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# Hydrohalogenation of *N*-Acetyl(aroyl)-1,4-benzoquinone Monoimines

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**Abstract**—New *N*-acetyl-1,4-benzoquinone monoimines alkyl-substituted in the quinoid ring were synthesized. The hydrohalogenation of N-acetyl(aroyl)-1,4-benzoquinone monoimines proceeds exclusively in keeping with the 1,4-addition. The hydrochlorination occurs along the ionic mechanism, in the hydrobromination grows the role of the radical mechanism.

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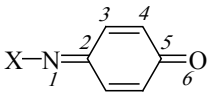
The hydrohalogenation of versatile N-substituted *p*-quinone monoimines is fairly well understood [1–3]. The halogen addition occurs mostly into the positions *2* and *6* of the quinoid ring by the 1,4-addition scheme [1, 2]. In the case of *N*-aryl-1,4-benzoquinone monoimines depending on the substituent in the *para*-position of the aryl fragment the halogen atom enters into the position *2* or *3* of the quinoid ring by the route of 1,4- or 6.3-addition [3]. In describing the orientation of the nucleophile addition to quinone imines the following numeration of the atoms in the quinone imine molecule is applied: The first digit indicates the atom adding the proton (or another electrophile), the second digit determines the atom adding the acid anion (or another nucleophil) [4].




The 4-amino-*N*-acetylphenol (paracetamol) is an efficient analgesic, and its oxidation product, *N*-acetyl-1,4-benzoquinone imine, is an intermediate compound in the chain of transformations leading to the hepatotoxicity of the paracetamol [5]. In this connection large number of publications concerns the study of the oxidation of 4-amino-*N*-acetylphenol to *N*-acetyl-1,4-benzoquinone imine [6, 7] and the reactivity of *N*-acetyl-1,4-benzoquinone imine with respect to biological objects [8], thiols [9], dimethylamine [10], and halogens [11]. The other investigated reactions were the halogenation of 4-amino-*N*-acetylphenol [12], reactions of *N*-acetyl-2,6(3,5)-dimethyl-1,4-benzoquinone monoimines with aniline, ethanol, water, hydrogen chloride, ethanethiol [13]. It was established that the reactions of *N*-acetyl-1,4-benzoquinone imine with dimethylamine [10], thiols [9] and of *N*-acetyl-3,5-dimethyl-1,4-benzoquinone monoimine with hydrogen chloride and ethanethiol [13] followed the scheme of the 1,4-addition, and the *N*-acetyl-2,6-dimethyl-1,4-benzoquinone monoimine reacted with hydrogen chloride along the 6,3-addition path [13]. The hydrohalogenation of unsubstituted in the quinoid ring, monoalkyl, and 2,5-dialkyl-substituted *N*-acetyl-1,4-benzoquinone monoimines was not examined.

4-Amino-*N*-aroylphenols are close analogs of paracetamol, and they are also tested for pharmaceuticals [14]. Their oxidation leads to the formation of *N*-aroyl-1,4-benzoquinone monoimines whose reactivity is fairly well studied. The reactions of various *N*-aroyl-1,4-benzoquinone monoimines with halogens [15], sodium arylsulfinates [16], and potassium thiocyanate [17] were investigated. Yet the hydrohalogenation of unsubstituted in the quinoid ring and monoalkyl-substituted *N*-aroyl-1,4-benzoquinone monoimines due to their instability was not previously studied.

It was previously suggested that the hydrochlorination

of the *N*-acetyl(aroyl)-1,4-benzoquinone monoimines unsubstituted in the quinoid ring might proceed both as 1,4- and 6,3-addition [18]. Therefore the goal of the present research was the establishment of the direction of the halogen addition in the hydrohalogenation of *N*-aroyl- and *N*-acetyl-1,4-benzoquinone monoimines.

*N*-Acetyl(aroyl)-1,4-benzoquinone monoimines **IIa–IIf** were obtained in situ by the oxidation of 4-amino-*N*-acetyl(aroyl)phenols **Ia–If** (Scheme 1). Chloroform was used as solvent during the oxidation. The solvent was selected to provide a good solubility of quinone imines **IIa–IIf** without their decomposition which was observed in acetone and acetic acid. On the other hand, initial 4-amino-*N*-acetyl(aroyl)phenols **Ia–If** are insoluble in chloroform that simplifies thair separation from the obtained quinone imines. The oxidation of aminophenols **Ia–If** was performed with silver(I) oxide. The application to this end of lead tetraacetate gave unsuitable results. The formation of quinone monoimines **IIa–IIf** was proved by the IR spectra of the obtaind solutions of quinone imines. The IR spectra contained the absorption band characteristic of groups C=O, C=N (1650, 1580 $cm^{-1}$) and lacked the absorption in the region 3200–3500 $cm^{-1}$ characteristic of groups NH, OH.

The hydrochlorination was carried out by passing the gaseous hydrogen chloride through the chloroform solution of quinone imines **IIa–IIf**. The hydrochlorination products were filtered off and in order to detect all possible reaction products their NMR spectra were registered without additional purification. To ensure the precise identification of compounds by an independent synthesis we obtained from 4-amino-2-chloro- and -3-chlorophenols **V** and **VI** treated with acetyl(aroyl) chlorides 4-amino-*N*-acetyl(aroyl)-2-chloro- and -3-chlorophenols **IIIa–IIIf** and **IVa–IVf** (Scheme 1).

The analysis of the $^1H$ NMR spectra of the products of hydrochlorination of quinone imines **IIa–IIf** showed that only 4-amino-*N*-acetyl(aroyl)-2-chlorophenols **IIIa–IIIf** formed, and no products of 6,3-addition, aminophenols **IVa–IVf**, were detected (Scheme 1), but the reaction mixtures contained impurities of the reduced forms of quinone monoimines, aminophenols **Ia–If**, and hydrolysis products.

