIa** and **XXXIb** was often accompanied by hydrolysis, so that 5,6-dichloro-2,3-dimethylcyclohex-2-ene-1,4-dione (**XL**) was formed in high yield in many cases. Depending on the conditions, halogenation of *N*-aroyl-4-

amino-2,3-dimethylphenols **XXXIIa** and **XXXIIb** led to the formation of *N*-(5-halo-4-hydroxy-2,3-dimethylphenyl)benzamides **XXXIIIa**, **XXXIIIb**, **XXXIVa**, and **XXXIVb**, *N*-(3,5,6-trichloro-5,6-dimethyl-4-oxocyclohex-2-en-1-ylidene)benzamides **XXXVIIa** and **XXXVIIb**, or mixtures of bromine addition products **XXXVIIIa** and **XXXIX** at different C=C bonds of the quinoid ring. Aminophenols **XXXIIIa**, **XXXIIIb**, **XXXIVa**, and **XXXIVb** were also synthesized by hydrohalogenation of quinone imines **XXXIa** and **XXXIb** (Scheme 5).

Surprisingly, the bromination of *N*-(5-bromo-2,3-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methylbenzamide (**XXXVIb**) with 8 equiv of bromine in DMF–AcOH at 55°C was accompanied by electrophilic replacement of hydrogen in the *p*-tolyl ring, and the product was 3-bromo-4-methyl-*N*-(5,5,6,6-tetrabromo-2,3-dimethylcyclohex-2-en-1-ylidene)benzamide (**XXXVIIIc**) (Scheme 5). Analogous process, i.e., chlorination of the 4-methoxyphenylsulfonyl residue, was observed previously only in the chlorination of *N*-(4-methoxyphenyl)sulfonyl-1,4-benzoquinone imines [8].

The 6-H proton in quinone imines **XXXV** and **XXXVI** resonated in the ^{1}H NMR spectra at δ 7.03–7.32 ppm; also, signals from protons in the two methyl groups were observed at δ 2.16–2.17 and 2.29–2.30 ppm as doublets with a coupling constant *J* of 0.9–1.2 Hz. Cyclohexene derivatives **XXXVIIa** and **XXXVIIb** displayed in the ^{1}H NMR spectra a singlet at δ 7.01–7.03 ppm due to proton at the double C=C bond, and the methyl groups gave rise to two singlets at δ 2.04 and 2.13–2.14 ppm. The spectra of **XXXVIIIa** and **XXXVIIIc** contained two singlets from protons in the methyl groups at δ 1.88–1.89 and 2.20–2.21 ppm, indicating that these groups are attached to sp^2-carbon atoms. The corresponding signals of compound **XXXIX**, in which the methyl groups are attached to sp^3-hybridized carbon atoms, are located in a stronger field, at δ 1.73 and 1.34 ppm. 5,6-Dichloro-2,3-dimethylcyclohex-2-ene-1,4-dione (**XL**) showed in the ^{1}H NMR spectrum an upfield singlet (δ 4.68 ppm) from the equivalent 5-H and 6-H protons and a singlet at δ 2.09 ppm from the equivalent methyl groups.

Molecules **VII**, **VIIIb**, **VIIIc**, **IX**, **XXIIIa**–**XXIIIc**, **XXIVa**, **XXIVc**, **XXVa**–**XXVc**, **XXVIa**–**XXVIc**, **XXVIIa**, **XXVIIc**, and **XXVIII** possess an asymmetric carbon atom. The presence of a chiral center in isopropyl-substituted derivatives **VIIIb**, **VIIIc**, **IX**, **XXVa**–**XXVc**, **XXVIa**–**XXVIc**, **XXVIIa**, and **XXVIIc**, as well as in bromomethyl-substituted compound **XXVIII**, follows from their ^{1}H NMR spectra where protons in the isopropyl group give rise to two doublets (the CH_2Br protons in **XXVIII** appear as a doublet of doublets). These compounds attract interest from the viewpoint of studying spontaneous enantiomer resolution, which was revealed by us previously [9].

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were measured on a Varian VXR-300 spectrometer at 300 and 75.4 MHz, respectively, using $CDCl_3$ as solvent and tetramethylsilane as internal reference. The reaction mixtures were analyzed by thin-layer chromatography on Silufol UV-254 plates using benzene–hexane (10:1) as eluent; spots were visualized under UV light.

***N*-(2,5-Dialkyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamides Ia–Ic, IIa–IIc, IIIa–IIIc, XXXIa, and XXXIb and *N*-(2,5-dialkyl-4-hydroxyphenyl)-benzamides IVa–IVc, Va–Vc, VIa–VIc, XXXIIa, and XXXIIb** were synthesized according to the procedures described in [10, 11], and were recrystallized from acetic acid.

***N*-(2,5-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide (Ia).** Yield 92%, mp 97–99°C. ^{1}H NMR spectrum, δ, ppm: 1.94 d (3H, 5-Me, *J* = 1.2 Hz), 2.28 d (3H, 2-Me, *J* = 1.2 Hz), 6.59 q (1H, 3-H, *J* = 1.2 Hz), 6.66 q (1H, 6-H, *J* = 1.2 Hz), 7.48–7.92 m (5H, Ph). Found, %: N 5.58, 5.82. $C_{15}H_{13}NO_2$. Calculated, %: N 5.85.

***N*-(2,5-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methylbenzamide (Ib).** Yield 89%, mp 116–118°C. ^{1}H NMR spectrum, δ, ppm: 1.93 d (3H, 5-Me, *J* = 1.2 Hz), 2.24 s (3H, 4-**Me**C_6H_4), 2.27 d (3H, 2-Me, *J* = 1.2 Hz), 6.58 q (1H, 3-H, *J* = 1.2 Hz), 6.64 q (1H, 6-H, *J* = 1.2 Hz), 7.28–7.80 d.d (4H, C_6H_4, *J* = 8.4 Hz). Found, %: N 5.10, 5.51. $C_{16}H_{15}NO_2$. Calculated, %: N 5.53.

***N*-(2,5-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-nitrobenzamide (Ic).** Yield 94%, mp 187–188°C. ^{1}H NMR spectrum, δ, ppm: 1.97 d (3H, 5-Me, *J* = 1.5 Hz), 2.29 d (3H, 2-Me, *J* = 1.8 Hz), 6.62 q (1H, 3-H, *J* = 1.8 Hz), 6.66 q (1H, 6-H, *J* = 1.5 Hz), 8.08–8.35 d.d (4H, C_6H_4, *J* = 9.0 Hz). Found, %: N 9.58, 9.90. $C_{15}H_{12}N_2O_4$. Calculated, %: N 9.85.

***N*-(5-Isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide (IIa).** Yield 88%, mp 110–

111°C. ^{1}H NMR spectrum, δ, ppm: 1.02 d (6H, 5-CH**Me**$_2$, J = 6.9 Hz), 2.27 d (3H, 2-Me, J = 1.5 Hz), 2.91–3.05 m (1H, 5-CH), 6.56 d (1H, 6-H, J = 0.9 Hz), 6.58 q (1H, 3-H, J = 1.5 Hz), 7.48–7.92 m (5H, Ph). Found, %: N 5.08, 5.29. $C_{17}H_{17}NO_2$. Calculated, %: N 5.24.

***N*-(5-Isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methylbenzamide (IIb).** Yield 91%, mp 110–111°C. ^{1}H NMR spectrum, δ, ppm: 1.02 d (6H, 5-CH**Me**$_2$, J = 6.9 Hz), 2.27 d (3H, 2-Me, J = 1.5 Hz), 2.44 s (3H, 4-**Me**C_6H_4), 2.91–3.05 m (1H, 5-CH), 6.56 d (1H, 6-H, J = 0.9 Hz), 6.58 q (1H, 3-H, J = 1.5 Hz), 7.28–7.81 d.d (4H, C_6H_4, J = 8.4 Hz). Found, %: N 4.77, 5.10. $C_{18}H_{19}NO_2$. Calculated, %: N 4.98.

