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Halogenation of N-substituted *p*-Quinone Monoimines and *p*-Quinonemonooxime Ethers: XII.* Halogenation of *N*-Aroyl-2(3)-methyl-1,4-benzoquinone Monoimines and Their Reduced Forms

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Abstract—A strong acceptor substituent at the nitrogen atom of the N-substituted *p*-quinone monoimine decreases the stability of the halogen-containing cyclohexene structures formed at the addition of a halogen molecule to the C=C bond of the quinoid ring. As a result of the bromination of *N*-benzoyl-2-methyl-1,4-benzoquinone monoimine alongside the usual products of addition and substitution the 5-benzoyloxy-2,3,6-tribromo-6-methylcyclohex-2-ene-1,4-dione was isolated.

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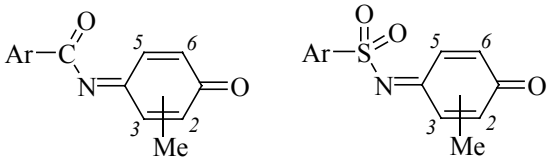
This study is a continuation of the research on the halogenation processes of N-substituted 1,4-benzoquinone monoimines. We formerly investigated in detail the halogenation of various *N*-arylsulfonyl-1,4-benzoquinone monoimines and their reduced forms [2–4], 4-amino-*N*-aroylphenol without substituents in the ring of the aminophenol [5], and *N*-aroyl-1,4-benzoquinone monoimines with two alkyl substituents in the ring [6, 7]. The *N*-aroyl-1,4-benzoquinone monoimines unsubstituted in the quinoid ring were not previously examined due to their instability [5, 8].

In this study *N*-aroyl-2(3)-methyl-1,4-benzoquinone monoimines **I, II** and 4-amino-*N*-aroyl-2(3)-methylphenols **III, IV** were chosen as the objects of the investigation. In contrast to the corresponding *N*-arylsulfonyl-2-methyl-1,4-benzoquinone monoimines [3] the ^{1}H NMR spectra of *N*-aroyl-2-methyl-1,4-benzoquinone monoimines **Ia, Ib** contain a single set of signals. It was established formerly that the *N*-aroyl-1,4-benzoquinone monoimines had a lower barrier to the *Z*,*E*-isomerization [9] ($\Delta G^{\neq}_{298K}$ 44–46 kJ mol^{-1}), than N-arylsulfonyl derivatives [10] ($\Delta G^{\neq}_{298Q}$ 65–80 kJ mol^{-1}). Therefore in the solutions of compounds **Ia, Ib** already at the room temperature the fast *Z*,*E*-isomerization occurs, and notwithstanding the existence of two isomeric forms the ^{1}H NMR spectrum contains a single set of signals, namely, the degenerate *Z*,*E*-isomerization is observed. It was earlier established that the presence of the *Z*,*E*-isomerization significantly affected the halogenation course of the *N*-arylsulfonyl-1,4-benzoquinone monoimines [3].

The difference in the chemical shifts of protons H^5 and H^6 (H^2 and H^3) of the quinoid ring is not so pronounced in the ^{1}H NMR spectra of compounds **I, II** as in the case of N-arylsulfonyl derivatives. This is due to the fact that the chemical shifts of the protons of the quinoid ring of N-aroyl derivatives **A** because of the fast *Z,E*-isomerization depend mainly on the position of this proton in the ring and on the character of the substituents in the neighboring positions. In N-arylsulfonyl derivatives **B** the chemical shifts of the protons in the quinoid ring are strongly affected by the position of the substituent at the nitrogen atom (*cis*- or *trans*-): the signal of the proton in the position 5 of the quinoid ring is shifted downfield and appears in the region 7.92–8.18 [3], of the proton H^3, in the region 6.81–6.93 ppm. In aroyl derivatives A the signal of the atom H^5 of quinone imines **Ia**, **Ib** is shifted upfield compared with the sulfonyl derivatives and appears in the region 7.02–7.08, and that of the atom H^3,

* For Communication XI, see [1].

at 6.85–6.87 ppm.



A **B**

The special feature of *p*-quinone monoimines consists in the dependence of their redox potential on the nature of the substituent at the nitrogen atom [11]. The presence of a strong acceptor substituent at the nitrogen atom in the *N*-aroyl-1,4-benzoquinone monoimines significaly increases their redox potential, and this should inevitably affect the halogenation, for the redox processes play there a significant part.

The goal of this study is the investigation of the halogenation of the *N*-aroyl-2(3)-methyl-1,4-benzoquinone monoimines and the comparison of the results obtained with the previously examined halogenation processes of the corresponding *N*-arylsulfonyl-1,4-benzoquinone monoimines.

The halogenation of *N*-aroyl-2(3)-methyl-1,4-benzoquinone monoimines **Ia, Ib** and **IIa, IIb**, 4-amino-*N*-aroyl-2(3)-methylphenols **IIIa–IIIc** and **IVa–IVc** was carried out using gaseous chlorine and molecular bromine in $CHCl_3$, AcOH, DMF, a mixture DMF–AcOH, 1:5, at various ratios initial substrate–halogen.

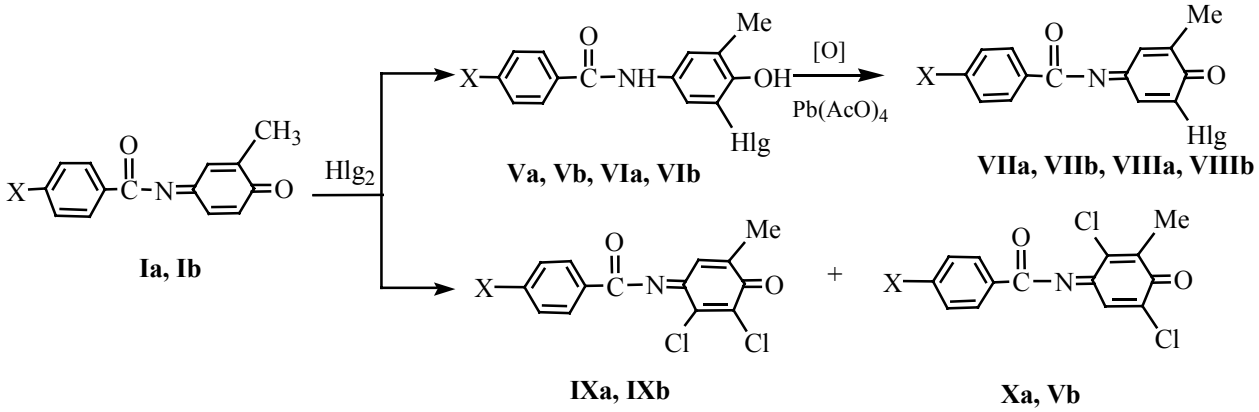
N-Aroyl-2(3)-methyl-1,4-benzoquinone monoimines were obtained by the oxidation of the corresponding aminophenols with lead tetraacetate in acetic acid, but we failed to isolate the respective quinone monoimines after the oxidation of 4-amino-*N*-aroyl-2-methylphenols **IIIa, IIIc** and 4-amino-*N*-benzoyl-3-methylphenol (**IVa**) for the reaction products were uncrystallizable oily substances. We succeeded to isolate in the crystalline state only bromo- and nitrobenzoyl derivatives **Ia, Ib** and *N*-aroyl-3-methyl-1,4-benzoquinone monoimines **IIb, IIc**.