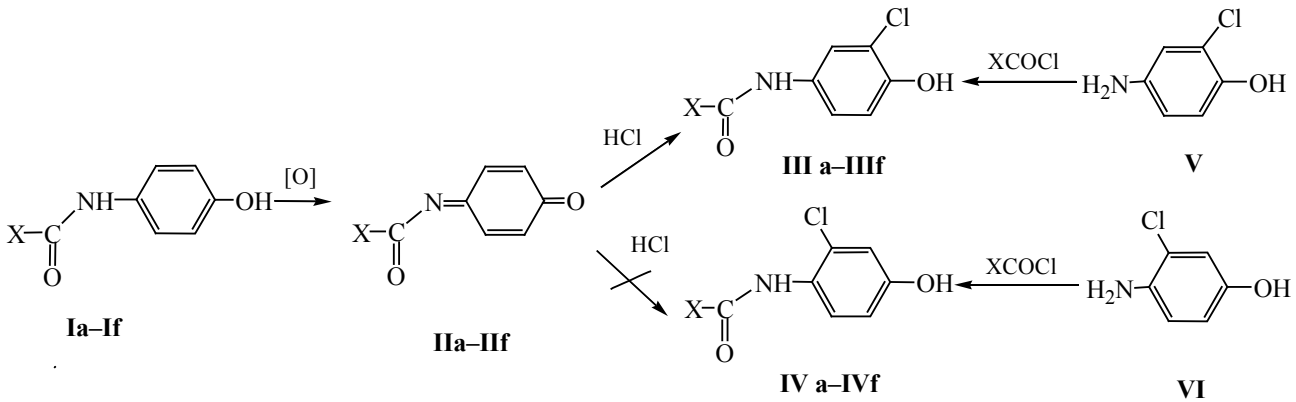
Aiming at elucidation of the hydrochlorination mechanism of compounds **IIa–IIf** we performed quantum-chemical calculations. For quinone monoimines **IIa** and **IId** by method DFT (B3LYP) with the use of basis set 6-31+G(d) a complete optimization was carried out of all geometric parameters of initial quinone monoimines and probable transition states that might form in the course of the hydrochlorination.

Proceeding from [19, 20] a conclusion is presumable that in the hydrohalogenation of the N-substituted 1,4-benzoquinone monoimines the transition states may be either anion-radical, radical, or protonated species.

The hydrogen chloride is not prone to the formation of radical species [21], therefore the hydrochlorination apparently proceeds through the protonation of the initial quinone monoimine.

In the first stage the initial quinone monoimine undergoes protonation, and depending on the properties of the substituent at the nitrogen it may occur both at the nitrogen and the oxygen [20]. According to the calcula-

**Scheme 1.**




X = Me (**a**), 4-$MeOC_6H_4$ (**b**), 4-$MeC_6H_4$ (**c**), Ph (**d**), 4-$ClC_6H_4$ (**e**), 4-$NO_2C_6H_4$ (**f**).

tions in the event of imines **IIa–IIf** the protonation at the nitrogen atom is more favorable (Scheme 2) than at the oxygen atom. The energy of the protonated form **A** of quinone monoimine **IIa** attains –514.58628, of quinone monoimine **IId**, –706.34282 a.u., of the protonated form **B** of quinone monoimine **IIa**, –514.57866, of quinone monoimine **IId**, –706.32120 a.u. Namely, for quinone monoimine **IIa** the energy of the transition state **A** is less than the energy of the form **B** protonated at the oxygen atom by 20 kJ mol$^{-1}$, and for quinone monoimine **IId**, by 56.8 kJ mol$^{-1}$.

In the second stage the chloride anion adds to cation **A**. In keeping with the calculations, the energies of the possible transition states **C–F** (with accounting for the spatial position of the CO group with respect to the ring) are at X = Me: –975.06881(**C**), –97.06827 (**D**), –975.1035 (**E**), –974.98688 (**F**) a.u., and at X = Ph: –1166.81199 (**C**), – 1166.81139 (**D**), –1166.75576 (**E**), –116.73110 (**F**) a.u.. Hence from the energy viewpoint the structures **C**, **D** (Scheme 2) are more favorable, and their energies are virtually equal [the difference 1.4 (X = Me), 1.6 kJ mol$^{-1}$ (X = Ph)], whereas the energy of structure **E** exceeds that of structure **D** by 152.1 (X = Me), 140.6 kJ mol$^{-}$ (X = Ph), and the energy of structure **F** exceeds that of structure **C** by 215.1 (X = Me), 212.4 kJ mol$^{-1}$ (X = Ph).

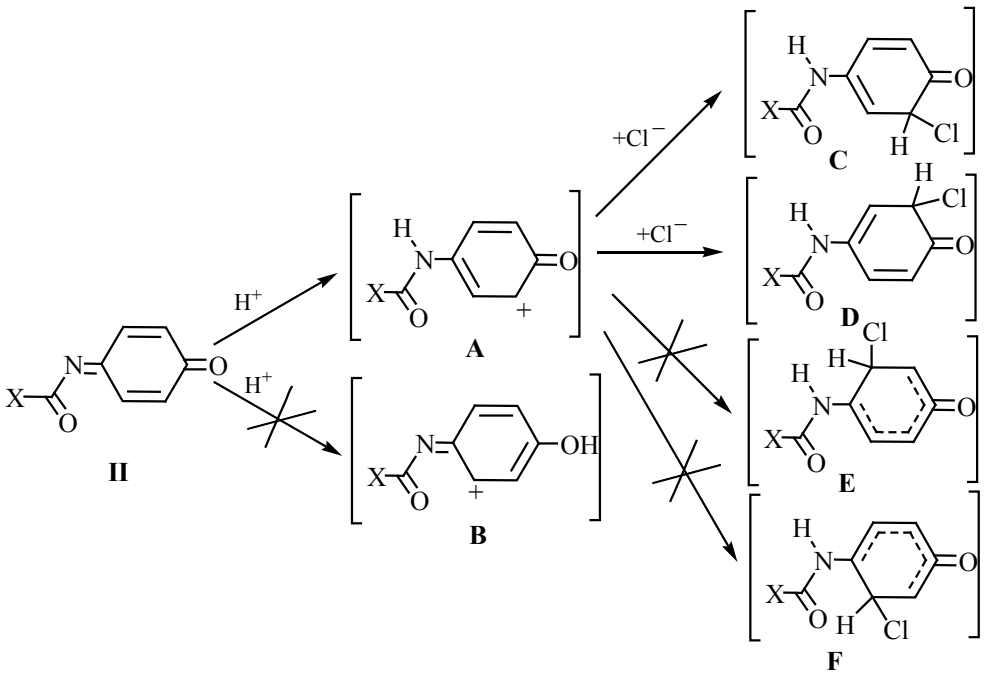
Hence at the hydrochlorination of the *N*-acetyl(aroyl)-1,4-benzoquinone monoimines first occurs the protonation of the more basic nitrogen atom, and then the addition of the chloride anion to the *ortho*-position of the carbonyl carbon atom. The addition of the chloride anion to the *ortho*-position with respect to the imine carbon atom is unfavorable by the energy, therefore the hydrochlorination of the *N*-acetyl(aroyl)-1,4-benzoquinone monoimines yields only the products of 1,4-addition.

The *N*-acetyl(aroyl)-1,4-benzoquinone monoimines containing a single methyl group in the quinoid ring are more stable compounds than the unsubstituted acetyl(aroyl) derivatives due to their reduced redox potential [22]. They have in the quinoid ring a free C=C bond excluding the effect of the steric factor on the halide ion addition to the carbon atom of this bond.