***N*-(5-Isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-nitrobenzamide (IIc).** Yield 76%, mp 154–156°C. ^{1}H NMR spectrum, δ, ppm: 1.04 d (6H, 5-CH**Me**$_2$, J = 7.2 Hz), 2.28 d (3H, 2-Me, J = 1.5 Hz), 2.93–3.07 m (1H, 5-CH), 6.55 q (1H, 6-H, J = 1.2 Hz), 6.62 q (1H, 3-H, J = 1.5 Hz), 8.10–8.37 d.d (4H, C_6H_4, J = 9.0 Hz). Found, %: N 8.71, 8.94. $C_{17}H_{16}N_2O_4$. Calculated, %: N 8.97.

***N*-(2-Isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide (IIIa).** Yield 93%, mp 80–81°C. ^{1}H NMR spectrum, δ, ppm: 1.28 d (6H, 2-CH**Me**$_2$, J = 6.9 Hz), 1.94 d (3H, 5-Me, J = 1.5 Hz), 3.30–3.44 m (1H, 2-CH), 6.56 d (1H, 3-H, J = 0.6 Hz), 6.66 q (1H, 6-H, J = 1.5 Hz), 7.48–7.91 m (5H, Ph). Found, %: N 5.10, 5.17. $C_{17}H_{17}NO_2$. Calculated, %: N 5.24.

***N*-(2-Isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methylbenzamide (IIIb).** Yield 77%, mp 64–66°C. ^{1}H NMR spectrum, δ, ppm: 1.27 d (6H, 2-CH**Me**$_2$, J = 6.6 Hz), 1.93 d (3H, 5-Me, J = 1.5 Hz), 2.44 s (3H, 4-**Me**C_6H_4), 3.29–3.43 m (1H, 2-CH), 6.55 d (1H, 3-H, J = 0.6 Hz), 6.65 q (1H, 6-H, J = 1.5 Hz), 7.28–7.79 d.d (4H, C_6H_4, J = 8.4 Hz). Found, %: N 4.57, 4.89. $C_{18}H_{19}NO_2$. Calculated, %: N 4.98.

***N*-(2-Isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-nitrobenzamide (IIIc).** Yield 85%, mp 124–126°C. ^{1}H NMR spectrum, δ, ppm: 1.28 d (6H, 2-CH**Me**$_2$, J = 6.9 Hz), 1.97 d (3H, 5-Me, J = 1.8 Hz), 3.27–3.41 m (1H, 2-CH), 6.60 d (1H, 3-H, J = 0.6 Hz), 6.66 q (1H, 6-H, J = 1.8 Hz), 8.08–8.37 d.d (4H, C_6H_4, J = 9.0 Hz). Found, %: N 8.80, 8.91. $C_{17}H_{16}N_2O_4$. Calculated, %: N 8.97.

***N*-(4-Hydroxy-2,5-dimethylphenyl)benzamide (IVa).** Yield 73%, mp 257–259°C. Found, %: N 5.15, 5.59. $C_{15}H_{15}NO_2$. Calculated, %: N 5.80.

***N*-(4-Hydroxy-2,5-dimethylphenyl)-4-methylbenzamide (IVb).** Yield 78%, mp 266–268°C. Found, %: N 5.24, 5.37. $C_{16}H_{17}NO_2$. Calculated, %: N 5.49.

***N*-(4-Hydroxy-2,5-dimethylphenyl)-4-nitrobenzamide (IVc).** Yield 96%, mp 198–200°C. Found, %: N 9.53, 9.85. $C_{15}H_{14}N_2O_4$. Calculated, %: N 9.78.

***N*-(4-Hydroxy-5-isopropyl-2-methylphenyl)benzamide (Va).** Yield 93%, mp 185–186°C. Found, %: N 5.02, 5.45. $C_{17}H_{19}NO_2$. Calculated, %: N 5.20.

***N*-(4-Hydroxy-5-isopropyl-2-methylphenyl)-4-methylbenzamide (Vb).** Yield 95%, mp 150–152°C. Found, %: N 4.29, 4.78. $C_{18}H_{21}NO_2$. Calculated, %: N 4.94.

***N*-(4-Hydroxy-5-isopropyl-2-methylphenyl)-4-nitrobenzamide (Vc).** Yield 73%, mp 190–193°C. Found, %: N 8.71, 8.89. $C_{17}H_{18}N_2O_4$. Calculated, %: N 8.91.

***N*-(4-Hydroxy-2-isopropyl-5-methylphenyl)benzamide (VIa).** Yield 87%, mp 196–198°C. Found, %: N 5.05, 5.37. $C_{17}H_{19}NO_2$. Calculated, %: N 5.20.

***N*-(4-Hydroxy-2-isopropyl-5-methylphenyl)-4-methylbenzamide (VIb).** Yield 81%, mp 163–165°C. Found, %: N 4.10, 4.67. $C_{18}H_{21}NO_2$. Calculated, %: N 4.94.

***N*-(4-Hydroxy-2-isopropyl-5-methylphenyl)-4-nitrobenzamide (VIc).** Yield 90%, mp 137–140°C. Found, %: N 8.64, 8.98. $C_{17}H_{18}N_2O_4$. Calculated, %: N 8.91.

***N*-(2,3-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide (XXXIa).** Yield 93%, mp 94–96°C. ^{1}H NMR spectrum, δ, ppm: 2.10 d (3H, 3-Me, J = 1.2 Hz), 2.29 d (3H, 2-Me, J = 1.2 Hz), 6.48 d (1H, 5-H, J = 10.2 Hz), 6.83 q (1H, 6-H, J = 10.2 Hz), 7.46–7.90 m (5H, Ph). Found, %: N 5.78, 5.91. $C_{15}H_{13}NO_2$. Calculated, %: N 5.85.

***N*-(2,3-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methylbenzamide (XXXIb).** Yield 97%, mp 104–106°C. ^{1}H NMR spectrum, δ, ppm: 2.10 d (3H, 3-Me, J = 0.9 Hz), 2.28 d (3H, 2-Me, J = 0.9 Hz), 2.43 s (3H, 4-**Me**C_6H_4), 6.47 d (1H, 5-H, J = 10.2 Hz), 6.81 d (1H, 6-H, J = 10.2 Hz), 7.27–7.78 d.d (4H, C_6H_4, J = 8.1 Hz). Found, %: N 5.51, 5.67. $C_{16}H_{15}NO_2$. Calculated, %: N 5.53.

***N*-(4-Hydroxy-2,3-dimethylphenyl)benzamide (XXXIIa).** Yield 89%, mp 210–211°C. Found, %: N 5.73, 5.84. $C_{15}H_{15}NO_2$. Calculated, %: N 5.80.

***N*-(4-Hydroxy-2,3-dimethylphenyl)-4-methylbenzamide (XXXIIb).** Yield 95%, mp 224.5–226°C.

Found, %: N 5.40, 5.49. $C_{16}H_{17}NO_2$. Calculated, %: N 5.49.

Chlorination of quinone imines Ia–Ic, IIa–IIc, IIIa–IIIc, XVIa–XVIc, XVIIIa–XVIIIc, XXa–XXc, XXXIa, XXXIb, XXXVa, and XXXVb and aminophenols IVa–IVc, Va–Vc, VIa–VIc, Xa–Xc, XIIa–XIIc, XIVa–XIVc, XXXIIa, XXXIIb, XXXIIIa, and XXXIIIb (*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 quinone imine or aminophenol in 3 ml of chloroform, acetic acid, dimethylformamide, or dimethylformamide–acetic acid mixture (1:5), maintained at 30–40°C. The amount of chlorine was controlled by the gain in weight until a substrate-to-chlorine ratio of 1:1 to 1:3. The precipitate was filtered off and recrystallized from acetic acid.