The equimolar chlorination of quinone monoimines **Ia, Ib** in acetic acid afforded 6-chlorophenols **Va, Vb**, and in DMF, a mixture of 5,6- and 3,6-dichloro-1,4-benzoquinone monoimines **IXa, IXb** and **Xa, Xb** with the prevalence of the latter (Scheme 1). At the increased excess of chlorine to 1:2 uncrystallizable oily intractable mixtures of compounds were obtained.

The structures of quinone monoimines **IXa, IXb** and **Xa, Xb** were identified from the ^{1}H NMR spectra. The quartet signal of atom H^3 of quinone monoimines **IXa, IXb** appeared in the region 6.82–6.86 ppm. The location of the signal confirmed the whereabouts of the proton in the *ortho*-position to the C=N fragment of the quinoid ring, its form was due to the coupling with the protons of the CH_3 group whose doublet was observed at 2.06–2.09 ppm. In the ^{1}H NMR spectra of quinone monoimines **Xa, Xb** the singlet of the atom H^5 located in the *ortho*-position to the imine carbon atom appeared in the region 7.16–7.21 ppm and was shifted downfield compared to the signal of the proton H^3 of quinone monoimines **IXa, IXb**. The protons of CH_3 group give rise to a singlet at 2.33–2.35 ppm confirming the presence of the chlorine atom in the position *3* of the quinoid ring.

The equimolar bromination of quinone monoimines **Ia, Ib** in $CHCl_3$, DMF, a mixture DMF–AcOH, 1 : 5, resulted only in 6-bromophenols **VIa, VIb** (Scheme 1).

Scheme 1.



Ia, Ib **Va, Vb, VIa, VIb** **VIIa, VIIb, VIIIa, VIIIb** **IXa, IXb** **Xa, Vb**

X = Br (**a**), NO_2 (**b**); Hlg = Cl (**V, VII**), Br (**VI, VIII**).

At increasing the ratio initial compound–bromine from 1 : 2 to 1 : 5 only oily substances were obtained which we failed to identify.

The structure of compounds **Va, Vb, VIa, VIb** was established from the ^{1}H NMR spectra of *N*-aroyl-2-methyl-6-bromo(chloro)-1,4-benzoquinone monoimines **VIIa, VIIb** and **VIIIa, VIIIb** obtained by the oxidation of aminophenols **Va, Vb, VIa, VIb** with lead tetraacetate in acetic acid.

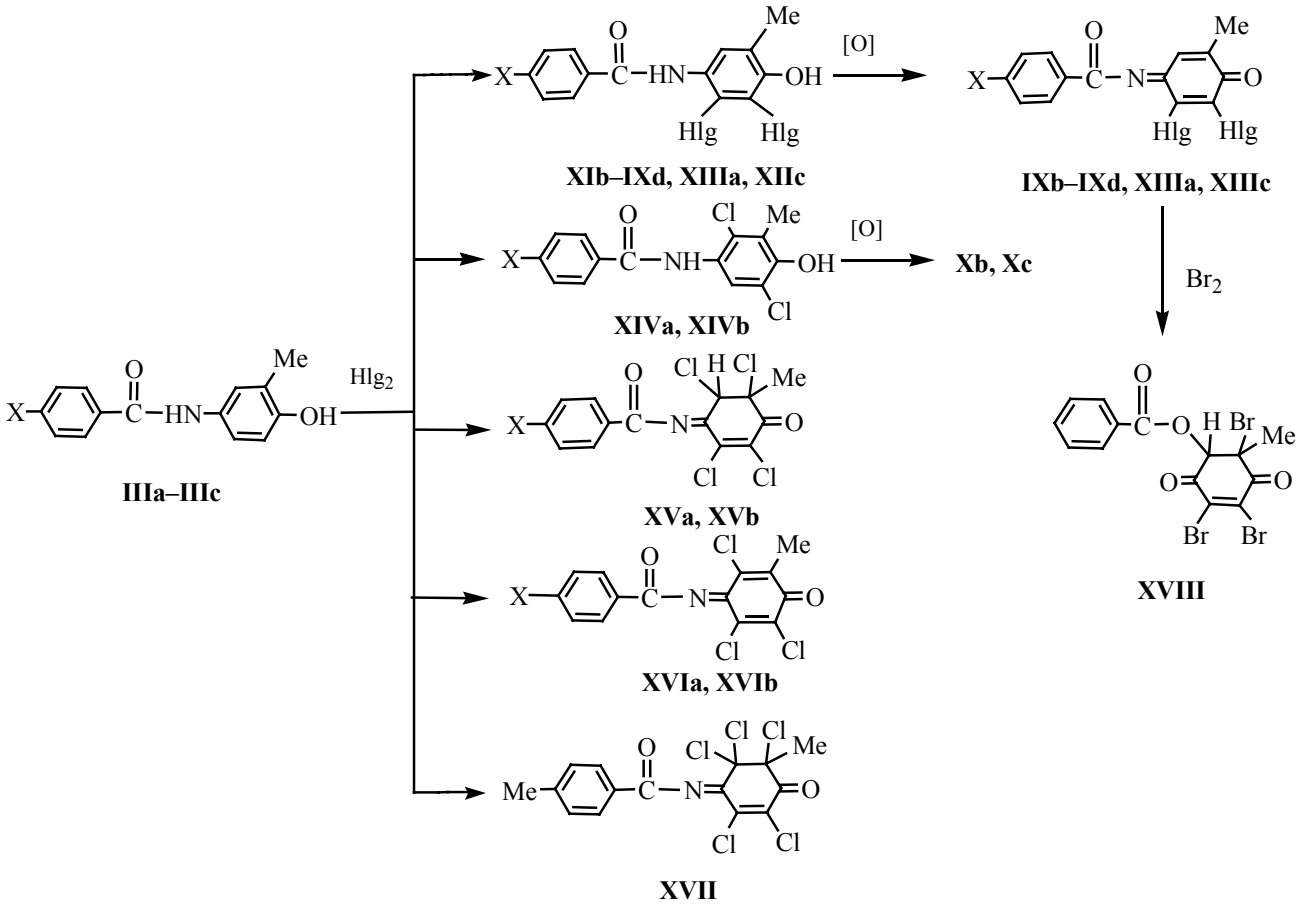
In the ^{1}H NMR spectra of quinone monoimines **VIIa, VIIb** and **VIIIa, VIIIb** the quartet signal of the atom H^3 was observed at 6.89–6.92, and the doublet of the atom H^5, in the region 7.25–7.55 ppm. The doublet of the protons of the CH_3 group appeared at 2.11–2.14 ppm in good agreement with the assumed structure.

The chlorination of 2-methylphenols **IIIa–IIIc** in $CHCl_3$, AcOH, DMF at the ratio initial substrate–chlorine 1:1 resulted in 2-methyl-5,6-dichlorophenols **XIa–XIc** (Scheme 2).

The equimolar chlorination of aminophenols **IIIa, IIIb** in the mixture DMF–AcOH, 1 : 5, led to the formation of substituted 5,6- and 3,6-dichlorophenols **XIa**, **XIb** and **XIVa, XIVb** with the prevalence of the former. At increasing the ratio initial substrate–chlorine to 1 : 3 in $CHCl_3$, AcOH, the mixture DMF–AcOH we obtained stable 4-aroylimino-6-methyl-2,3,5,6-tetrachloro-cyclohex-2-en-1-ones **XVa, XVb**. At the chlorination of aminophenols **IIIb, IIIc** in DMF with the triple excess of chlorine 3,5,6-trichloro derivatives **XVIb, XVIc** were isolated originating from the dehydrochlorination of 4-aroylimino-6-methyl-2,3,5,6-tetrachlorocyclohex-2-en-1-ones **XV**. By increasing the ratio initial substrate–chlorine to 1 : 5 in DMF stable 6-methyl-4-(4-methyl-benzoyl)imino-2,3,5,5,6-pentachlorocyclohex-2-en-1-one (**XVII**) was obtained.