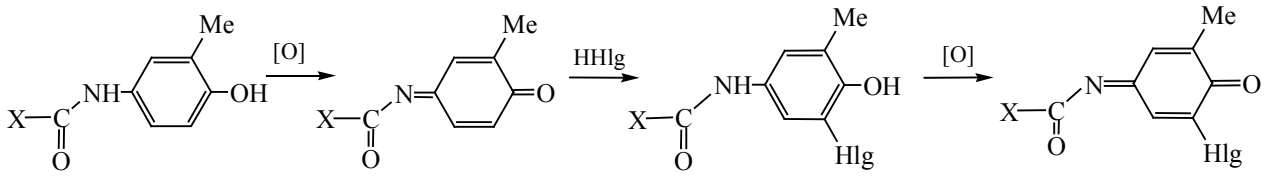
*N*-Acetyl(aroyl)-2-methyl- and -3-methyl-1,4-benzoquinone monoimines **VIIIa–VIIIf, Xa–Xf** were obtained by oxidation of the corresponding 4-aminomethylphenols **VIIa–VIIf, IXa–IXf** (Scheme 3). We succeeded to isolate in the crystalline state quinone monoimines **VIIIe,VIIIf, Xa–Xc, Xe**. The formation in the solution of quinone monoimines **VIIIa–VIIId, Xd** was proved by IR spectra.

In contrast to *N*-arylsulfonyl-2-methyl-1,4-benzoquinone monoimines [23] existing in solution as two isomers in the $^1$H NMR spectra of N-aroyl derivatives **VIIIe** and **VIIIf** a single set of signals is present. It was

**Scheme 2.**



**Scheme 3.**




**VIIa–VIIf** **VIIIa–VIIIf** **XIa–XIf, XIIa–XIIf** **XIIIb–XIIIf, XIVe, XIVf**

X = Me (**a**), 4-$MeOC_6H_4$ (**b**), 4-$MeC_6H_4$ (**c**), Ph (d), 4-$BrC_6H_4$ (**e**), 4-$NO_2C_6H_4$ (**f**); Hlg = Cl (**XI, XIII**), Br (**XII, XIV**).

formerly established that *N*-aroyl-1,4-benzoquinone monoimines have lower barrier to the *Z*,*E*-isomerization ($\Delta G^{\neq}_{298K}$ 44–46 kJ mol$^{-1}$) [24] than the arylsulfonyl derivatives ($\Delta G^{\neq}_{298K}$ 65–80 kJ mol$^{-1}$) [25]. Therefore in the solutions of compounds **VIIIa–VIIIf** already at the room temperature fast *Z*,*E*-isomerization occurred, and notwithstanding the existence of two isomeric forms the $^1$H NMR spectra contain a single set of signals.

The hydrochlorination of quinone monoimines **VIIIa–VIIIf, Xa–Xf** was performed with gaseous hydrogen chloride in chloroform, the hydrobromination, in AcOH by adding an equimolar amount of 40% HBr.

The hydrochlorination of quinone monoimines **VIIIa–VIIId, Xd** was carried out without their isolqation from the solution just after the oxidation of the corresponding aminophenols **VIIa–VIId, IXd** with silver(I) oxide in chloroform, and the hydrobromination was performed after oxidation with lead tetraacetate in AcOH.

The experiment demonstrated that the hydrohalogenation of quinone monoimines **VIIIa–VIIIf** afforded only the products of 1,4-addition **XIa–XIf, XIIb–XIIf** (Scheme 3) as in the case of the corresponding N-arylsulfonyl derivatives [23]. No products of 6,3-addition were detected. We failed to isolate the reaction product of the hydrobromination of *N*-acetyl-2-methyl-1,4-benzoquinone monoimine (**VIIIa**), only the hydrolysis products were obtained. In the $^1$H NMR spectra of compounds **XIa–XIf, XIIb–XIIf** two characteristic doublets were observed at δ 7.43–7.48 and 7.71–7.86 ppm with the *meta*-coupling constant which corresponded to atoms $H^3$ and $H^5$.

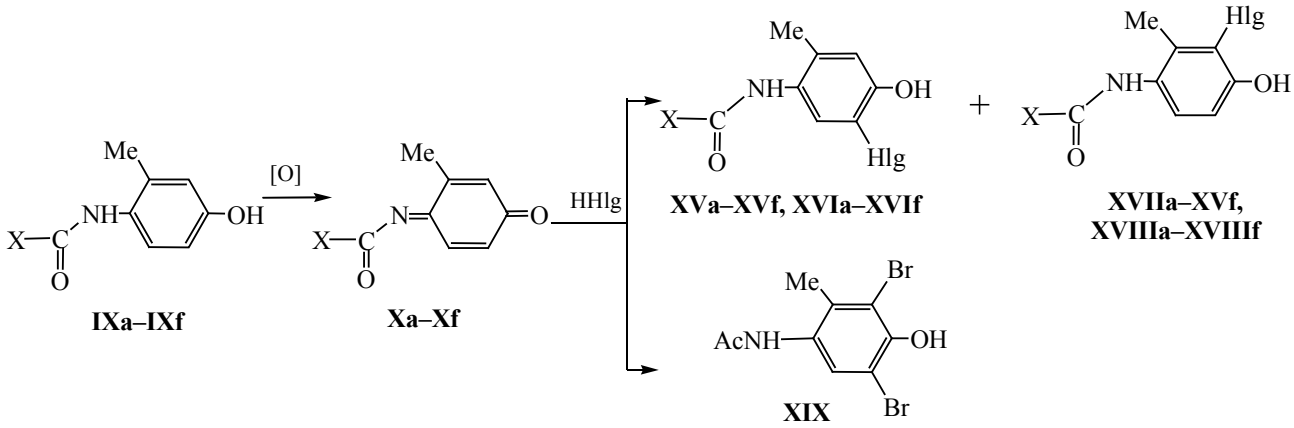
In order to prove the structure of aminophenols **XIa–XIf, XIIb–XIIf** they were oxidized with lead tetraacetate in acetic acid into the corresponding quinone monoimines **XIIIb–XIIIf**, **XIVe, XIVf**. We did not succeed in isolating quinone monoimines **XIIIa, XIVa–XIVd** in the crystalline state, same as initial quinone monoimines **VIIIa–VIIId**. In the $^1$H NMR spectra of quinone monoimines **XIIIb–XIIIf**, **XIVe, XIVf** a quartet of atom $H^3$ is observed in the region δ 6.92 and 6.89 ppm and a doublet of atom $H^5$ with the *meta*-coupling constant in the region δ 7.25 and 7.52 ppm, confirming the structure of imines.