Compound **VII** was obtained by chlorination of quinone imine **Ia** in chloroform at a substrate-to-chlorine ratio of 1:3; compounds **Xa**–**Xc**, **XIIa**–**XIIc**, and **XIVa**–**XIVc** were obtained by chlorination of aminophenols **IVa**–**IVc**, **Va**–**Vc**, and **VIa**–**VIc** in AcOH or DMF–AcOH (1:5) at a substrate-to-chlorine ratio of 1:1; compounds **XVIa**–**XVIc**, **XVIIIa**–**XVIIIc**, and **XXa**–**XXc** were obtained by chlorination of quinone imines **Ia**–**Ic**, **IIa**–**IIc**, and **IIIa**–**IIIc** in AcOH at a substrate-to-chlorine ratio of 1:2; compounds **XXIIIa**–**XXIIIc**, **XXVa**–**XXVc**, and **XXVIa**–**XXVIc** were obtained by chlorination of quinone imines **Ia**–**Ic**, **IIa**–**IIc**, and **IIIa**–**IIIc** or aminophenols **IVa**–**IVc**, **Va**–**Vc**, and **VIa**–**VIc** in DMF–AcOH (1:5) at a substrate-to-chlorine ratio of 1:3 or by chlorination of aminophenols **Xa**–**Xc**, **XIIa**–**XIIc**, and **XIVa**–**XIVc** or quinone imines **XVIa**–**XVIc**, **XVIIIa**–**XVIIIc**, and **XXa**–**XXc** in AcOH or DMF–AcOH 1:5 at a substrate-to-chlorine ratio of 1:1; compounds **XXXIIIa** and **XXXIIIb** were obtained by chlorination of aminophenols **XXXIIa** and **XXXIIb** in AcOH, DMF, or DMF–AcOH (1:5) at a substrate-to-chlorine ratio of 1:1; compounds **XXXVIIa** and **XXXVIIb** were obtained by chlorination of aminophenols **XXXIIIa** and **XXXIIIb** or quinone imines **XXXIa**, **XXXIb**, **XXXVa**, and **XXXVb** in DMF or DMF–AcOH (1:5) at a substrate-to-chlorine ratio of 1:1; compound **XL** was obtained by chlorination of quinone imines **XXXIa** and **XXXIb** in $CHCl_3$.

***N*-(5,6-Dichloro-2,5-dimethyl-4-oxocyclohex-2-en-1-ylidene)benzamide (VII).** Yield 60%, mp 126–128°C. ^{1}H NMR spectrum, δ, ppm: 1.79 s (3H, 5-Me), 2.30 d (3H, 2-Me, J = 1.2 Hz), 4.83 s (1H, 6-H), 6.52 q (1H, 3-H, J = 1.2 Hz), 7.48–7.97 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 18.48 (2-Me), 22.00 (5-Me), 58.58 (C^6), 64.99 (C^5), 128.77 ($C^{2'}$), 129.62 ($C^{3'}$), 131.03 (C^3), 131.43 ($C^{1'}$), 134.19 ($C^{4'}$), 148.65 (C^2), 159.80 (C^1), 178.49 (NC=O), 188.15 (C^4). Found, %: Cl 22.53, 22.90. $C_{15}H_{13}Cl_2NO_2$. Calculated, %: Cl 22.86.

***N*-(3-Chloro-4-hydroxy-2,5-dimethylphenyl)-benzamide (Xa).** Yield 61%, mp 218–219°C. Found, %: Cl 12.46, 12.81. $C_{15}H_{14}ClNO_2$. Calculated, %: Cl 12.86.

***N*-(3-Chloro-4-hydroxy-2,5-dimethylphenyl)-4-methylbenzamide (Xb).** Yield 58%, mp 197–198°C. Found, %: Cl 11.92, 12.10. $C_{16}H_{16}ClNO_2$. Calculated, %: Cl 12.24.

***N*-(3-Chloro-4-hydroxy-2,5-dimethylphenyl)-4-nitrobenzamide (Xc).** Yield 70%, mp 241–242°C. Found, %: Cl 10.69, 11.12. $C_{15}H_{13}ClN_2O_4$. Calculated, %: Cl 11.05.

***N*-(3-Chloro-4-hydroxy-5-isopropyl-2-methylphenyl)benzamide (XIIa).** Yield 57%, mp 173–175°C. Found, %: Cl 11.29, 11.60. $C_{17}H_{18}ClNO_2$. Calculated, %: Cl 11.67.

***N*-(3-Chloro-4-hydroxy-5-isopropyl-2-methylphenyl)-4-methylbenzamide (XIIb).** Yield 45%, mp 192–194°C. Found, %: Cl 10.63, 11.04. $C_{18}H_{20}ClNO_2$. Calculated, %: Cl 11.16.

***N*-(3-Chloro-4-hydroxy-5-isopropyl-2-methylphenyl)-4-nitrobenzamide (XIIc).** Yield 74%, mp 240–242.5°C. Found, %: Cl 9.70, 10.20. $C_{17}H_{17}ClN_2O_4$. Calculated, %: Cl 10.16.

***N*-(3-Chloro-4-hydroxy-2-isopropyl-5-methylphenyl)benzamide (XIVa).** Yield 32%, mp 182–184°C. Found, %: Cl 11.30, 11.75. $C_{17}H_{18}ClNO_2$. Calculated, %: Cl 11.67.

***N*-(3-Chloro-4-hydroxy-2-isopropyl-5-methylphenyl)-4-methylbenzamide (XIVb).** Yield 69%, mp 202–204°C. Found, %: Cl 11.24, 11.58. $C_{18}H_{20}ClNO_2$. Calculated, %: Cl 11.16.

***N*-(3-Chloro-4-hydroxy-2-isopropyl-5-methylphenyl)-4-nitrobenzamide (XIVc).** Yield 69%, mp 173–174°C. Found, %: Cl 9.89, 10.32. $C_{17}H_{17}ClN_2O_4$. Calculated, %: Cl 10.16.

***N*-(3-Chloro-2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide (XVIa).** Yield 87%, mp 101–103°C. ^{1}H NMR spectrum, δ, ppm: 2.01 d (3H, 5-Me, J = 1.2 Hz), 2.44 s (3H, 2-Me), 6.71 q (1H, 6-H, J = 1.2 Hz), 7.48–7.90 m (5H, Ph). Found, %: Cl 12.88, 13.32. $C_{15}H_{12}ClNO_2$. Calculated, %: Cl 12.95.

***N*-(3-Chloro-2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methylbenzamide (XVIb).** Yield 73%, mp 140–142°C. ^{1}H NMR spectrum, δ, ppm: 2.00 d (3H, 5-Me, *J* = 1.5 Hz), 2.44 s (3H, 4-**Me**C_6H_4), 2.44 s (3H, 2-Me), 6.69 q (1H, 6-H, *J* = 1.5 Hz), 7.28–7.79 d.d (4H, C_6H_4, *J* = 8.1 Hz). Found, %: Cl 12.08, 12.49. $C_{16}H_{14}ClNO_2$. Calculated, %: Cl 12.32.

***N*-(3-Chloro-2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-nitrobenzamide (XVIc).** Yield 63%, mp 196–198°C. ^{1}H NMR spectrum, δ, ppm: 2.05 d (3H, 5-Me, *J* = 1.8 Hz), 2.46 s (3H, 2-Me), 6.72 q (1H, 6-H, *J* = 1.8 Hz), 8.09–8.36 d.d (4H, C_6H_4, *J* = 9.3 Hz). Found, %: Cl 10.93, 11.25. $C_{15}H_{11}ClN_2O_4$. Calculated, %: Cl 11.12.

***N*-(3-Chloro-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide (XVIIIa).** Yield 57%, mp 94–96°C. ^{1}H NMR spectrum, δ, ppm: 1.04 d (6H, 5-CH**Me**$_2$, *J* = 6.9 Hz), 2.44 s (3H, 2-Me), 2.96–3.10 m (1H, 5-CH), 6.61 d (1H, 6-H, *J* = 1.2 Hz), 7.48–7.91 m (5H, Ph). Found, %: Cl 11.80, 12.32. $C_{17}H_{16}ClNO_2$. Calculated, %: Cl 11.75.

***N*-(3-Chloro-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methylbenzamide (XVIIIb).** Yield 61%, mp 96–98°C. ^{1}H NMR spectrum, δ, ppm: 1.03 d (6H, 5-CH**Me**$_2$, *J* = 6.9 Hz), 2.43 s (3H, 2-Me), 2.44 s (3H, 4-**Me**C_6H_4), 2.96–3.10 (1H, 5-CH), 6.60 d (1H, 6-H, *J* = 0.9 Hz), 7.28–7.79 d.d (4H, C_6H_4, *J* = 8.1 Hz). Found, %: Cl 11.04, 11.59. $C_{18}H_{18}ClNO_2$. Calculated, %: Cl 11.23.