The structure of compounds **XVa, XVb, XVIb, XVIc, XVII** was proved by the data of ^{1}H and ^{13}C NMR spectra. The singlet of the atom H^5 of the structures **XVa, XVb**

Scheme 2.



III, **XI–XVI**, X = H (**a**), NO_2 (**b**), Me (**c**); **IX,** X = NO_2 (**b**), Me (**c**), H (**d**); **X**, X = NO_2 (**b**), H (**c**); Hlg = Cl (**IX, XI**), Br (**XII, XIII**).

appears in the region 5.01–5.03 ppm characteristic of the protons attached to the sp^3-hybridized carbon atom in the *ortho*-position to the C=N fragment, the proton signal of the CH_3 group is observed as a singlet at 1.90–1.93 ppm. In the case of quinone monoimines **XVIb, XVIc** the singlet of the methyl protons is shifted downfield compared to the methyl signal of the protons of **XVa, XVb** structure and is observed at 2.22–2.27 ppm. In the spectrum of compound **XVII** the methyl singlet is located at 2.18 ppm.

The ^{13}C NMR spectra of compounds **XVa, XVII** contain characteristic upfield signals of two sp^3-hybridized carbon atoms: 64.81, 57.88 in the spectrum of compound **XVa** (from fragments $CClCH_3$, CHCl) and 88.77, 72.27 ppm for compound **XVII** (CClCl and $CClCH_3$). In the ^{13}C NMR spectrum of compound **XVIc** the signals of sp^3- hybridized carbon atoms are absent, and the observed signals are totally consistent with the assumed structure.

The bromination of aminophenols **IIIa, IIIc** in $CHCl_3$, AcOH, the mixture DMF–AcOH furnished 4-amino-*N*-aroyl-5,6-dibromo-2-methylphenols **XIIa, XIIc** (Scheme 2). We failed to obtain products of deeper bromination. It may be caused by the higher redox potential of aroyl derivatives and impossible for bromine to oxidize the obtained aminophenols **XIIa, XIIc** unlike the previously observed behavior of arylsulfonyl derivatives [3].

In order to identify aminophenols **XIa–XIc, XIIa, XIIc** they were oxidized with lead tetraacetate in acetic acid into the corresponding 1,4-benzoquinone monoimines **IXb–IXd, XIIIa, XIIIc** since the ^1H NMR spectra of quinone monoimines were more informative. The mixture of compounds **XIa, XIb** and **XIVa, XIVb** also was analyzed after oxidation which yielded a mixture of quinone monoimines **IXb, IXd** and 3,6-dichloro-1,4-benzoquinone monoimines **Xb, Xc**.

In the ^1H NMR spectrum of quinone monoimines **IXb–IXd**, **XIIIa, XIIIc** the quartet of the proton H^3 appeared in the region 6.82–6.88, and the doublet of the methyl protons, at 2.04–2.05 ppm, unambiguously confirming the structure of these compounds. In the spectra of quinone monoimines **Xb, Xc** the singlet of the atom H^5 is present in the region 7.16–7.21 ppm, and the singlet of the methyl protons, at 2.33–2.35 ppm, in agreement with the assumed structure.

The bromination of aminophenol **XIIa** and quinone monoimine **XIIIa** in DMF and its mixture with ACOH at the ratio substrate–bromine 1 : 10 provided 5-benzoyloxy-2,3,6-tribromo-6-methylcyclohex-2-en-1,4-dione (**XVIII**). Formerly at the bromination of the analogous 4-amino-*N*-arylsulfonyl-2-methylphenols no compounds of similar structure were isolated [3], but they were obtained at the bromination of *N*-aroyl-2,6(2,5)-dimethyl-1,4-benzoquinone monoimines [7].

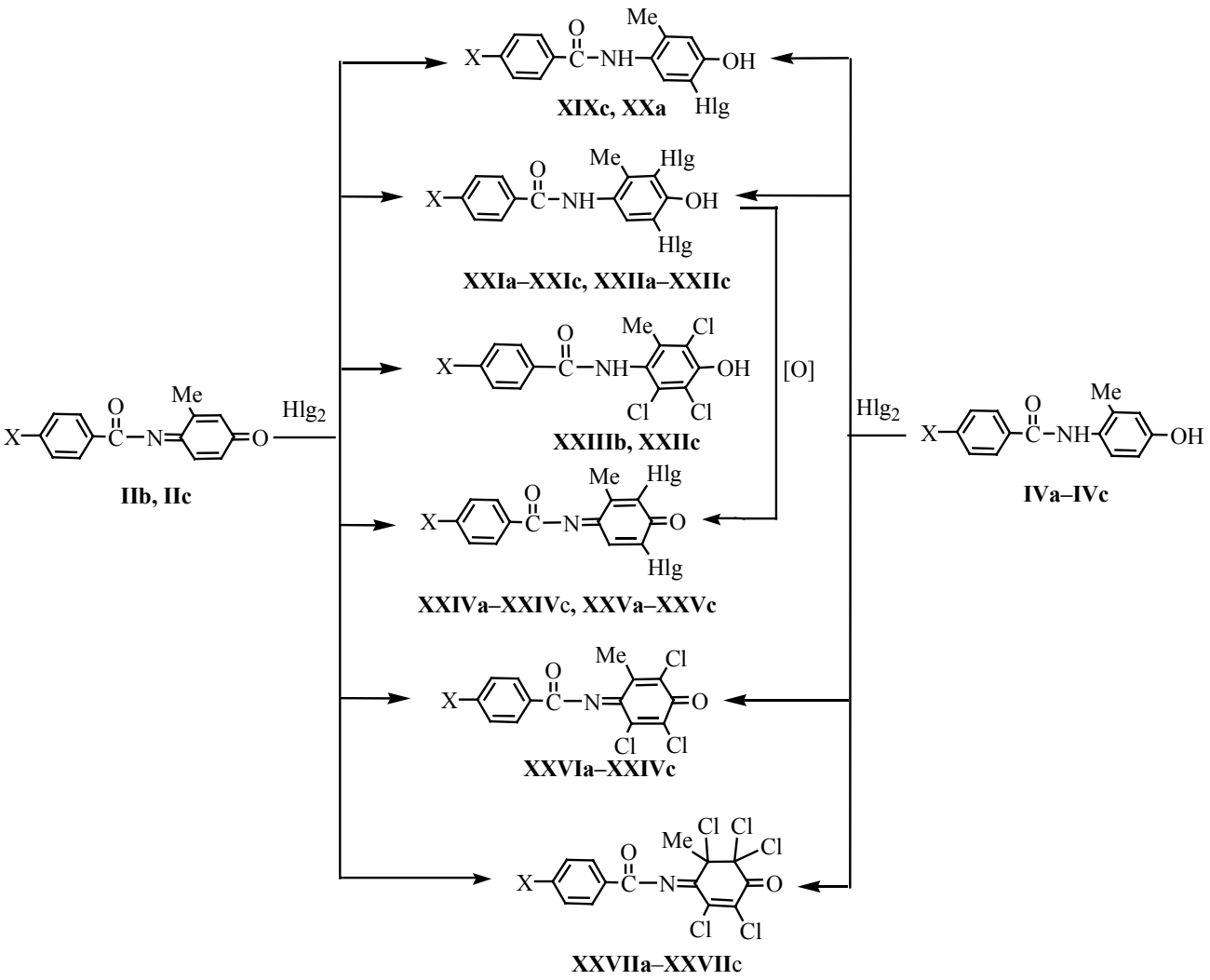
The structure of compound **XVIII** was proved by the data of ^1H and ^{13}C NMR spectra. The characteristic feature of this compound is the presence in the ^1H NMR spectrum of a signal from the H^5 proton linked to the sp^3-hybridized carbon atom in the region 6.20, and the singlet of the methyl protons at 2.01 ppm [7]. In the ^{13}C NMR spectrum of compound **XVIII** two characteristic peaks of the carbonyl atoms C^1 and C^4 appeared at 181.46 and 180.33 ppm, and two signals of sp^3-hybridized carbon atoms were observed in the strong field (77.18 and 56.65 ppm).