The hydrohalogenation of quinone monoimines **Xa–Xf** provided two isomers: 4-amino-*N*-acetyl(aroyl)-6-halo- (**XVa–XVf, XVIb–XVIf**) and -2-halo-3-methylphenols (**XVIIa–XVIIf, XVIIIb–XVIIIf**), also forming by 1,4-addition (Scheme 4). The reaction products were analyzed by $^1$H NMR without preliminary purification. In the $^1$H NMR spectra of aminophenols **XVa–XVf, XVIb–XVIf** two singlet signals of atoms $H^2$ and $H^5$ were observed at δ 6.85 and 7.27 ppm respectively. The $^1$H NMR spectra of aminophenols **XVIIa–XVIIf, XVIIIb–XVIIIf** are characterized by the presence of two doublets with the ortho-coupling constant, δ 6.83 ($H^6$) and 7.04 ($H^5$) ppm. The similar regioselective addition of hydrogen halides was previously observed in the hydrohalogenation of the *N*-arylsulfonyl-3-methyl-1,4-benzoquinone monoimines [23]. In the hydrobromination of imine **Xa** 2,6-dibromo derivative **XIX** was also isolated.

The analysis of the $^1$H NMR spectra of the reaction products showed that nearly in all cases in the mixtures 6-halo derivatives **XVa–XVf, XVIb–XVIf** prevailed (see the table), therewith at the hydrobromination the content of the second isomer, 2-bromo derivative **XVIIIb–XVIIIf** was higher than at the hydrochlorination, especially in the case of *N*-(4-nitrobenzoyl)-substituted imine **Xf**. It indicates that the steric factor (the presence of Me group at the C=C bond of the quinoid ring) does not significantly affect the hydrohalogenation of imines **Xa–Xf**.

In order to make a correct comparison of the processes of hydrochlorination and hydrobromination of quinone monoimines **Xa–Xf** the hydrochlorination of these quinone monoimines was carried out under the treatment with HCl in aqueous AcOH. The reaction products were

**Scheme 4.**




X = Me (**a**), 4-$MeOC_6H_4$ (**b**), 4-$MeC_6H_4$ (**c**), $C_6H_5$ (**d**), 4-$ClC_6H_4$ (**e**), 4-$NO_2C_6H_4$ (**f**); Hlg = Cl (**XV, XVII**), Br (**XVI, XVIII**).

analyzed by $^1H$ NMR without preliminary purification. The isomer ratio remained the same within the error limits of the experiment as at the hydrochlorination with gaseous HCl in chloroform, therefore the nature of the solvent did not considerably affect the course of the hydrochlorination.

The different isomer ratio in the products of the hydrochlorination and hydrobromination of the *N*-acyl-(aroyl)-3-methyl-1,4-benzoquinonemonoimines may be attributed to two routes of hydrohalogenation.

The hydrochlorination of quinone monoimines **Xa–Xf** starts with the protonation of the initial reagents, same as with quinone monoimines **IIa–IIf** unsubstituted in the quinoid ring (Scheme 5, route *a*). The transition state that forms in this event may be presented as two boundary structures **G** and **H**. The analysis of the charge distribution in the protonated form obtained by the quantum-chemical calculations shows that structure **G** is more favorable, and in this structure the charge on the atom $C^6$ is more positive [+0.010 (X = Me), –0.058 (X = Ph)] than on the atom $C^2$ [–0.815 (X = Me), –0.360 (X = Ph)].

Composition of products of hydrohalogenation of *N*-acetyl(aroyl)-3-methyl-1,4-benzoquinone monoimines **Xa–Xf**

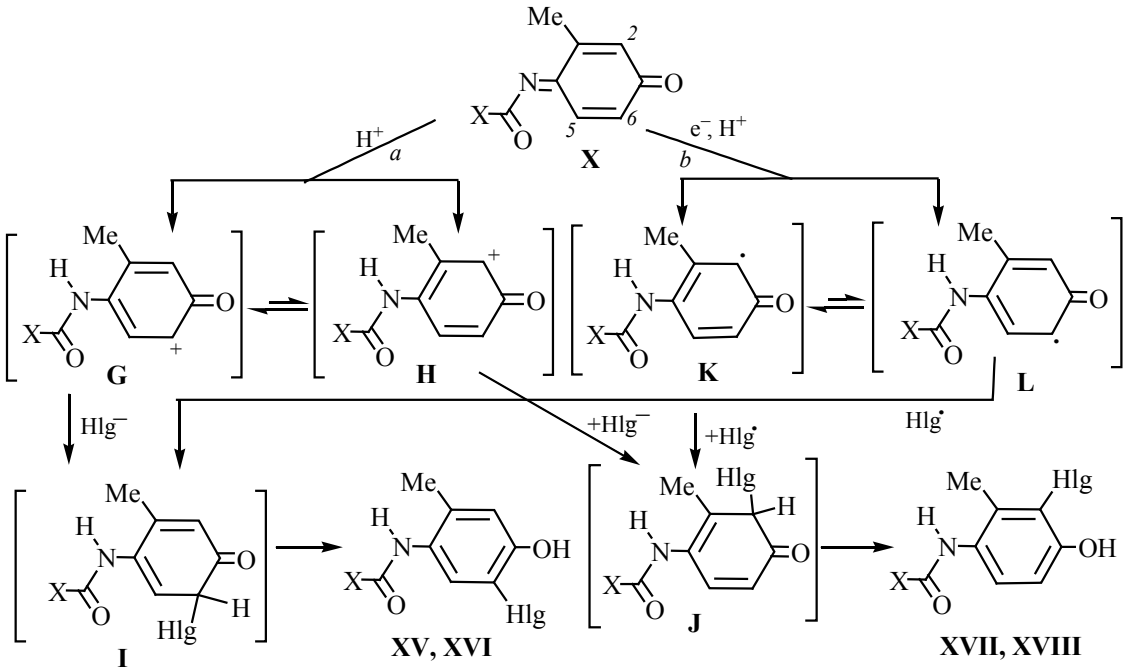
| Quinone imine | Content of isomers, % | | | |
|---|---|---|---|---|
| | hydrochlorination products | | hydrobromination products | |
| | **XV** | **XVII** | **XVI** | **XVIII** |
| **Xa** | 70 | 30 | – | – |
| **Xb** | 80 | 20 | 90 | 10 |
| **Xc** | 73 | 27 | 65 | 35 |
| **Xd** | 75 | 25 | 74 | 26 |
| **Xe** | 77 | 23 | 59 | 41 |
| **Xf** | 70 | 30 | 48 | 52 |

The subsequent addition of the chloride anion may take two directions, into positions *2* or *6* of the ring, since the energy of the transition states **I** and **J** is materially the same, the energy difference equals only 1.4 (X = Me) and 4.2 kJ $mol^{-1}$ (X = Ph). The addition of the chloride anion into the position *5* is unfavorable by energy: The energy of this structure exceeds the energy of the transition state **I** by 215.1 (X = Me), 177.1 kJ $mol^{-1}$ (X = Ph).