***N*-(3-Chloro-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-nitrobenzamide (XVIIIc).** Yield 60%, mp 169–170°C. ^{1}H NMR spectrum, δ, ppm: 1.07 d (6H, 5-CH**Me**$_2$, *J* = 6.6 Hz), 2.45 s (3H, 2-Me), 2.98–3.12 m (1H, 5-CH), 6.61 d (1H, 6-H, *J* = 0.9 Hz), 8.10–8.37 d.d (4H, C_6H_4, *J* = 9.3 Hz). Found, %: Cl 9.88, 10.34. $C_{17}H_{15}ClN_2O_4$. Calculated, %: Cl 10.22.

***N*-(3-Chloro-2-isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide (XXa).** Yield 31%, mp 84–86°C. ^{1}H NMR spectrum, δ, ppm: 1.48 d (6H, 2-CH**Me**$_2$, *J* = 6.9 Hz), 1.99 d (3H, 5-Me, *J* = 1.5 Hz), 3.72–3.86 m (1H, 2-CH), 6.65 q (1H, 6-H, *J* = 1.5 Hz), 7.48–7.89 m (5H, Ph). Found, %: Cl 11.40, 11.79. $C_{17}H_{16}ClNO_2$. Calculated, %: Cl 11.75.

***N*-(3-Chloro-2-isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methylbenzamide (XXb).** Yield 21%, mp 102–104°C. ^{1}H NMR spectrum, δ, ppm: 1.47 d (6H, 2-CH**Me**$_2$, *J* = 7.5 Hz), 1.98 d (3H, 5-Me, *J* = 1.2 Hz), 2.44 s (3H, 4-C**H**$_3C_6H_4$), 3.72–3.86 m (1H, 2-CH), 6.64 q (1H, 6-H, *J* = 1.2 Hz), 7.29–7.77 d (4H, C_6H_4, *J* = 8.4 Hz). Found, %: Cl 11.01, 11.71. $C_{18}H_{18}ClNO_2$. Calculated, %: Cl 11.23.

***N*-(3-Chloro-2-isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-nitrobenzamide (XXc).** Yield 61%, mp 136–138°C. ^{1}H NMR spectrum, δ, ppm: 1.48 d (6H, 2-CH**Me**$_2$, *J* = 7.2 Hz), 2.02 d (3H, 5-Me, *J* = 1.5 Hz), 3.72–3.86 m (1H, 2-CH), 6.65 q (1H, 6-H, *J* = 1.5 Hz), 8.06–8.38 d.d (4H, C_6H_4, *J* = 9.0 Hz). Found, %: Cl 9.76, 10.25. $C_{17}H_{15}ClN_2O_4$. Calculated, %: Cl 10.22.

***N*-(3,5,6-Trichloro-2,5-dimethyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXIIIa).** Yield 11%, mp 128–129°C. ^{1}H NMR spectrum, δ, ppm: 1.86 s (3H, 5-Me), 2.47 s (3H, 2-Me), 4.87 s (1H, 6-H), 7.48–7.97 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 16.57 (2-Me), 23.18 (5-Me), 58.05 (C^6), 64.65 (C^5), 128.79 ($C^{2'}$), 129.59 ($C^{3'}$), 131.28 ($C^{1'}$), 134.29 ($C^{4'}$), 137.15 (C^3), 144.89 (C^2), 158.42 (C^1), 178.12 (NC=O), 181.63 (C^4). Found, %: Cl 30.94, 31.81. $C_{15}H_{12}Cl_3NO_2$. Calculated, %: Cl 30.86.

4-Methyl-*N*-(3,5,6-trichloro-2,5-dimethyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXIIIb). Yield 59%, mp 90–91°C. ^{1}H NMR spectrum, δ, ppm: 1.85 s (3H, 5-Me), 2.44 s (3H, 4-**Me**C_6H_4, *J* = 8.4 Hz), 2.46 s (3H, 2-Me), 4.86 s (1H, 6-H), 7.28–7.85 d.d (4H, C_6H_4, *J* = 8.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 16.61 (2-Me), 21.83 (**Me**C_6H_4), 22.58 (5-Me), 58.20 (C^6), 64.68 (C^5), 128.54 ($C^{1'}$), 129.53 ($C^{2'}$), 129.73 ($C^{3'}$), 137.12 (C^3), 145.04 ($C^{4'}$), 145.42 (C^2), 158.20 (C^1), 178.13 (NC=O), 181.72 (C^4). Found, %: Cl 29.31, 29.79. $C_{16}H_{14}Cl_3NO_2$. Calculated, %: Cl 29.66.

4-Nitro-*N*-(3,5,6-trichloro-2,5-dimethyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXIIIc). Yield 59%, mp 160–162°C. ^{1}H NMR spectrum, δ, ppm: 1.88 s (3H, 5-Me), 2.48 s (3H, 2-Me), 4.88 s (1H, 6-H), 8.13–8.37 d.d (4H, C_6H_4, *J* = 9.0 Hz). Found, %: Cl 26.98, 27.33. $C_{15}H_{11}Cl_3N_2O_4$. Calculated, %: Cl 27.30.

***N*-(3,5,6-Trichloro-5-isopropyl-2-methyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXVa).** Yield 43%, mp 139–141°C. ^{1}H NMR spectrum, δ, ppm: 0.88–1.11 d.d (6H, 5-CH**Me**$_2$, *J* = 6.3 Hz), 2.24–2.38 m (1H, 5-CH), 2.45 s (3H, 2-Me), 5.10 s (1H, 6-H), 7.48–7.93 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 16.36 and 17.20 (CH**Me**$_2$), 18.77 (2-Me), 36.08 (**C**HMe$_2$), 59.96 (C^6), 82.86 (C^5), 128.88 ($C^{2'}$), 129.54 ($C^{3'}$), 130.90 ($C^{1'}$), 134.50 ($C^{4'}$), 138.69 (C^3), 144.54 (C^2), 158.76 (C^1), 178.23 (NC=O), 183.50 (C^4). Found,

%: Cl 28.10, 28.37. $C_{17}H_{16}Cl_3NO_2$. Calculated, %: Cl 28.54.

4-Methyl-*N*-(3,5,6-trichloro-5-isopropyl-2-methyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXVb). Yield 47%, mp 168–170°C. ^{1}H NMR spectrum, δ, ppm: 0.87–1.11 d.d (6H, 5-CH**Me**$_2$, J = 6.6 Hz), 2.23–2.37 m (1H, 5-CH), 2.44 s (3H, 4-**Me**C_6H_4), 2.44 s (3H, 2-Me), 5.09 s (1H, 6-H), 7.28–7.82 d.d (4H, C_6H_4, J = 8.4 Hz). Found, %: Cl 27.45, 27.78. $C_{18}H_{18}Cl_3NO_2$. Calculated, %: Cl 27.50.

4-Nitro-*N*-(3,5,6-trichloro-5-isopropyl-2-methyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXVc). Yield 60%, mp 157–159°C. ^{1}H NMR spectrum, δ, ppm: 0.90–1.17 d.d (6H, 5-CH**Me**$_2$, J = 6.6 Hz), 2.25–2.39 m (1H, 5-CH), 2.47 s (3H, 2-Me), 5.14 s (1H, 6-H), 8.10–8.38 d.d (4H, C_6H_4, J = 9.0 Hz). Found, %: Cl 25.10, 25.59. $C_{17}H_{15}Cl_3N_2O_4$. Calculated, %: Cl 25.46.

***N*-(3,5,6-Trichloro-2-isopropyl-5-methyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXVIa).** Yield 84%, mp 122–123°C. ^{1}H NMR spectrum, δ, ppm: 1.45–1.51 d.d (6H, 2-CH**Me**$_2$, J = 7.2 Hz), 1.83 s (3H, 5-Me), 3.63–3.77 m (1H, 2-CH), 4.79 s (1H, 6-H), 7.48–7.96 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 18.78 and 19.86 (CH**Me**$_2$), 22.52 (5-Me), 31.81 (**C**HMe$_2$), 59.19 (C^6), 64.39 (C^5), 128.81 (C$^{2'}$), 129.61 (C$^{3'}$), 131.35 (C$^{1'}$), 134.24 (C$^{4'}$), 135.97 (C^3), 152.00 (C^2), 157.27 (C^1), 177.63 (NC=O), 182.10 (C^4). Found, %: Cl 28.12, 28.51. $C_{17}H_{16}Cl_3NO_2$. Calculated, %: Cl 28.54.