The analysis of the experimental data of this study and the former investigations [5–7] shows that the formation of aminophenols **XI**, **XII** occurs as a result of the oxidation of aminophenols **III** with a halogen molecule into quinone monoimines **I** which add the molecule Hlg_2 to the free bond C=C of the quinoid ring giving 4-aroylimino-5,6-dihalo-2-methylcyclohex-2-en-1-ones. We failed to isolate the latter for due to the fast in the NMR scale *Z*,*E*-isomerization they were very unstable and suffered a prototropic rearrangement to provide aminophenols **XI**, **XII**. Aminophenols **XI**, **XII** may also form as a result of the electrophilic substitution of hydrogen atoms by halogen in the molecules of aminophenols **III**. Aminophenols **XIV** result from the electrophilic substitution of hydrogen atoms by chlorine in the ring of aminophenols **III**.

The maximally chlorinated compound **XVII** is likely to form through a sequence of transformations: (1) The oxidation of aminophenol **III** to quinone monoimine **I** with a halogen molecule; (2) addition of the molecule Cl_2 to the free bond C=C of the quinoid ring of quinone monoimine **I** with the formation of the unstable cyclohexene structure which in the course of the reaction suffers the prototropic rearrangement into aminophenol **XI**; (3) aminophenol **XI** undergoes the oxidation and adds the molecule Cl_2 to the methyl-substituted C=C bond giving compound **XV**; (4) tetrachlorocyclohexene structure **XV** suffers the dehydrochlorination to form trichloroquinone monoimine **XVI** that adds the molecule Cl_2 to the methyl-substituted C=C bond affording the compound of the maximum degree of chlorination the pentachlorocyclohexene structure **XVII**.

The chlorination of quinone monoimines **IIa, IIb** and aminophenols **IVa–IVc** in various solvents at different

Scheme 3.



X = H (**a**), Me (**b**), Cl (**c**), Hlg = Cl (**XIX, XXI, XXIV**), Br (**XX, XXII, XXV**).

ratios initial substance–chlorine led to the formation of compounds shown in Scheme 3. In a single case, at the chlorination of 3-methyl-*N*-(4-chlorobenzoyl)-1,4-benzoquinone monoimine (**IIc**) at the ratio initial substance–chlorine 1 : 1 in $CHCl_3$ or the mixture DMF–AcOH, 1 : 5 we obtained 6-chloro derivative **XIXc** in a mixture with 2,6-dichlorocompound **XXIc** (Scheme 3).

Individual aminophenols **XXIa–XXIc** were obtained by the equimolar chlorination of quinone monoimines **IIa**, **IIb** in AcOH and aminophenols **IVa–IVc** in $CHCl_3$, AcOH, DMF, the mixture DMF–AcOH. The chlorination of quinone monoimines **IIb**, **IIc** in $CHCl_3$ gave a mixture of 2,6-dichloro- (**XXIb**, **XXIc**) and 2,5,6-trichlorophenols (**XXIIIb**, **XXIIIc**) (Scheme 3). The oxidation of aminophenols **XXIa–XXIc** with lead tetraacetate in acetic acid leads to the formation of *N*-aroyl-3-methyl-2,6-dichloro-1,4-benzoquinone monoimines **XXIVa–XXIVb** which were also obtained by the chlorination of quinone monoimines **IIb**, **IIc** in DMF at the ratio initial substance–chlorine 1 : 1. At the excess of the chlorinating agent (1 : 3.5) the chlorination of the quinone monoimines **IIb**, **IIc** and aminophenols **IVa–IVc** in $CHCl_3$, AcOH, the mixture DMF–AcOH, 1 : 5, resulted in *N*-aroyl-3-methyl-2,5,6-trichloro-1,4-benzoquinone monoimines **XXVIa–XXVIc**. The products of the highest chlorination degree **XXVIIa–XXVIIc** were obtained at the chlorination of quinone monoimines **IIb**, **IIc** and aminophenols **IVa–IVc** only in DMF at the highest ratio initial sub-

stance–chlorine (1 : 6.5).

The structure of compounds **XXVIa–XXVIc, XXVIIa–XXVIIc** was proved by the ^{1}H and ^{13}C NMR spectra. In the spectra of quinone monoimines **XXVIIa–XXVIIc** the proton signal from the methyl group is observed at 2.29–2.30 ppm upfield from the signal of the methyl protons of compounds **XXVIa–XXVIc**. In the ^{13}C NMR spectrum of compound **XXVIIb** the characteristic signals of two sp^3-hybridized carbon atoms appear at 88.40 (CClCl) and 74.51 ppm ($CClCH_3$).

The bromination of quinone monoimines **IIa**, **IIb** and aminophenols **IVa–IVc** at the ratio initial substrate–bromine from 1 : 3 to 1 : 5 in $CHCl_3$, AcOH, the mixture DMF–AcOH, 1 : 5, resulted in the formation of 2,6-dibromophenols **XXIIa–XXIIc**. The oxidation of the latter and also the bromination of quinone monoimines **IIa**, **IIb** in DMF at the ratio initial substrate–bromine 1 : 1 led to the formation of 2,6-dibromo-1,4-benzoquinone monoimines **XXVa–XXVc**. The bromination of aminophenol **IVa** in AcOH, DMF at the same ratio initial substrate–bromine yielded 6-bromophenol **XXa** (Scheme 3).

In the ^{1}H NMR spectra of aminophenols **XIX**, **XX** the singlet of the atom H^2 is observed at 6.85–6.87, the singlet of the atom H^5, in the region 7.28–7.41 ppm, and the singlet of the methyl protons, at 2.13 ppm, confirming the structure of these compounds.

In the ^{1}H NMR spectra of quinone monoimines **XXIVa–XXIVc**, **XXVa–XXVc** the singlet of the atom H^5 is present in the region 7.11–7.38 ppm, and the singlet of the methyl protons, at 2.47– 2.51 ppm. The structure of compounds **XXIIIb**, **XXIIIc** was established after the oxidation to the corresponding quinone monoimines **XXVIb**, **XXVIc** whose structure was proved by the ^{1}H NMR spectra.

Analysis of the results of the halogenation of quinone monoimines **I** and **II** and aminophenols **III** and **IV** shows that in general the direction and the course of the halogenation of quinone monoimines **I** and **II** are analogous to those of *N*-arylsulfonyl-2(3)-methyl-1,4-benzoquinone monoimines, but the presence of a strong acceptor substituent at the nitrogen atom results in some deviations. We failed to obtain from quinone monoimines **I** and **II** a large variety of cyclohexene structures, in particular, products of addition of one halogen molecule, as were obtained from the corresponding N-arylsulfonyl derivatives. This is due to the stronger electron-acceptor properties of the ArCO group and consequently to the higher C–H-acidity of protons in the ortho-position to the imine carbon atom leading to a high reactivity of the cyclohexene compounds and to the fast dehydrohalogenation of the latter. As a result of the dehydrohalogenation or a prototropic rearrangement the cyclohexene compounds convert into the corresponding quinone monoimines or aminophenols. On the other hand, by the chlorination of quinone monoimines **II** and aminophenols **III, IV** we obtained the product of the maximum degree of halogenation, compounds **XVII** and **XXVII** that we had failed to prepare from the corresponding N-arylsulfonyl derivatives of *p*-quinone monoimines. This can be ascribed to the stronger electron-acceptor properties of the aroyl group compared to the $ArSO_2$ group and consequently to the lower stability of the cyclohexene structures resulting in the readily occurring processes of dehydrohalogenation and further to the formation of quinone imines of the maximum degree of halogenation.