Since the energy of the transition states **I** and **J** is materially the same and in the protonated form atom $C^6$ is more positive, the addition of the chloride anion occurs both to the position *2* giving aminophenols **XVII** and to the position *6* forming aminophenols **XV**, and the latter direction prevails (Scheme 5). Namely, the hydrochlorination of the *N*-acetyl(aroyl)-3-methyl-1,4-benzoquinone monoimines proceeds along the ionic mechanism with the charge control.

The hydrohalogenation of quinone monoimines **Xa–Xf** was carried out at room temperature in air. As already mentioned, HCl is not oxidized by the air oxygen and difficultly forms radical species, and HBr under these conditions readily forms radical species [21]. *N*-Aroyl-1,4-benzoquinone monoimines possess the highest redox potentials among all known quinone monoimines [26], therefore they considerably easier are reduced

**Scheme 5.**



X = Me, Ph; Hlg = Cl, Br.

and form anion-radical species. In the series of quinone monoimines **Xb–Xc–Xd–Xe–Xf** with decreasing donor and increasing acceptor properties of the substituent in the para-position of the aryl fragment the redox potential of quinone monoimines **Xb–Xf** should grow [27], and this should result in the easier formation of anion-radical species. According to the experimental data, in this series grows the content of isomer **XVIII** (Scheme 5, route *b*) formed in the hydrobromination. Yet in the case of the hydrochlorination the content of the corresponding isomer **XVII** changes insignificantly.

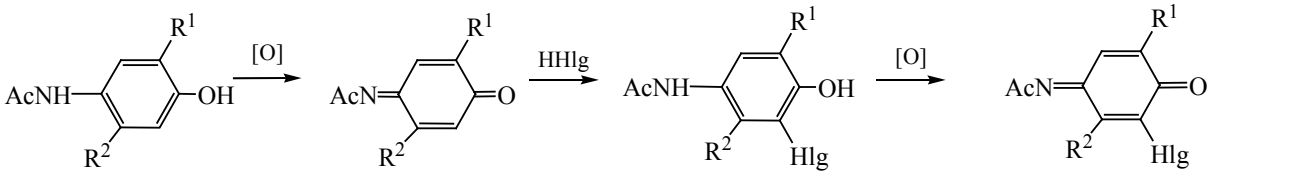
The experimental data and the quantum-chemical calculations lead to the conclusion that the hydrobromination of quinone monoimines **Xa–Xf** occurs along two parallel routes, along the ionic and the radical mechanisms (Scheme 5, routes *a* and *b*).

In event of the ionic mechanism, like in the hydrochlorination in the first stage the protonation occurs of the initial quinone monoimine at the nitrogen atom, and then the addition of the bromide anion. Also positions *2* and *6* of the ring are favorable by the energy: The energy of the transition states **I** and **J** is virtually the same, the energy difference equals only 0.13 (X = Me), 2.15 kJ mol$^{-1}$ (X = Ph). The energy of the transition state with the addition of the bromide anion into the position *5* exceeds the energy of the transition state **I** by 189.24 (X = Me), 129.4 kJ mol$^{-1}$ (X = Ph). Thus if the hydrobromination proceeded only by the ionic mechanism in all cases like in the hydrochlorination the main product should be aminophenol **XVI** in contrast to the experimental data.

As already stated, since HBr is prone to the formation of radical species the contribution of the radical mechanism to the hydrobromination becomes significant. At the radical mechanism in the first stage occurs one-electron transfer and the protonation at the nitrogen atom providing a radical species of the initial quinone monoimine with the boundary structures **K** and **L** (Scheme 5, route *b*). According to the calculations structure **K** is preferable, therewith the density of the localization of the partially free LUMO is larger on the atom C$^{2}$ [0.228 (X = Me), 0.347 (X = Ph)], than on the atom C$^{6}$ [0.140 (X = Me), 0.260 (X = Ph)]. Consequently, the subsequent addition of the radical species Br$^{\bullet}$ occurs predominantly into the position *2* with the orbital control: The partially free LUMO of the radical species of the quinone monoimine interacts with the partially occupied HOMO of the radical bromine species. As a result forms the transition structure **J** that in its turn transforms into aminophenol **XVIII**.

The most stable representatives of *N*-acetyl-

**Scheme 6.**




$R^1 = R^2 =$ Me (**a**), $R^1 =$ Pr-*i*, $R^2 =$ Me (**b**), $R^1 =$ Me, $R^2 =$ Pr-*i* (**c**); Hlg = Cl (**XXII, XXIV**), Br (**XXIII, XXV**).

(aroyl)-1,4-benzoquinone monoimines are the quinone monoimines with two alkyl substituents in the quinoid ring. In the hydrohalogenation of 2,5-dialkyl-*N*-aroyl-1,4-benzoquinone monoimines only products of 1,4-addition were found [28], the hydrohalogenation of 2,5-dialkyl-*N*-acetyl-1,4-benzoquinone monoimines was not previously studied.

2,5-Dialkyl-*N*-acetyl-1,4-benzoquinone monoimines **XXIa–XXIc** were obtained by oxidation of the corresponding aminophenols **XXa–XXc** with silver oxide in chloroform (Scheme 6).

The hydrochlorination of 2,5-dialkyl-*N*-acetyl-1,4-benzoquinone monoimines **XXIa–XXIc** was performed with gaseous hydrogen chloride in chloroform, the hydrobromination was carried out in acetic acid by adding equimolar quantity of the 40% hydrobromic acid. The reaction products were analyzed by NMR without preliminary purification.

In all cases only products of 1,4-addition were obtained, 2,5-dialkyl-4-amino-*N*-acetyl-6-halophenols **XXIIa–XXIIc, XXIIIa–XXIIIc**. Notwithstanding the presence of the bulky isopropyl group the hydrohalogenation of quinine monoimine **XXIc** proceeded just at the C=C bond containing this group. In order to more exact establishment of the structure of the obtained compounds they were oxidized with silver(I) oxide in chloroform into the corresponding imines **XXIVa–XXIVc, XXVa–XXVc** for the spectra of the oxidized forms were more informative.

In the $^1$H NMR spectra of quinone monoimines **XXIVa**, **XXVa** quartets appear from the atom $H^3$ (δ 6.71 and 6.69 ppm), doublets from the protons of the 2-Me group (δ 2.08 and 2.09 ppm), and two singlets of protons of groups 5-Me and MeCO. The characteristic feature of the $^1$H NMR spectra of quinone monoimines **XXIVb, XXVb** is the presence of singlet signals from hydrogen atoms of the groups 3-Me and MeCO and of the doublet from the atom $H^5$ in the region δ 6.52 and 6.58 ppm. In the spectra of quinone monoimines **XXIVc, XXVc** quartets are observed from the atom $H^3$ (δ 6.66 and 6.64 ppm), doublets of the hydrogen atoms of the 2-Me group (δ 2.05 and 2.07 ppm), and a singlet of protons from the group MeCO (δ 2.31 ppm). The character of these spectra unambiguously confirms the assumed structure of quinone monoimines **XXIVa–XXIVc, XXVa–XXVc**.