4-Methyl-*N*-(3,5,6-trichloro-2-isopropyl-5-methyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXVIb). Yield 63%, mp 138–140°C. ^{1}H NMR spectrum, δ, ppm: 1.44–1.51 d.d (6H, 2-CH**Me**$_2$, J = 7.2 Hz), 1.83 s (3H, 5-Me), 2.44 s (3H, 4-**Me**C_6H_4), 3.62–3.76 m (1H, 2-CH), 4.78 s (1H, 6-H), 7.29–7.84 d.d (4H, C_6H_4, J = 8.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.78 and 19.85 (CH**Me**$_2$), 21.81 (4-**Me**C_6H_4), 22.52 (5-Me), 31.78 (**C**HMe$_2$), 59.13 (C^6), 64.40 (C^5), 128.70 (C$^{1'}$), 129.52 (C$^{2'}$), 129.69 (C$^{3'}$), 135.79 (C^3), 145.31 (C$^{4'}$), 152.09 (C^2), 157.01 (C^1), 177.59 (NC=O), 182.14 (C^4). Found, %: Cl 27.41, 27.93. $C_{18}H_{18}Cl_3NO_2$. Calculated, %: Cl 27.50.

4-Nitro-*N*-(3,5,6-trichloro-2-isopropyl-5-methyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXVIc). Yield 70%, mp 159–162°C. ^{1}H NMR spectrum, δ, ppm: 1.44–1.52 d.d (6H, 2-CH**Me**$_2$, J = 7.2 Hz), 1.85 s (3H, 5-Me), 3.62–3.76 m (1H, 2-CH), 4.78 s (1H, 6-H), 8.11–8.38 d.d (4H, C_6H_4, J = 9.0 Hz). Found, %: Cl 25.04, 25.40. $C_{17}H_{15}Cl_3N_2O_4$. Calculated, %: Cl 25.46.

***N*-(5-Chloro-4-hydroxy-2,3-dimethylphenyl)-benzamide (XXXIIIa).** Yield 80%, mp 176–178°C. Found, %: Cl 12.65, 12.89. $C_{15}H_{14}ClNO_2$. Calculated, %: Cl 12.86.

***N*-(5-Chloro-4-hydroxy-2,3-dimethylphenyl)-4-methylbenzamide (XXXIIIb).** Yield 53%, mp 226–228°C. Found, %: Cl 12.01, 12.29. $C_{16}H_{16}ClNO_2$. Calculated, %: Cl 12.24.

***N*-(5-Chloro-2,3-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide (XXXVa).** Yield 15%, mp 136–138°C. ^{1}H NMR spectrum, δ, ppm: 2.16 d (3H, 3-Me, J = 1.2 Hz), 2.30 d (3H, 2-Me, J = 1.2 Hz), 7.05 s (1H, 6-H), 7.47–7.90 m (5H, Ph). Found, %: Cl 12.84, 12.99. $C_{15}H_{12}ClNO_2$. Calculated, %: Cl 12.95.

***N*-(5-Chloro-2,3-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methylbenzamide (XXXVb).** Yield 21%, mp 169–170°C. ^{1}H NMR spectrum, δ, ppm: 2.15 d (3H, 3-Me, J = 1.2 Hz), 2.30 d (3H, 2-Me, J = 1.2 Hz), 2.44 s (3H, 4-**Me**C_6H_4), 7.03 s (1H, 6-H), 7.28–7.78 d.d (4H, C_6H_4, J = 8.1 Hz). Found, %: Cl 12.31, 12.45. $C_{16}H_{14}ClNO_2$. Calculated, %: Cl 12.32.

***N*-(3,5,6-Trichloro-5,6-dimethyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXXVIIa).** Yield 11%, mp 61–63°C. ^{1}H NMR spectrum, δ, ppm: 2.04 s (3H, 5-Me), 2.14 s (3H, 6-Me), 7.03 s (1H, 2-H), 7.48–7.93 m (5H, Ph). Found, %: Cl 30.76, 30.79. $C_{15}H_{12}Cl_3NO_2$. Calculated, %: Cl 30.86.

4-Methyl-*N*-(3,5,6-trichloro-5,6-dimethyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXXVIIb). Yield 68%, mp 79–80°C. ^{1}H NMR spectrum, δ, ppm: 2.04 s (3H, 5-Me), 2.13 s (3H, 6-Me), 2.44 s (3H, 4-**Me**C_6H_4), 7.01 s (1H, 2-H), 7.29–7.82 d.d (4H, C_6H_4, J = 8.4 Hz). Found, %: Cl 29.58, 29.68. $C_{16}H_{14}Cl_3NO_2$. Calculated, %: Cl 29.66.

5,6-Dichloro-2,3-dimethylcyclohex-2-ene-1,4-dione (XL). Yield 83%, sublimes at 158°C. ^{1}H NMR spectrum, δ, ppm: 2.09 s (6H, Me), 4.68 s (2H, 5-H, 6-H). Found, %: Cl 34.10, 34.22. $C_8H_8Cl_2O_2$. Calculated, %: Cl 34.29.

Bromination of quinone imines Ia–Ic, IIa–IIc, IIIa–IIIc, XVIIa–XVIIc, XIXa–XIXc, XXIa–XXIc, XXXIa, XXXIb, XXXVIa, and XXXVIb and aminophenols IVa–IVc, Va–Vc, VIa–VIc, XIa–XIc, XIIIa–XIIIc, XVa–XVc, XXXIIa, XXXIIb, XXXIVa, and XXXIVb (*general procedure*). A solution of bromine in chloroform, acetic acid, dimethylformamide, or dimethylformamide–acetic acid (1 : 5)

was added dropwise under stirring at 30–40°C to a solution of 2 mmol of the corresponding substrate in 3 ml of the same solvent until a required substrate-to-bromine ratio was attained (1:1 to 1:10). The precipitate was filtered off and recrystallized from acetic acid.

Compounds **VIIIb** and **VIIIc** were obtained by bromination of quinone imines **IIIb** and **IIIc** in AcOH at a substrate-to-bromine ratio of 1:3; compound **IX** was obtained by bromination of quinone imine **IIc** in DMF–AcOH (1:5) at a substrate-to-bromine ratio of 1:1; compounds **XIa**–**XIc**, **XIIIa**–**XIIIc**, and **XVa**–**XVc** were obtained by bromination of quinone imines **Ia**–**Ic**, **IIa**–**IIc**, and **IIIa**–**IIIc** in AcOH or aminophenols **IVa**–**IVc**, **Va**–**Vc**, and **VIa**–**VIc** in AcOH, DMF–AcOH (1:5), DMF, or $CHCl_3$ at a substrate-to-bromine ratio of 1:1; compounds **XVIIa**–**XVIIc**, **XIXa**–**XIXc**, and **XXIa**–**XXIc** were obtained by bromination of quinone imines **Ia**–**Ic**, **IIa**–**IIc**, and **IIIa**–**IIIc** or aminophenols **IVa**–**IVc**, **Va**–**Vc**, and **VIa**–**VIc** in DMF at a substrate-to-bromine ratio of 1:2; compounds **XXIIa**–**XXIIc** were obtained by bromination of quinone imines **XVa**–**XVc** in DMF at a substrate-to-bromine ratio of 1:2; compounds **XXIVa**, **XXIVc**, **XXVIIa**, and **XXVIIc** were obtained by bromination of quinone imines **Ia**, **Ic**, **IIIa**, **IIIc**, **XVIIa**, **XVIIc**, **XXIa**, and **XXIc** or aminophenols **IVa**, **IVc**, **VIa**, **VIc**, **XIa**, **XIc**, **XVa**, and **XVc** in AcOH or DMF–AcOH (1:5) at a substrate-to-bromine ratio of 1:5; compound **XXVIII** was obtained by bromination of aminophenol **XIa** in AcOH at a substrate-to-bromine ratio of 1:10; compounds **XXIX** and **XXX** were obtained by bromination of aminophenols **XIa** and **XIIIa** in DMF at a substrate-to-bromine ratio of 1:6; compounds **XXXIVa** and **XXXIVb** were obtained by bromination of quinone imines **XXXIa** and **XXXIb** or aminophenols **XXXIIa** or **XXXIIb** in $CHCl_3$ or AcOH at a substrate-to-bromine ratio of 1:1; compounds **XXXVIa** and **XXXVIb** were obtained by bromination of quinone imines **XXXIa** and **XXXIb** or aminophenols **XXXIIa** and **XXXIIb** in AcOH or DMF–AcOH (1:5) at a substrate-to-bromine ratio of 1:5; compounds **XXXVIIIa**, **XXXVIIIc**, and **XXXIX** were obtained by bromination of quinone imines **XXXIa**, **XXXIb**, **XXXVIa**, and **XXXVIb** or aminophenols **XXXIIa**, **XXXIIb**, **XXXIVa**, and **XXXIVb** in DMF–AcOH (1:5) at a substrate-to-bromine ratio of 1:10; we failed to separate compounds **XXXVIIIa** and **XXXIX**.