EXPERIMENTAL

IR spectra of compounds synthesized were recorded on a spectrophotometer UR-20 from pellets with KBr. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Varian VXR-300 (300 and 75.4 MHz) from solutions in $CDCl_3$, internal reference TMS.

The reaction mixtures were analyzed by TLC on Silufol UV-254 plates, eluent benzene–hexane, 10 **:** 1, benzene–ethyl acetate, 10:1, development by UV irradiation.

4-Amino-*N*-aroyl-2(3)-methylphenols IIIa–IIIc, IVa–IVc were obtained by the reaction of 4-amino-2(3)-methylphenols with the corresponding carboxylic acids chlorides in the mixture DMF–AcOH, 1 **:** 5, in the presence of AcONa by procedure [12].

***N*-Aroyl-2(3)-methyl-1,4-benzoquinone monoimines Ia, Ib, IIb, IIc** were obtained by the oxidation of 4-amino-*N*-aroyl-2(3)-methylphenols with $Pb(OAc)_4$ in AcOH [12]. The products were recrystallized from AcOH.

***N*-(4-Bromobenzoyl)-2-methyl-1,4-benzoquinone monoimine (Ia).** Yield 79%, mp 116–118°C. ^{1}H NMR spectrum, δ, ppm: 2.04 d (3H, 2-Me, *J* 1.2 Hz), 6.66 d (1H, H^6, *J* 10.2 Hz), 6.85 q (1H, H^3, *J* 2.7 Hz), 7.02–7.06 d.d (1H, H^5, *J* 10.2, 2.7 Hz), 7.62 d, 7.80 d (4H, C_6H_4, *J* 8.7 Hz). Found, %: N 4.56, 4.59. $C_{14}H_{10}BrNO_2$. Calculated, %: N 4.61.

2-Methyl-*N*-(4-nitrobenzoyl)-1,4-benzoquinone monoimine (Ib). Yield 71%, mp 121–123°C. ^{1}H NMR spectrum, δ, ppm: 2.06 d (3H, 2-Me, *J* 1.5 Hz), 6.70 d (1H,

H^6, *J* 9.6 Hz), 6.88 q (1H, H^3, *J* 2.4 Hz), 7.05–7.08 d.d (1H, H^5, *J* 9.6, 2.4 Hz), 8.11 d, 8.35 d (4H, C_6H_4, *J* 9.0 Hz). Found, %: N 10.33, 10.36. $C_{14}H_{10}N_2O_4$. Calculated, %: N 10.37.

3-Methyl-*N*-(4-methylbenzoyl)-1,4-benzoquinone monoimine (IIb). Yield 81%, mp 88–89°C. ^{1}H NMR spectrum, δ, ppm: 2.30 d (3H, 3-Me), 2.44 s (3H, 4-Me), 6.44–6.48 d.d (1H, H^6, *J* 2.4 Hz), 6.61 q (1H, H^2, *J* 1.5 Hz), 6.85 d (1H, H^5, *J* 10.2 Hz), 7.28 d, 7.78 d (4H, C_6H_4, *J* 8.4 Hz). Found, %: N 5.79, 5.82. $C_{15}H_{13}NO_2$. Calculated, %: N 5.85.

3-Methyl-*N*-(4-chlorobenzoyl)-1,4-benzoquinone monoimine (IIc). Yield 83%, mp 112–114°C. ^{1}H NMR spectrum, δ, ppm: 2.29 d (3H, 3-Me), 6.47– 6.51 d.d (1H, H^6, *J* 2.7 Hz), 6.62 q (1H, H^2, *J* 1.2 Hz), 6.86 d (1H, H^5, *J* 10.3 Hz), 7.74 d, 7.90 d (4H, C_6H_4, *J* 8.4 Hz). Found, %: N 5.29, 5.33. $C_{14}H_{10}ClNO_2$. Calculated, %: N 5.39.

4-Amino-*N*-benzoyl-2-methylphenol (IIIa). Yield 82%, mp 202–204°C. Found, %: N 6.08, 6.13. $C_{14}H_{13}NO_2$. Calculated, %: N 6.16.

4-Amino-2-methyl-*N*-(4-nitrobenzoyl)phenol (IIIb). Yield 91%, mp 263–264°C. Found, %: N 9.93, 10.18. $C_{14}H_{12}N_2O_4$. Calculated, %: N 10.29.

4-Amino-2-methyl-*N*-(4-methylbenzoyl)phenol (IIIc). Yield 86%, mp 228–230°C. Found, %: N 5.74, 5.79. $C_{15}H_{15}NO_2$. Calculated, %: N 5.80.

4-Amino-*N*-benzoyl-3-methylphenol (IVa). Yield 89%, mp 202–204°C. Found, %: N 6.09, 6.14. $C_{14}H_{13}NO_2$. Calculated, %: N 6.16.

4-Amino-3-methyl-*N*-(4-methylbenzoyl)phenol (IVb). Yield 75%, mp 208–210°C. Found, %: N 5.71, 5.77. $C_{15}H_{15}NO_2$. Calculated, %: N 5.80.

4-Amino-3-methyl-*N*-(4-chlorobenzoyl)phenol (IVc). Yield 81%, mp 205–206°C. Found, %: N 5.30, 5.34. $C_{14}H_{12}ClNO_2$. Calculated, %: N 5.35.

Chlorination of quinone monoimines Ia, Ib, IIb, IIc and aminophenols IIIa–IIIc, IVa–IVc. Through the solution of 2 mmol of compounds under study in 3 ml $CHCl_3$, AcOH, DMF, or a mixture DMF–AcOH, 1 : 5, was passes a flow of dry chlorine at the rate 15–20 ml min^{-1} at 25–30°C. The ratio initial compound–chlorine was monitored by the weight gain, and it was varied in the range from 1 **:** 1 to 1 **:** 6.5. After several hours the reaction products were filtered off and recrystallized from acetic acid.

4-Amino-*N*-(4-bromobenzoyl)-2-methyl-6-chlorophenol (Va). Yield 84%, mp 160–162°C. Found, %: Br + Cl 33.79, 33.85. $C_{14}H_{11}BrClNO_2$. Calculated, %: Br + Cl 33.87.

4-Amino-2-methyl-*N*-(4-nitrobenzoyl)-6-chlorophenol (Vb). Yield 42%, mp 256–258°C. Found, %: Cl 11.48, 11.52. $C_{14}H_{11}ClN_2O_4$. Calculated, %: Cl 11.56.

***N*-(4-Bromobenzoyl)-2-methyl-6-chloro-1,4-benzoquinone monoimine (VIIa).** Yield 69%, mp 128–130°C. ^{1}H NMR spectrum, δ, ppm: 2.12 d (3H, 2-Me), 6.89 q (1H, H^3, *J* 2.1, 1.5 Hz), 7.25 d (1H, H^5), 7.63 d, 7.80 d (4H, C_6H_4, *J* 9.0 Hz). Found, %: Br + Cl 34.01, 34.05. $C_{14}H_9BrClNO_2$. Calculated, %: Br + Cl 34.07.