Thus our research permitted the establishment of the fact that the hydrohalogenation of *N*-acetyl(aroyl)-1,4-benzoquinone monoimines independent of the substituents in the quinoid ring occurred exclusively as 1,4-addition. The hydrochlorination proceeds by the ionic mechanism, whereas the hydrobromination, both by ionic and radical mechanism.

## EXPERIMENTAL

IR spectra of compounds synthesized were recorded on a spectrophotometer UR-20 from pellets with KBr or solutions in chloroform. $^1$H and $^{13}$C NMR spectra were registered on a spectrometer Varian VXR-300 at operating frequencies 300 ($^1$H) and 75.4 MHz ($^{13}$C) with respect to TMS. TLC was carried out on Silufol UV-254 plates. Chloroform was used as solvent, eluent benzene–hexane, 1:10, development under UV irradiation.

Quantum-chemical calculations were performed with the use of Firefly QC software[29] that is partially underlain by the initial code of GAMESS (US) package [30]. The search for the transition states was carried out along the standard procedure of the structure optimization.

4-Amino-*N*-acetyl(aroyl)phenols **Ia–If**, 4-amino-*N*-acetyl(aroyl)-2-chlorophenols **IIIa–IIIf**, 4-amino-*N*-acetyl(aroyl)-3-chlorophenols **IVa–IVf**, and 4-amino-*N*-aroyl-2(3)-methylphenols **VIIa–VIIf**, **IXa–IXf** were obtained by procedure [31], 4-amino-*N*-acetyl-2,5-dimethylphenol (**XXa**), 4-amino-*N*-acetyl-6-isopropyl-

3-methylphenol (XXb), 4-amino-*N*-acetyl-5-isopropyl-2-methyl-phenol (XXc), by method [32].

The characteristics of aminophenols **Ia–If** are in agreement with the published data: Ia, mp 168–169°C (169°C [33]); Ib, mp 223–225°C (226–230°C [34, 35]); Ic, mp 214–216°C (190°C [36]); Id, mp 212–214°C (221°C [36]); Ie, mp 255–256°C (250°C [37]); If, mp 271–272°C (258°C [38]); IVb, mp 199–200°C (200–201°C [35]); VIIa, mp 181–183°C (179–180°C [39]); IXa, mp 125–127°C (129–130°C [35, 39]); IXb, mp 216–218°C (223–225°C [35]).

**4-Amino-*N*-acetyl-3-chlorophenol (IVa).** Yield 35%, mp 123–124°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.01 s (3H, Me), 6.69–6.72 d.d (1H, H$^6$, $J$ 2.4 Hz), 6.84 d (1H, H$^2$, $J_{2,6}$ 1.5 Hz), 7.29 d (1H, H$^5$, $J_{5,6}$ 8.4 Hz), 9.32 s (1H, OH), 9.78 s (1H, NH). Found, %: C 51.75, 51.93; H 4.28, 4.40; Cl 18.99, 19.16; N 7.54, 7.90. $C_8H_8ClNO_2$. Calculated, %: C 51.77; H 4.34; Cl 19.10; N 7.55.

**4-Amino-*N*-(4-methylbenzoyl)-3-chlorophenol (IVc).** Yield 48%, mp 213–214.5°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.38 s (3H, Me), 6.76–6.79 d.d (1H, H$^6$, $J$ 2.1 Hz), 6.92 q (1H, H$^2$, $J$ 2.7 Hz), 7.28 d (1H, H$^5$, $J_{5,6}$ 7.8 Hz), 7.04–7.96 d.d (4H, 4-MeC$_6$H$_4$, $J$ 7.8 Hz), 9.77 s (1H, OH), 9.89 s (1H, NH). Found, %: C 64.23, 64.57; H 4.31, 4.68; Cl 13.49, 13.70; N 5.29, 5.62. $C_{14}H_{12}ClNO_2$. Calculated, %: C 64.25; H 4.62; Cl 13.55; N 5.35.

**4-Amino-*N*-benzoyl-3-chlorophenol (IVd).** Yield 44%, mp 195–197°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 6.77–6.81 d.d (1H, H$^6$, $J$ 2.1 Hz), 6.93 q (1H, H$^2$, $J$ 2.4 Hz), 7.31 d (1H, H$^5$, $J_{5,6}$ 9.0 Hz), 7.49–7.99 m (5H, Ph), 9.86 s (1H, OH), 9.91 s (1H, NH). Found, %: C 63.07, 63.51; H 4.09, 4.28; Cl 14.16, 14.37; N 5.62, 5.80. $C_{13}H_{10}ClNO_2$. Calculated, %: C 63.04; H 4.07; Cl 14.31; N 5.66.

**4-Amino-*N*-(4-chlorobenzoyl)-3-chlorophenol (IVe).** Yield 52%, mp 204–205°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 6.77–6.80 d.d (1H, H$^6$, $J$ 2.4 Hz), 6.93 q (1H, H$^2$, $J$ 2.4 Hz), 7.29 d (1H, H$^5$, $J$ 9.0 Hz), 7.60–7.99 d.d (4H, 4-ClC$_6$H$_4$, $J$ 8.4 Hz), 9.94 s (1H, OH), 9.98 s (1H, NH). Found, %: C 55.47, 55.68; H 3.20, 3.49; Cl 25.07, 25.19; N 4.68, 4.90. $C_{13}H_9Cl_2NO_2$. Calculated, %: C 55.34; H 3.22; Cl 25.13; N 4.96.

**4-Amino-*N*-(4-nitrobenzoyl)-3-chlorophenol (IVf).** Yield 44%, mp 224–226°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 6.78–6.82 d.d (1H, H$^6$, $J$ 2.1 Hz), 6.94 q (1H, H$^2$, $J$ 2.4 Hz), 7.32 d (1H, H$^5$, $J_{5,6}$ 8.7 Hz), 8.19–8.38 d.d (4H, 4-NO$_2$C$_6$H$_4$, $J$ 9.0 Hz), 9.98 s (1H, OH), 10.25 s (1H, NH). Found, %: C 53.29, 53.41; H 3.12, 3.60; Cl 12.17, 12.48; N 9.34, 9.50. $C_{13}H_9ClN_2O_4$. Calculated, %: C 53.35; H 3.10; Cl 12.11; N 9.57.