***N*-(5,6-Dibromo-2-isopropyl-5-methyl-4-oxocyclohex-2-en-1-ylidene)-4-methylbenzamide (VIIIb).** Yield 95%, mp 119–121°C. ^{1}H NMR spectrum, δ, ppm: 1.26–1.31 d.d (6H, 2-CH**Me**$_2$, J = 6.9 Hz), 1.97 s (3H, 5-Me), 2.44 s (3H, 4-**Me**C_6H_4), 3.25–3.39 m (1H, 2-CHMe$_2$), 5.07 s (1H, 6-H), 6.40 s (1H, 3-H), 7.27–7.88 d.d (4H, C_6H_4, J = 8.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 20.82 and 21.45 (CH**Me**$_2$), 21.86 (4-**Me**C_6H_4), 24.73 (5-Me), 28.35 (**C**HMe$_2$), 49.37 (C^6), 57.52 (C^5), 127.11 (C^3), 128.79 ($C^{1'}$), 129.44 ($C^{2'}$), 129.73 ($C^{3'}$), 145.16 ($C^{4'}$), 157.80 (C^2), 158.87 (C^1), 178.75 (NC=O), 188.94 (C^4). Found, %: Br 36.01, 36.39. $C_{18}H_{19}Br_2NO_2$. Calculated, %: Br 36.22.

***N*-(5,6-Dibromo-2-isopropyl-5-methyl-4-oxocyclohex-2-en-1-ylidene)-4-nitrobenzamide (VIIIc).** Yield 66%, mp 144–146°C. ^{1}H NMR spectrum, δ, ppm: 1.27–1.33 d.d (6H, 2-CH**Me**$_2$, J = 6.9 Hz), 2.00 s (3H, 5-Me), 3.23–3.37 m (1H, 2-CH), 5.08 s (1H, 6-H), 6.46 s (1H, 3-H), 8.15–8.37 d.d (4H, C_6H_4, J = 8.7 Hz). Found, %: Br 33.45, 33.91. $C_{17}H_{16}Br_2N_2O_4$. Calculated, %: Br 33.85.

***N*-(5,6-Dibromo-3-isopropyl-6-methyl-4-oxocyclohex-2-en-1-ylidene)-4-nitrobenzamide (IX).** Yield 35%, mp 119–120°C. ^{1}H NMR spectrum, δ, ppm: 1.02–1.08 d.d (6H, 3-CH**Me**$_2$, J = 6.9 Hz), 2.31 s (3H, 6-Me), 2.91–3.05 m (1H, 3-CH), 4.92 s (1H, 5-H), 6.42 s (1H, 2-H), 8.12–8.37 d.d (4H, C_6H_4, J = 9.0 Hz). Found, %: Br 33.54, 33.91. $C_{17}H_{16}Br_2N_2O_4$. Calculated, %: Br 33.85.

***N*-(3-Bromo-4-hydroxy-2,5-dimethylphenyl)-benzamide (XIa).** Yield 98%, mp 204–206°C. Found, %: Br 24.42, 24.59. $C_{15}H_{14}BrNO_2$. Calculated, %: Br 24.96.

***N*-(3-Bromo-4-hydroxy-2,5-dimethylphenyl)-4-methylbenzamide (XIb).** Yield 86%, mp 201–203°C. Found, %: Br 23.55, 24.01. $C_{16}H_{16}BrNO_2$. Calculated, %: Br 23.91.

***N*-(3-Bromo-4-hydroxy-2,5-dimethylphenyl)-4-nitrobenzamide (XIc).** Yield 78%, mp 242–244.5°C. Found, %: Br 21.49, 21.78. $C_{15}H_{13}BrN_2O_4$. Calculated, %: Br 21.88.

***N*-(3-Bromo-4-hydroxy-5-isopropyl-2-methylphenyl)benzamide (XIIIa).** Yield 95%, mp 173–175°C. Found, %: Br 22.30, 22.81. $C_{17}H_{18}BrNO_2$. Calculated, %: Br 22.94.

***N*-(3-Bromo-4-hydroxy-5-isopropyl-2-methylphenyl)-4-methylbenzamide (XIIIb).** Yield 59%, mp 148–150°C. Found, %: Br 21.49, 21.76. $C_{18}H_{20}BrNO_2$. Calculated, %: Br 22.06.

***N*-(3-Bromo-4-hydroxy-5-isopropyl-2-methylphenyl)-4-nitrobenzamide (XIIIc).** Yield 88%,

mp 232– 233.5°C. Found, %: Br 20.03, 20.44. $C_{17}H_{17}BrN_2O_4$. Calculated, %: Br 20.32.

***N*-(3-Bromo-4-hydroxy-2-isopropyl-5-methylphenyl)benzamide (XVa).** Yield 75%, mp 198–200°C. Found, %: Br 22.04, 22.73. $C_{17}H_{18}BrNO_2$. Calculated, %: Br 22.94.

***N*-(3-Bromo-4-hydroxy-2-isopropyl-5-methylphenyl)-4-methylbenzamide (XVb).** Yield 99%, mp 218–220°C. Found, %: Br 21.60, 22.04. $C_{18}H_{20}BrNO_2$. Calculated, %: Br 22.06.

***N*-(3-Bromo-4-hydroxy-5-isopropyl-2-methylphenyl)-4-nitrobenzamide (XVc).** Yield 96%, mp 202–203°C. Found, %: Br 20.10, 20.49. $C_{17}H_{17}BrN_2O_4$. Calculated, %: Br 20.32.

***N*-(3-Bromo-2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide (XVIIa).** Yield 36%, mp 116–118°C. ^{1}H NMR spectrum, δ, ppm: 2.02 d (3H, 5-Me, J = 1.5 Hz), 2.49 s (3H, 2-Me), 6.70 q (1H, 6-H, J = 1.5 Hz), 7.48–7.90 m (5H, Ph). Found, %: Br 23.83, 24.65. $C_{15}H_{12}BrNO_2$. Calculated, %: Br 25.11.

***N*-(3-Bromo-2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methylbenzamide (XVIIb).** Yield 23%, mp 110–112°C. ^{1}H NMR spectrum, δ, ppm: 2.01 d (3H, 5-Me, J = 1.5 Hz), 2.44 s (3H, 4-C**H**$_3$C$_6$H$_4$), 2.48 s (3H, 2-Me), 6.69 q (1H, 6-H, J = 1.5 Hz), 7.28–7.79 d.d (4H, C_6H_4, J = 7.8 Hz). Found, %: Br 23.41, 23.87. $C_{16}H_{14}BrNO_2$. Calculated, %: Br 24.05.

***N*-(3-Bromo-2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-nitrobenzamide (XVIIc).** Yield 61%, mp 192–194°C. ^{1}H NMR spectrum, δ, ppm: 2.06 d (3H, 5-Me, J = 1.5 Hz), 2.50 s (3H, 2-Me), 6.71 q (1H, 6-H, J = 1.5 Hz), 8.09–8.37 d.d (4H, C_6H_4, J = 9.0 Hz). Found, %: Br 21.53, 21.89. $C_{15}H_{11}BrN_2O_4$. Calculated, %: Br 22.00.