2-Methyl-*N*-(4-nitrobenzoyl)-6-chloro-1,4-benzoquinone monoimine (VIIb). Yield 58%, mp 148–150°C. ^{1}H NMR spectrum, δ, ppm: 2.14 d (3H, 2-Me), 6.92 q (1H, H^3, *J* 3.0, 1.5 Hz), 7.28 d (1H, H^5), 8.11 d, 8.36 d (4H, C_6H_4, *J* 9.3 Hz). Found, %: Cl 11.59, 11.62. $C_{14}H_9ClNO_2$. Calculated, %: Cl 11.64.

***N*-(4-Bromobenzoyl)-2-methyl-5,6-dichloro-1,4-benzoquinone monoimine (IXa).** Yield 22%. ^{1}H NMR spectrum, δ, ppm: 2.06 d (3H, 2-Me), 6.82 q (1H, H^3, *J* 1.5 Hz), 7.61 d, 7.97 d (4H, C_6H_4, *J* 8.4 Hz).

2-Methyl-*N*-(4-nitrobenzoyl)-5,6-dichloro-1,4-benzoquinone monoimine (IXb). ^{1}H NMR spectrum, δ, ppm: 2.09 d (3H, 2-Me, *J* 1.5 Hz), 6.86 q (1H, H^3, *J* 1.5 Hz), 8.12 d, 8.37 d (4H, C_6H_4, *J* 8.4 Hz).

2-Methyl-*N*-(4-methylbenzoyl)-5,6-dichloro-1,4-benzoquinone monoimine (IXc). Yield 72%, mp 149–150°C. ^{1}H NMR spectrum, δ, ppm: 2.04 d (3H, 2-Me), 2.45 s (3H, 4-MeC_6H_4), 6.82 q (1H, H^3, *J* 1.5 Hz), 7.29 d, 7.82 d (4H, C_6H_4, *J* 8.4 Hz). Found, %: Cl 22.97, 23.00. $C_{15}H_{11}Cl_2NO_2$. Calculated, %: Cl 23.01.

***N*-Benzoyl-2-methyl-5,6-dichloro-1,4-benzoquinone monoimine (IXd).** Yield 79%, mp 92–94°C. ^{1}H NMR spectrum, δ, ppm: 2.05 d (3H, 2-Me), 6.83 q (1H, H^3, *J* 1.8 Hz), 7.49–7.93 m (5H, Ph). Found, %: Cl 24.06, 24.09. $C_{14}H_9Cl_2NO_2$. Calculated, %: Cl 24.11.

***N*-(4-Bromobenzoyl)-2-methyl-3,6-dichloro-1,4-benzoquinone monoimine (Xa).** Yield 78%. ^{1}H NMR spectrum, δ, ppm: 2.33 s (3H, 2-Me), 7.16 s (1H, H^5), 7.64 d, 7.81 d (4H, C_6H_4, *J* 8.7 Hz).

2-Methyl-*N*-(4-nitrobenzoyl)-3,6-dichloro-1,4-benzoquinone monoimine (Xb). ^{1}H NMR spectrum, δ, ppm: 2.35 s (3H, Me^2), 7.21 s (1H, H^5), 8.12 d, 8.37 d (4H, C_6H_4, *J* 9.0 Hz).

***N*-Benzoyl-2-methyl-3,6-dichloro-1,4-benzoquinone monoimine (Xc).** ^{1}H NMR spectrum, δ, ppm: 2.10 s (3H, 2-Me), 7.17 s (1H, H^5), 7.49–7.93 m (5H, Ph).

4-Amino-*N*-benzoyl-2-methyl-5,6-dichlorophenol (XIa). Yield 74%, mp 221–222°C. Found, %: Cl 23.86, 23.91. $C_{14}H_{11}Cl_2NO_2$. Calculated, %: Cl 23.94.

4-Amino-2-methyl-*N*-(4-nitrobenzoyl)-5,6-dichlorophenol (XIb). Yield 80%, mp 244–246°C. Found, %: Cl 19.96, 21.03. $C_{14}H_{10}Cl_2N_2O_4$. Calculated, %: Cl 20.78.

4-Amino-2-methyl-*N*-(4-methylbenzoyl)-5,6-dichlorophenol (XIc). Yield 66%, mp 210–212°C. Found, %: Cl 22.77, 22.83. $C_{15}H_{13}Cl_2NO_2$. Calculated, %: Cl 22.86.

4-Benzoylimino-6-methyl-2,3,5,6-tetrachlorocyclohex-2-en-1-one (XVa). Yield 13%, mp 100–102°C. ^{1}H NMR spectrum, δ, ppm: 1.90 s (3H, 6-Me), 5.01 s (1H, H^5), 7.49–7.98 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 22.59 (6-Me), 57.88 (C^5), 64.81 (C^6), 129.04 (C$^{2'}$), 129.81 (C$^{3'}$), 131.23 (C$^{1'}$), 134.67 (C$^{4'}$), 138.30 (C^2), 142.71 (C^3), 154.24 (C^4), 177.36 (C=O$_{aroyl}$), 180.27 (C^1). Found, %: Cl 38.79, 38.84. $C_{14}H_9Cl_4NO_2$. Calculated, %: Cl 38.85.

6-Methyl-4-(4-nitrobenzoyl)imino-2,3,5,6-tetrachlorocyclohex-2-en-1-one (XVb). Yield 55%, mp 153–154°C. ^{1}H NMR spectrum, δ, ppm: 1.93 s (3H, 6-Me), 5.03 s (1H, H^5), 8.14 d, 8.38 d (4H, C_6H_4, *J* 9.0 Hz). Found, %: Cl 33.92, 35.06. $C_{14}H_8Cl_4N_2O_4$. Calculated, %: Cl 34.58.

2-Methyl-*N*-(4-nitrobenzoyl)-3,5,6-trichloro-1,4-benzoquinone monoimine (XVIb). ^{1}H NMR spectrum, δ, ppm: 2.22 s (3H, 2-Me), 8.04 d, 8.38 d (4H, C_6H_4, *J* 8.7 Hz).

2-Methyl-*N*-(4-methylbenzoyl)-3,5,6-trichloro-1,4-benzoquinone monoimine (XVIc). Yield 70%, mp 210–212°C. ^{1}H NMR spectrum, δ, ppm: 2.27 s (3H, 2-Me), 2.44 (3H, 4-Me), 7.28 d, 7.73 d (4H, C_6H_4, *J* 8.1 Hz). ^{13}C NMR spectrum, δ, ppm: 21.77 (4'-Me), 23.15 (2-Me), 128.72 (C$^{2'}$), 129.18 (C$^{1'}$), 129.56 (C$^{3'}$), 138.74 (C^6), 138.81 (C^5), 139.02 (C^3), 143.74 (C^4), 144.59 (C$^{4'}$), 144.60 (C^2), 175.27 (C=O$_{aroyl}$), 175.46 (C^1). Found, %: Cl 30.99, 31.01. $C_{15}H_{10}Cl_3NO_2$. Calculated, %: Cl 31.04.