**4-Amino-2-methyl-*N*-(4-methoxybenzoyl)phenol (VIIb).** Yield 83%, mp 192–194°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.12 s (3H, 2-Me), 3.83 s (3H, MeO), 6.74 d (1H, H$^6$, $J$ 8.7 Hz), 7.33–7.36 d.d (1H, H$^5$, $J$ 9.0 Hz), 7.42 q (1H, H$^3$, $J$ 1.2 Hz), 7.04–7.94 d.d (4H, 4-MeOC$_6$H$_4$, $J$ 8.7 Hz), 9.18 s (1H, OH), 9.80 s (1H, NH). Found, %: C 70.11, 70.34; H 5.86, 6.22; N 5.42, 5.79. $C_{15}H_{15}NO_3$. Calculated, %: C 70.02; H 5.88; N 5.44.

**4-Amino-2-methyl-*N*-(4-methylbenzoyl)phenol (VIIc).** Yield 86%, mp 228.5–230°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.16 s (3H, 2-Me), 2.42 s (3H, Me), 6.70 d (1H, H$^6$, $J$ 8.7 Hz), 7.31–7.35 d.d (1H, H$^5$, $J$ 8.7 Hz), 7.41 q (1H, H$^3$, $J$ 1.5 Hz), 7.04–7.96 d.d (4H, 4-MeC$_6$H$_4$, $J$ 9.0 Hz), 8.81 s (1H, OH), 9.65 s (1H, NH). Found, %: C 74.55, 74.82; H 6.31, 6.49; N 5.80, 6.16. $C_{15}H_{15}NO_2$. Calculated, %: C 74.67; H 6.27; N 5.81.

**4-Amino-*N*-benzoyl-2-methylphenol (VIId).** Yield 82%, mp 203–204°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.13 s (3H, 2-Me), 6.74 d (1H, H$^6$, $J$ 8.4 Hz), 7.35–7.38 d.d (1H, H$^5$, $J$ 9.0 Hz), 7.44 q (1H, H$^3$, $J$ 1.2 Hz), 7.48–7.94 m (5H, Ph), 9.16 s (1H, OH), 9.96 s (1H, NH). Found, %: C 73.92, 74.35; H 5.68, 5.91; N 6.18, 6.44. $C_{14}H_{13}NO_2$. Calculated, %: C 73.99; H 5.77; N 6.16.

**4-Amino-2-methyl-*N*-(4-bromobenzoyl)phenol (VIIe).** Yield 81%, mp 208.5–210°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.14 s (3H, 2-Me), 6.71 d (1H, H$^6$, $J$ 9.0 Hz), 7.29–7.33 d.d (1H, H$^5$, $J$ 8.7 Hz), 7.39 q (1H, H$^3$, $J$ 1.2 Hz), 7.64–7.91 d.d (4H, 4-BrC$_6$H$_4$, $J$ 9.0 Hz), 8.88 s (1H, OH), 9.82 s (1H, NH). Found, %: C 54.67, 54.82; H 3.90, 4.21; N 4.67, 4.88. $C_{14}H_{12}BrNO_2$. Calculated, %: C 54.92; H 3.95; N 4.58.

**4-Amino-2-methyl-*N*-(4-nitrobenzoyl)phenol (VIIf).** Yield 78%, mp 262–263.5°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.13 s (3H, 2-Me), 6.76 d (1H, H$^6$, $J$ 8.7 Hz), 7.36–7.39 d.d (1H, H$^5$, $J$ 9.0 Hz), 7.45 q (1H, H$^3$, $J$ 1.5 Hz), 8.16–8.35 d.d (4H, 4-NO$_2$C$_6$H$_4$, $J$ 9.0 Hz), 9.22 s (1H, OH), 10.27 s (1H, NH). Found, %: C 61.80, 62.05; H 4.39, 4.57; N 10.18, 10.43. $C_{14}H_{12}N_2O_4$. Calculated, %: C 61.76; H 4.44; N 10.29.

**4-Amino-3-methyl-*N*-(4-methylbenzoyl)phenol (IXc).** Yield 75%, mp 208–210°C. Found, %: C 74.58, 74.90; H 6.23, 6.51; N 5.53, 5.89. $C_{15}H_{15}NO_2$. Calculated, %: C 74.67; H 6.27; N 5.81.

**4-Amino-*N*-benzoyl-3-methylphenol (IXr).** Yield 89%, mp 202–204°C. Found, %: C 74.03, 74.29; H 5.68,

5.91; N 6.14, 6.32. $C_{14}H_{13}NO_2$. Calculated, %: C 73.99; H 5.77; N 6.16.

**4-Amino-3-methyl-*N*-(4-chlorobenzoyl)phenol (IXe).** Yield 85%, mp 203–204°C. Found, %: C 64.09, 64.28; H 4.53, 4.79; N 5.38, 5.61. $C_{14}H_{12}ClNO_2$. Calculated, %: C 64.25; H 4.62; N 5.35.

**4-Amino-3-methyl-*N*-(4-nitrobenzoyl)phenol (IXf).** Yield 68%, mp 236–238°C. Found, %: C 61.66, 61.90; H 4.28, 4.53; N 10.27, 10.54. $C_{14}H_{12}N_2O_4$. Calculated, %: C 61.76; H 4.44; N 10.29.

***N*-Acetyl-4-amino-2,5-dimethylphenol (XXa).** Yield 30%, mp 174–176°C. Found, %: C 67.10, 67.32; H 7.14, 7.50; N 7.62, 7.89. $C_{10}H_{13}NO_2$. Calculated, %: C 67.02; H 7.31; N 7.82.

**4-Amino-*N*-acetyl-6-isopropyl-3-methylphenol (XXb).** Yield 43%, mp 177–178°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 1.12 d (6H, 6-CH$\underline{Me}_2$, *J* 6.6 Hz), 1.97 s (3H, 3-Me), 2.02 s (3H, MeCO), 3.07–3.17 m (1H, 6-C$\underline{H}Me_2$), 6.58 s (1H, H$^5$), 6.92 s (1H, H$^2$), 9.04 s (1H, NH), 9.06 s (1H, OH). Found, %: C 69.44, 69.71; H 8.28, 8.53; N 6.70, 6.22. $C_{12}H_{17}NO_2$. Calculated, %: C 69.54; H 8.27; N 6.76.

**4-Amino-*N*-acetyl-5-isopropyl-2-methylphenol (XXc).** Yield 37%, mp 180°C. Found, %: C 69.54, 69.83; H 8.12, 8.57; N 6.70, 6.94. $C_{12}H_{17}NO_2$. Calculated, %: C 69.54; H 8.27; N 6.76.

***N*-Acetyl(aroyl)-1,4-benzoquinone monoimines IIa–IIf, VIIIa–VIIIf, Xa–Xf, XXIa–XXIc.** *a*. Into 10 ml of dry chloroform was added 0.01 mol of the corresponding 4-amino-*N*-acetyl(aroyl)phenol, and at stirring was added 0.012 mol of silver(I) oxide. The dispersion was heated to 40°C at vigorous stirring over 30 min, the solution turned yellow. The silver precipitate was filtered off from the reaction mixture, the solvent was distilled off in a vacuum. The formed precipitate of the quinone imine was recrystallized from the mixture benzene–hexane. *N*-Acetyl(aroyl)-1,4-benzoquinone monoimines **IIa–IIf, VIIIa–VIIId** were not isolated from the reaction solution obtained by removing the silver precipitate. The reaction solution was purified by column chromatography, the solvent was evaporated, the quinone imine obtained as uncrystallizable oily substance was dissolved in an appropriate solvent (chloroform or acetic acid) and was used for further hydrohalogenation.