***N*-(3-Bromo-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide (XIXa).** Yield 20%, mp 92–93°C. ^{1}H NMR spectrum, δ, ppm: 1.04 d (6H, 5-CH**Me**$_2$, J = 6.9 Hz), 2.48 s (3H, 2-Me), 2.97–3.11 m (1H, 5-CH), 6.60 d (1H, 6-H), 7.28–7.79 m (5H, Ph). Found, %: Br 23.01, 23.25. $C_{17}H_{16}BrNO_2$. Calculated, %: Br 23.08.

***N*-(3-Bromo-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methylbenzamide (XIXb).** Yield 35%, mp 100–101°C. ^{1}H NMR spectrum, δ, ppm: 1.03 d (6H, 5-CH**Me**$_2$, J = 6.9 Hz), 2.44 s (3H, 4-**Me**C$_6$H$_4$), 2.48 s (3H, 2-Me), 2.96–3.10 m (1H, 5-CH), 6.59 d (1H, 6-H, J = 0.9 Hz), 7.28–7.79 d.d (4H, C_6H_4, J = 8.4 Hz). Found, %: Br 21.74, 22.22. $C_{18}H_{18}BrNO_2$. Calculated, %: Br 22.18.

***N*-(3-Bromo-5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-nitrobenzamide (XIXc).** Yield 83%, mp 166–167°C. ^{1}H NMR spectrum, δ, ppm: 2.06 d (6H, 5-CH**Me**$_2$, J = 6.9 Hz), 2.49 s (3H, 2-Me), 3.00–3.14 m (1H, 5-CH), 6.60 d (1H, 6-H, J = 0.9 Hz), 8.09–8.37 d.d (4H, C_6H_4, J = 9.0 Hz). Found, %: Br 20.03, 20.46. $C_{17}H_{15}BrN_2O_4$. Calculated, %: Br 20.42.

***N*-(3-Bromo-2-isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide (XXIa).** Yield 13%, mp 92–94°C. ^{1}H NMR spectrum, δ, ppm: 1.50 d (6H, 2-CH**Me**$_2$, J = 6.9 Hz), 1.99 d (3H, 5-Me, J = 1.5 Hz), 3.71–3.85 m (1H, 2-CH), 6.63 q (1H, 6-H, J = 1.5 Hz), 7.49–7.89 m (5H, Ph). Found, %: Br 23.04, 24.02. $C_{17}H_{16}BrNO_2$. Calculated, %: Br 23.08.

***N*-(3-Bromo-2-isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methylbenzamide (XXIb).** Yield 19%, mp 110–112°C. ^{1}H NMR spectrum, δ, ppm: 1.49 d (6H, 2-CH**Me**$_2$, J = 6.6 Hz), 1.98 d (3H, 5-Me, J = 1.2 Hz), 2.44 s (3H, 4-C**H**$_3$C$_6$H$_4$), 3.71–3.85 m (1H, 2-CH), 6.62 q (1H, 6-H, J = 1.2 Hz), 7.29–7.77 d.d (4H, C_6H_4, J = 8.4 Hz). Found, %: Br 22.11, 22.35. $C_{18}H_{18}BrNO_2$. Calculated, %: Br 22.18.

***N*-(3-Bromo-2-isopropyl-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-nitrobenzamide (XXIc).** Yield 20%, mp 103–105.5°C. ^{1}H NMR spectrum, δ, ppm: 1.50 d (6H, 2-CH**Me**$_2$, J = 6.9 Hz), 2.03 d (3H, 5-Me, J = 1.5 Hz), 3.75–3.89 m (1H, 2-CH), 6.62 q (1H, 6-H, J = 1.5 Hz), 8.06–8.38 d.d (4H, C_6H_4, J = 9.0 Hz). Found, %: Br 20.10, 20.46. $C_{17}H_{15}BrN_2O_4$. Calculated, %: Br 20.42.

***N*-(5,5,6-Tribromo-3-isopropyl-6-methyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXIIa).** ^{1}H NMR spectrum, δ, ppm: 1.00–1.10 d.d (6H, 3-CH**Me**$_2$, J = 6.9 Hz), 2.10 s (3H, 6-Me), 2.95–3.09 m (1H, 3-CH), 6.58 s (1H, 2-H), 7.43–7.92 m (5H, Ph).

4-Methyl-*N*-(5,5,6-tribromo-3-isopropyl-6-methyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXIIb). Yield 35%, mp 134–136°C. ^{1}H NMR spectrum, δ, ppm: 1.00–1.09 d.d (6H, 3-CH**Me**$_2$, J = 6.6 Hz), 2.08 s (3H, 6-Me), 2.40 s (3H, 4-C**H**$_3$C$_6$H$_4$), 2.94–3.08 m (1H, 3-CH), 6.58 s (1H, 2-H), 7.21–7.80 d.d (4H, C_6H_4, J = 8.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 17.58 (6-Me), 20.60 and 20.71 (CH**Me**$_2$), 21.75 (4-**Me**C$_6$H$_4$), 28.60 (**C**HMe$_2$), 70.47 (C^6), 88.50

(C^5), 125.19 ($C^{1'}$), 129.39 ($C^{2'}$), 130.08 ($C^{3'}$), 130.83 (C^2), 145.21 ($C^{4'}$), 152.34 (C^3), 163.77 (C^1), 183.20 (NC=O), 189.46 (C^4). Found, %: Br 45.57, 46.03. $C_{18}H_{18}Br_3NO_2$. Calculated, %: Br 46.09.

4-Nitro-*N*-(5,5,6-tribromo-3-isopropyl-6-methyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXIIc). ^{1}H NMR spectrum, δ, ppm: 1.03–1.12 d.d (6H, 3-CH**Me**$_2$, J = 6.6 Hz), 2.12 s (3H, 6-Me), 2.96–3.10 m (1H, 3-CH), 6.59 s (1H, 2-H), 8.08–8.30 d.d (4H, C_6H_4, J = 8.7 Hz).

***N*-(3,5,6-Tribromo-2,5-dimethyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXIVa).** Yield 80%, mp 122–124°C. ^{1}H NMR spectrum, δ, ppm: 2.06 s (3H, 5-Me), 2.53 s (3H, 2-Me), 5.10 s (1H, 6-H), 7.48–7.98 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 19.98 (2-Me), 25.62 (5-Me), 47.70 (C^6), 56.40 (C^5), 128.78 ($C^{2'}$), 129.66 ($C^{3'}$), 131.30 (C^3), 131.57 ($C^{1'}$), 134.34 ($C^{4'}$), 145.69 (C^2), 158.63 (C^1), 179.13 (NC=O), 182.64 (C^4). Found, %: Br 50.05, 50.29. $C_{15}H_{12}Br_3NO_2$. Calculated, %: Br 50.15.

4-Nitro-*N*-(3,5,6-tribromo-2,5-dimethyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXIVc). Yield 54%, mp 179–180°C. ^{1}H NMR spectrum, δ, ppm: 2.08 s (3H, 5-Me), 2.54 s (3H, 2-Me), 5.11 s (1H, 6-H), 8.14–8.37 d.d (4H, C_6H_4, J = 9.0 Hz). Found, %: Br 45.59, 45.93. $C_{15}H_{11}Br_3N_2O_4$. Calculated, %: Br 45.84.

***N*-(3,5,6-Tribromo-2-isopropyl-5-methyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXVIIa).** Yield 26%, mp 122–124°C. ^{1}H NMR spectrum, δ, ppm: 1.45–1.53 d.d (6H, 2-CH**Me**$_2$, J = 7.2 Hz), 2.03 s (3H, 5-Me), 3.61–3.75 m (1H, 2-CH), 5.00 s (1H, 6-H), 7.48–7.98 m (5H, Ph). Found, %: Br 47.01, 47.32. $C_{17}H_{16}Br_3NO_2$. Calculated, %: Br 47.37.