6-Methyl-4-(4-methylbenzoyl)imino-2,3,5,5,6-pentachlorocyclohex-2-en-1-one (XVII). Yield 70%, mp 112–114°C. ^{1}H NMR spectrum, δ, ppm: 2.18 s (3H, 6-Me), 2.44 s (3H, 4-Me), 7.29 d, 7.77 d (4H, C_6H_4, *J* 8.1 Hz). ^{13}C NMR spectrum, δ, ppm: 20.55 (6-Me), 21.75 (4'-Me), 72.27 (C^6), 88.77 (C^5), 128.82 (C$^{2'}$), 129.04 (C$^{1'}$), 129.58 (C$^{3'}$), 138.17(C^2), 138.84 (C^3), 144.80 (C$^{4'}$), 147.53 (C^4), 173.97 (C^1), 178.61 (C=O$_{aroyl}$). Found, %: Cl 42.81, 42.85. $C_{15}H_{10}Cl_5NO_2$. Calculated, %: Cl 42.87.

4-Amino-3-methyl-6-chloro-*N*-(4-chlorobenzoyl) phenol (XIXc). Yield 80%, mp 204–206°C. ^{1}H NMR spectrum, δ, ppm: 2.13 s (3H, 3-Me), 6.87 s (1H, H^2), 7.28 s (1H, H^5), 7.60 d, 7.98 d (4H, C_6H_4, *J* 8.1 Hz). Found, %: Cl 23.88, 23.93. $C_{14}H_{11}Cl_2NO_2$. Calculated, %: Cl 23.94.

4-Amino-*N*-benzoyl-3-methyl-2,6-dichlorophenol (XXIa). Yield 69%, mp 206–208°C. Found, %: Cl 23.89, 23.92. $C_{14}H_{11}Cl_2NO_2$. Calculated, %: Cl 23.94.

4-Amino-3-methyl-*N*-(4-methylbenzoyl)-2,6-dichlorophenol (XXIb). Yield 77%, mp 208–210°C. Found, %: Cl 22.80, 22.84. $C_{15}H_{13}Cl_2NO_2$. Calculated, %: Cl 22.86.

4-Amino-3-methyl-2,6-dichloro-*N*-(4-chlorobenzoyl)phenol (XXIc). Yield 50%, mp 206–208°C. Found, %: Cl 32.13, 32.15. $C_{14}H_{10}Cl_3NO_2$. Calculated, %: Cl 32.17.

***N*-Benzoyl-3-methyl-2,6-dichloro-1,4-benzoquinone monoimine (XXIVa).** Yield 60%, mp 107–109°C. ^{1}H NMR spectrum, δ, ppm: 2.48 s (3H, 3-Me), 7.13 s (1H, H^5), 7.49–7.90 m (5H, Ph). Found, %: Cl 24.08, 24.10. $C_{14}H_9Cl_2NO_2$. Calculated, %: Cl 24.11.

3-Methyl-*N*-(4-methylbenzoyl)-2,6-dichloro-1,4-benzoquinone monoimine (XXIVb). Yield 63%, mp 150–152°C. ^{1}H NMR spectrum, δ, ppm: 2.45 s (3H, 4-Me), 2.48 s (3H, 3-Me), 7.11 s (1H, H^5), 7.30 d, 7.78 d (4H, C_6H_4, *J* 8.1 Hz). Found, %: Cl 22.97, 23.00. $C_{15}H_{11}Cl_2NO_2$. Calculated, %: Cl 23.01.

3-Methyl-2,6-dichloro-*N*-(4-chlorobenzoyl)-1,4-benzoquinone monoimine (XXIVc). Yield 71%, mp 158–160°C. ^{1}H NMR spectrum, δ, ppm: 2.47 s (3H, 3-Me), 7.12 s (1H, H^5), 7.48 d, 7.85 d (4H, C_6H_4, *J* 8.4 Hz). Found, %: Cl 32.30, 32.35. $C_{14}H_8Cl_3NO_2$. Calculated, %: Cl 32.37.

***N*-Benzoyl-3-methyl-2,5,6-trichloro-1,4-benzoquinone monoimine (XXVIa).** Yield 81%, mp 194–196°C. ^{1}H NMR spectrum, δ, ppm: 2.46 s (3H, 3-Me), 7.48–7.82 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 17.16 (3-Me), 128.66 (C$^{2'}$), 128.93 (C$^{3'}$), 131.77 (C$^{1'}$), 133.72 (C$^{4'}$), 137.32 (C^2), 137.36 (C^6), 138.92 (C^5), 144.05 (C^3), 147.17 (C^4), 170.64 (C^1), 175.41 (C=O$_{aroyl}$). Found, %: Cl 32.29, 32.35. $C_{14}H_8Cl_3NO_2$. Calculated, %: Cl 32.37.

3-Methyl-*N*-(4-methylbenzoyl)-2,5,6-trichloro-1,4-benzoquinone monoimine (XXVIb). Yield 50%, mp 200–202°C. ^{1}H NMR spectrum, δ, ppm: 2.44 s (3H, 4-Me), 2.45 s (3H, 3-Me), 7.28 d, 7.70 d (4H, C_6H_4, *J* 8.1 Hz). ^{13}C NMR spectrum, δ, ppm: 17.18 (3-Me), 21.77 (4′-Me), 128.72 (C$^{2'}$), 129.07 (C$^{1'}$), 129.66 (C$^{3'}$), 144.76 (C$^{4'}$), 137.22 (C^2), 137.49 (C^6), 138.83 (C^5),

144.76 (C^3), 147.00 (C^4), 170.70 (C^1), 175.46 ($C{=}O_{aroyl}$). Found, %: Cl 30.96, 31.03. $C_{15}H_{10}Cl_3NO_2$. Calculated, %: Cl 31.04.

3-Methyl-2,5,6-trichloro-*N*-(4-chlorobenzoyl)-1,4-benzoquinone monoimine (XXVIc). Yield 43%, mp 198–200°C. ^{1}H NMR spectrum, δ, ppm: 2.45 s (3H, 3-Me), 7.47 d, 7.76 d (4H, C_6H_4, *J* 8.4 Hz). Found, %: Cl 39.01, 39.05. $C_{14}H_7Cl_4NO_2$. Calculated, %: Cl 39.06.

4-Benzoylimino-5-methyl-2,3,5,6,6-pentachlorocyclohex-2-en-1-one (XXVIIa). Yield 36%, mp 98–100°C. ^{1}H NMR spectrum, δ, ppm: 2.30 s (3H, 5-Me), 7.49–7.85 m (5H, Ph). Found, %: Cl 44.32, 44.35. $C_{14}H_8Cl_5NO_2$. Calculated, %: Cl 44.37.

5-Methyl-4-(4-methylbenzoyl)imino-2,3,5,6,6-pentachlorocyclohex-2-en-1-one (XXVIIb). Yield 56%, mp 110–112°C. ^{1}H NMR spectrum, δ, ppm: 2.29 s (3H, 5-Me), 2.44 s (3H, 4-Me), 7.29 d, 7.73 d (4H, C_6H_4, *J* 8.1 Hz). ^{13}C NMR spectrum, δ, ppm: 21.77 (4'-Me), 23.15 (5-Me), 74.51 (C^5), 88.40 (C^6), 128.79 ($C^{2'}$), 129.15 ($C^{1'}$), 129.67 ($C^{3'}$), 136.81 (C^2), 139.67 (C^3), 144.90 ($C^{4'}$), 150.56 (C^4), 174.55 ($C{=}O_{aroyl}$), 174.18 (C^1). Found, %: Cl 42.79, 42.85. $C_{15}H_{10}Cl_5NO_2$. Calculated, %: Cl 42.87.

5-Methyl-4-(4-chlorobenzoyl)imino-2,3,5,6,6-pentachlorocyclohex-2-en-1-one (XXVIIc). Yield 59%, mp 103–104°C. ^{1}H NMR spectrum, δ, ppm: 2.29 s (3H, 5-Me), 7.48 d, 7.78 d (4H, C_6H_4, *J* 8.7 Hz). Found, %: Cl 48.13, 49.51. $C_{14}H_7Cl_6NO_2$ Calculated, %: Cl 49.02.

Bromination of compounds Ia, Ib, IIb, IIc, IIIa–IIIc, IVa–IVc. To a solution of 2 mmol of compound under study in 3 ml of $CHCl_3$, AcOH, DMF, or the mixture DMF–AcOH, 1 : 5, was added dropwise at stirring a solution of bromine in the corresponding solvent till the necessary ratio initial substance–bromine was attained (1 : 1, 1 : 3, 1 : 5, 1 : 10). After several hours the reaction products were filtered off, washed with acetic acid, and recrystallized from acetic acid.

4-Amino-6-bromo-*N*-(4-bromobenzoyl)-2-methylphenol (VIa). Yield 63%, mp 228–230°C. Found, %: Br 41.44, 41.49. $C_{14}H_{11}Br_2NO_2$. Calculated, %: Br 41.50.

4-Amino-6-bromo-*N*-(4-nitrobenzoyl)-2-methylphenol (VIb). Yield 59%, mp 262–263°C. Found, %: Br 22.61, 23.10. $C_{14}H_{11}BrN_2O_4$. Calculated, %: Br 22.75.

6-Bromo-*N*-(4-bromobenzoyl)-2-methyl-1,4-benzoquinone monoimine (VIIIa). Yield 55%, mp 150–152°C. ^{1}H NMR spectrum, δ, ppm: 2.11 d (3H, 2-Me, *J* 1.8 Hz), 6.89 q (1H, H^3, *J* 1.8 Hz), 7.52 d (1H, H^5, *J* 2.4 Hz), 7.63 d, 7.80 d (4H, C_6H_4, *J* 9.0 Hz). Found, %: Br 41.69, 41.71. $C_{14}H_9Br_2NO_2$. СычandСле-НО, %: Br 41.72.

6-Bromo-2-methyl-*N*-(4-nitrobenzoyl)-1,4-benzoquinone monoimine (VIIIb). Yield 61%, mp 170–172°C. ^{1}H NMR spectrum, δ, ppm: 2.14 d (3H, 2-Me, *J* 1.8 Hz), 6.93 q (1H, H^3, *J* 1.8 Hz), 7.55 d (1H, H^5, *J* 2.1 Hz), 8.11 d, 8.36 d (4H, C_6H_4, *J* 8.7 Hz). Found, %: Br 22.16, 23.09. $C_{14}H_9BrN_2O_4$. Calculated, %: Br 22.89.

4-Amino-*N*-benzoyl-5,6-dibromo-2-methylphenol (XIIa). Yield 94%, mp 200–202°C. Found, %: Br 41.46, 41.48. $C_{14}H_{11}Br_2NO_2$. Calculated, %: Br 41.50.

4-Amino-5,6-dibromo-2-methyl-*N*-(4-methylbenzoyl)phenol (XIIc). Yield 95%, mp 224–226°C. Found, %: Br 39.98, 40.01. $C_{15}H_{13}Br_2NO_2$. Calculated, %: Br 40.04.

***N*-Benzoyl-5,6-dibromo-2-methyl-1,4-benzoquinone monoimine (XIIIa).** Yield 63%, mp 114–116°C. ^{1}H NMR spectrum, δ, ppm: 2.05 d (3H, 2-Me), 6.88 q (1H, H^3, *J* 1.8 Hz), 7.49–7.93 m (5H, Ph). Found, %: Br 41.67, 41.70. $C_{14}H_9Br_2NO_2$. Calculated, %: Br 41.72.

5,6-Dibromo-2-methyl-*N*-(4-methylbenzoyl)-1,4-benzoquinone monoimine (XIIIc). Yield 69%, mp 155–156°C. ^{1}H NMR spectrum, δ, ppm: 2.04 d (3H, 2-Me, *J* 1.5 Hz), 2.44 s (3H, 4-Me), 6.87 q (1H, H^3), 7.29 d, 7.81 d (4H, C_6H_4, *J* 8.4 Hz). Found, %: Br 40.19, 40.23. $C_{15}H_{11}Br_2NO_2$. Calculated, %: Br 40.25.

5-Benzoyloxy-2,3,6-tribromo-6-methyl-cyclohex-2-en-1,4-dione (XVIII). Yield 15%, mp 156–158°C. ^{1}H NMR spectrum, δ, ppm: 2.01 s (3H, 6-Me), 6.20 s (1H, H^5), 7.45–7.95 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 23.36 (6-Me), 56.65 (C^6), 77.18 (C^5), 127.48 ($C^{1'}$), 128.83 ($C^{2'}$), 130.11 ($C^{3'}$), 134.42 ($C^{4'}$), 137.80 (C^3), 146.12 (C^2), 175.15 ($C{=}O_{aroyl}$), 180.33 (C^4), 181.46 (C^1). Found, %: Br 49.01, 50.19. $C_{14}H_9Br_3O_4$. Calculated, %: Br 49.84.

4-Amino-*N*-benzoyl-6-dibromo-3-methylphenol (XXa). Yield 37%, mp 247–249°C. Found, %: Br 26.11, 26.13. $C_{14}H_{12}BrNO_2$. Calculated, %: Br 26.14.

4-Amino-*N*-benzoyl-2,6-dibromo-3-methylphenol (XXIIa). Yield 59%, mp 208–210°C. Found, %: Br 41.42, 41.46. $C_{14}H_{11}Br_2NO_2$. Calculated, %: Br 41.50.

4-Amino-2,6-dibromo-3-methyl-*N*-(4-methylbenzoyl)phenol (XXIIb). Yield 78%, mp 217–218°C. Found, %: Br 39.96, 40.02. $C_{15}H_{13}Br_2NO_2$. Calculated, %: Br 40.04.

4-Amino-2,6-dibromo-3-methyl-*N*-(4-chlorobenzoyl)phenol (XXIIc). Yield 75%, mp 246–248°C. Found, %: Br + Cl 46.50, 46.52. $C_{14}H_{10}Br_2ClNO_2$. Calculated, %: Br + Cl 46.54.

***N*-Benzoyl-2,6-dibromo-3-methyl-1,4-benzoquinone monoimine (XXVa).** Yield 63%, mp 120–122°C. ^{1}H NMR spectrum, δ, ppm: 2.51 s (3H, 3-Me), 7.39 s (1H, H^5), 7.49–7.90 m (5H, Ph). Found, %: Br 41.69, 41.73. $C_{14}H_9Br_2NO_2$. Calculated, %: Br 41.72.

2,6-Dibromo-3-methyl-*N*-(4-methylbenzoyl)-1,4-benzoquinone monoimine (XXVb). Yield 48%, mp 160–162°C. ^{1}H NMR spectrum, δ, ppm: 2.45 s (3H, 4-Me), 2.51 s (3H, 3-Me), 7.37 s (1H, H^5), 7.32 d, 7.78 d (4H, C_6H_4, *J* 8.1 Hz). Found, %: Br 40.19, 40.23. $C_{15}H_{11}Br_2NO_2$. Calculated, %: Br 40.25.

2,6-Dibromo-3-methyl-*N*-(4-chlorobenzoyl)-1,4-benzoquinone monoimine (XXVc). Yield 65%, mp 140–142°C. ^{1}H NMR spectrum, δ, ppm: 2.50 s (3H, 3-Me), 7.38 s (1H, H^5), 7.48 d, 7.85 d (4H, C_6H_4, *J* 8.7 Hz). Found, %: Br + Cl 46.74, 46.76. $C_{14}H_8Br_2ClNO_2$. Calculated, %: Br + Cl 46.77.

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