4-Nitro-*N*-(3,5,6-tribromo-2-isopropyl-5-methyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXVIIc). Yield 45%, mp 187–189°C. ^{1}H NMR spectrum, δ, ppm: 1.45–1.54 d.d (6H, 2-CH**Me**$_2$, J = 7.2 Hz), 2.05 s (3H, 5-Me), 3.64–3.78 m (1H, 2-CH), 5.01 s (1H, 6-H), 8.14–8.38 d.d (4H, C_6H_4, J = 9.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.76 and 20.16 (CH**Me**$_2$), 25.48 (5-Me), 35.56 (**C**HMe$_2$), 49.24 (C^6), 56.45 (C^5), 123.99 ($C^{2'}$), 130.68 ($C^{3'}$), 131.59 ($C^{1'}$), 136.42 (C^3), 151.00 (C^2), 154.43 ($C^{4'}$), 158.85 (C^1), 175.62 (NC=O), 181.91 (C^4). Found, %: Br 43.06, 43.46. $C_{17}H_{15}Br_3N_2O_4$. Calculated, %: Br 43.50.

***N*-(2,5,5,6-Tribromo-6-bromomethyl-3-methyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXVIII).** Yield 30%, mp 134–136°C. ^{1}H NMR spectrum, δ, ppm: 2.16 s (3H, 3-Me), 4.39 q (2H, CH_2Br, J = 3.3, 9.0 Hz), 7.41–7.93 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 18.05 (3-Me), 25.60 (CH_2Br), 66.93 (C^6), 87.51 (C^5), 127.26 ($C^{1'}$), 128.78 ($C^{2'}$), 130.35 ($C^{3'}$), 134.55 ($C^{4'}$), 138.60 (C^3), 140.27 (C^2), 163.85 (C^1), 178.74 (NC=O), 183.51 (C^4). Found, %: Br 62.24, 62.69. $C_{15}H_{10}Br_5NO_2$. Calculated, %: Br 62.84.

4,6-Dibromo-3,6-dimethyl-2,5-dioxocyclohex-3-en-1-yl benzoate (XXIX). Yield 42%, mp 134–136°C. ^{1}H NMR spectrum, δ, ppm: 2.00 s (3H, 3-Me), 2.29 s (3H, 6-Me), 6.07 s (1H, 1-H), 7.45–8.00 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 17.98 (3-Me), 24.03 (6-Me), 58.09 (C^6), 78.73 (C^1), 128.00 ($C^{1'}$), 128.73 ($C^{2'}$), 130.05 ($C^{3'}$), 134.14 ($C^{4'}$), 137.44 (C^4), 149.07 (C^3), 164.15 (OC=O), 183.66 (C^5), 186.35 (C^2). Found, %: Br 38.01, 38.23. $C_{15}H_{12}Br_2O_4$. Calculated, %: Br 38.41.

4,6-Dibromo-6-isopropyl-3-methyl-2,5-dioxocyclohex-3-en-1-yl benzoate (XXX). ^{1}H NMR spectrum, δ, ppm: 1.48 d (6H, 6-CH**Me**$_2$, J = 7.2 Hz), 2.27 s (3H, 3-Me), 2.36–2.50 m (1H, 6-CH), 6.17 s (1H, 1-H), 7.41–8.03 m (5H, Ph).

***N*-(5-Bromo-4-hydroxy-2,3-dimethylphenyl)-benzamide (XXXIVa).** Yield 89%, mp 209–210°C. Found, %: Br 24.74, 24.92. $C_{15}H_{14}BrNO_2$. Calculated, %: Br 24.96.

***N*-(5-Bromo-4-hydroxy-2,3-dimethylphenyl)-4-methylbenzamide (XXXIVb).** Yield 94%, mp 225.5–228°C. Found, %: Br 23.75, 27.98. $C_{16}H_{16}BrNO_2$. Calculated, %: Br 23.91.

***N*-(5-Bromo-2,3-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide (XXXVIa).** Yield 73%, mp 140–142°C. ^{1}H NMR spectrum, δ, ppm: 2.17 d (3H, 3-Me, J = 1.2 Hz), 2.30 d (3H, 2-Me, J = 1.2 Hz), 7.32 (1H, 6-H), 7.48–7.90 m (5H, Ph). Found, %: Br 25.07, 25.36. $C_{15}H_{12}BrNO_2$. Calculated, %: Br 25.11.

***N*-(5-Bromo-2,3-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-4-methylbenzamide (XXXVIb).** Yield 15%, mp 151.5–153°C. ^{1}H NMR spectrum, δ, ppm: 2.17 d (3H, 3-Me, J = 0.9 Hz), 2.29 d (3H, 2-Me, J = 0.9 Hz), 2.44 s (3H, 4-**Me**C_6H_4), 7.31 s (1H, 6-H), 7.28–7.79 d.d (4H, C_6H_4, J = 8.4 Hz). Found, %: Br 24.02, 24.16. $C_{16}H_{14}BrNO_2$. Calculated, %: Br 24.05.

***N*-(5,5,6,6-Tetrabromo-2,3-dimethyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXXVIIIa).** ^{1}H NMR spectrum, δ, ppm: 1.89 s (3H, 3-Me), 2.21 s (3H, 2-Me), 7.42–7.84 m (5H, Ph).

3-Bromo-4-methyl-*N*-(5,5,6,6-tetrabromo-2,3-dimethyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXXVIIIc). ^{1}H NMR spectrum, δ, ppm: 1.88 s (3H, 3-Me), 2.20 s (3H, 2-Me), 2.48 s (3H, 4-**Me**C_6H_3), 7.34 d (1H, 5′-H, J = 9.6 Hz), 7.92–7.95 d.d (1H, 6′-H, J = 9.6 Hz), 8.27 d (1H, 2′-H, J = 1.8 Hz).

***N*-(2,3,5,6-Tetrabromo-5,6-dimethyl-4-oxocyclohex-2-en-1-ylidene)benzamide (XXXIX).** ^{1}H NMR spectrum, δ, ppm: 1.34 s (3H, 5-Me), 1.73 s (3H, 6-Me), 7.40–7.88 m (5H, Ph).

Hydrochlorination of quinone imines Ia–Ic, IIa–IIc, IIIa–IIIc, XVIa–XVIc, XVIIIa–XVIIIc, XXa–XXc, XXXIa, and XXXIb. A stream of dry gaseous hydrogen chloride was passed over a period of 15–20 min through a solution of the corresponding quinone imine in 5 ml of anhydrous chloroform. The solution became lighter, and a colorless solid separated. The precipitate was filtered off, washed with acetic acid, and recrystallized from acetic acid. Aminophenols **Xa**–**Xc**, **XIIa**–**XIIc**, **XIVa**–**XIVc**, **XXXIIIa**, and **XXXIIIb** thus obtained were identical to the corresponding chlorination products of quinone imines **Ia**–**Ic**, **IIa**–**IIc**, **IIIa**–**IIIc**, **XXXIa**, and **XXXIb** and aminophenols **IVa**–**IVc**, **Va**–**Vc**, **VIa**–**VIc**, **XXXIIa**, and **XXXIIb**.

Hydrobromination of quinone imines Ia–Ic, IIa–IIc, IIIa–IIIc, XVIIa–XVIIc, XIXa–XIXc, XXIa–XXIc, XXXIa, and XXXIb. The corresponding quinone imine, 0.01 mol, was dissolved in 10 ml of acetic acid, and 2 ml of 46% hydrobromic acid was added. The mixture became lighter. It was diluted with water, and a colorless solid separated. The precipitate was filtered off, washed with acetic acid, and recrystallized from acetic acid. Aminophenols **XIa**–**XIc**, **XIIIa**–**XIIIc**, **XVa**–**XVc**, **XXXIVa**, and **XXXIVb** thus obtained were identical to the corresponding bromination products of quinone imines **Ia**–**Ic**, **IIa**–**IIc**, **IIIa**–**IIIc**, **XXXIa**, and **XXXIb** and aminophenols **IVa**–**IVc**, **Va**–**Vc**, **VIa**–**VIc**, **XXXIIa**, and **XXXIIb**.

Quinone imines **I**–**III**, **XVI**–**XXI**, **XXXIa**, **XXXIb**, **XXXVa**, **XXXVb**, **XXXVIa**, and **XXXVIb** were also synthesized by oxidation of aminophenols **IV**–**VI**, **X**–**XV**, and **XXXII**–**XXXIV** with lead tetraacetate in acetic acid according to the procedure described in [11] and were recrystallized from acetic acid.

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