*b*. *N*-Acetyl(aroyl)-1,4-benzoquinone monoimines were obtained by the oxidation of appropriate aminophenols with lead tetraacetate in acetic acid [31] and were recrystallized from acetic acid or the mixture benzene–hexane.

***N*-(4-Bromobenzoyl)-2-methyl-1,4-benzoquinone monoimine (VIIIe).** Yield 79%, mp 118–120°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.04 d (3H, 2-Me, *J* 1.2 Hz), 6.66 d (1H, H$^6$, *J* 9.9 Hz), 6.85 q (1H, H$^3$, *J* 1.2 Hz), 7.02–7.06 d.d (1H, H$^5$, *J* 9.9 Hz), 7.63–7.80 d.d (4H, 4-Br$C_6H_4$, *J* 8.7 Hz). Found, %: C 55.14, 55.38; H 3.27, 3.50; N 4.61, 4.89. $C_{14}H_{10}BrNO_2$. СычандСлеНО, %: C 55.29; H 3.31; N 4.61.

**2-Methyl-*N*-(4-nitrobenzoyl)-1,4-benzoquinone monoimine (VIIIf).** Yield 79%, mp 118–120°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.06 d (3H, 2-Me, *J* 1.5 Hz), 6.70 d (1H, H$^6$, *J* 9.9 Hz), 6.87 q (1H, H$^3$, *J* 1.2 Hz), 7.05–7.08 d.d (1H, H$^5$, *J* 9.6 Hz), 8.12–8.34 d.d (4H, 4-Br$C_6H_4$, *J* 9.0 Hz). Found, %: C 62.08, 62.34; H 3.55, 3.89; N 10.17, 10.40. $C_{14}H_{10}N_2O_4$. Calculated, %: C 62.22; H 3.73; N 10.37.

***N*-Acetyl-3-methyl-1,4-benzoquinone monoimine (Xa).** Yield 61%, mp 118–120°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.16 d (3H, 3-Me, *J* 1.5 Hz), 2.31 s (3H, MeCO), 6.50–6.51 d.d (1H, H$^6$, *J* 1.2 Hz), 6.54 q (1H, H$^2$, *J* 1.5 Hz), 6.86 d (1H, H$^5$, *J* 9.0 Hz). Found, %: C 66.08, 66.34; H 5.55, 5.89; N 8.17, 8.40. $C_9H_9NO_2$. Calculated, %: C 66.25; H 5.56; N 8.58.

**3-Methyl-*N*-(4-methoxybenzoyl)-1,4-benzoquinone monoimine (Xb).** Yield 83%, mp 104–106°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.29 d (3H, 3-Me, *J* 1.2 Hz), 3.88 s (3H, MeO), 6.45–6.48 d.d (1H, H$^6$, *J* 9.9 Hz), 6.60 q (1H, H$^2$, *J* 1.5 Hz), 6.87 d (1H, H$^5$, $J_{5,6}$ 9.6 Hz), 6.96–7.84 d.d (4H, 4-MeO$C_6\underline{H}_4$, *J* 8.7 Hz). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 17.6 (3-Me), 55.5 (OMe), 114.0 (C$^{3'}$, C$^{5'}$), 124.5 (C$^{1'}$), 131.2 (C$^5$), 131.6 (C$^{2'}$, C$^{6'}$), 132.5 (C$^2$), 134.0 (C$^6$), 148.0 (C$^3$), 157.1 (C$^4$), 164.2 (C$^{4'}$), 179.3 (C=O), 186.6 (C$^1$). Found, %: C 70.42, 70.61; H 5.09, 5.37; N 5.33, 5.68. $C_{15}H_{13}NO_3$. Calculated, %: C 70.58; H 5.13; N 5.49.

**3-Methyl-*N*-(4-methylbenzoyl)-1,4-benzoquinone monoimine (Xc).** Yield 81%, mp 88–89°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.30 d (3H, 3-Me, *J* 1.5 Hz), 2.44 s (3H, 4-$\underline{Me}C_6H_4$), 6.44–6.48 d.d (1H, H$^6$, *J* 10.2 Hz), 6.61 q (1H, H$^2$, *J* 2.1 Hz), 6.85 d (1H, H$^5$, $J_{5,6}$ 10.2 Hz), 7.28–7.78 d.d (4H, 4-Me$C_6\underline{H}_4$, *J* 8.4 Hz). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 17.6 (3-Me), 21.7 ($\underline{Me}C_6H_4$), 129.3 (C$^{1'}$), 129.4 (C$^{3'}$, C$^{5'}$), 129.5 (C$^{2'}$, C$^{6'}$), 131.1 (C$^5$), 132.5 (C$^2$), 134.1 (C$^6$), 145.0 (C$^{4'}$), 147.8 (C$^3$), 157.0 (C$^4$), 179.7 (C=O), 186.5 (C$^1$). Found, %: C 74.92, 75.30; H 5.61, 5.84; N 5.80, 6.19. $C_{15}H_{13}NO_2$. Calculated, %: C 75.30; H 5.48; N 5.85.

***N*-Benzoyl-3-methyl-1,4-benzoquinone monoimine (Xd).** $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.31 d (3H, 3-Me, *J* 1.5 Hz), 6.46–6.49 d.d (1H, H$^6$, *J* 9.0 Hz), 6.61 q (1H, H$^2$, *J* 1.2 Hz), 6.87 d (1H, H$^5$, $J_{5,6}$ 10.2 Hz), 7.48–7.90 m (5H, Ph).

**3-Methyl-*N*-(4-chlorobenzoyl)-1,4-benzoquinone monoimine (Xe).** Yield 83%, mp 102–104°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.29 d (3H, 3-Me, *J* 1.2 Hz), 6.47–6.51 d.d (1H, H$^6$, *J* 10.6 Hz), 6.62 q (1H, H$^2$, *J* 1.5 Hz), 6.86 d (1H, H$^5$, $J_{5,6}$ 10.2 Hz), 7.48–7.85 d.d (4H, 4-$ClC_6H_4$, *J* 8.7 Hz). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 17.7 (3-Me), 129.2 (C$^{3'}$, C$^{5'}$), 130.4 (C$^{1'}$), 130.7 (C$^{2'}$, C$^{6'}$), 131.0 (C$^5$), 132.8 (C$^2$), 134.4 (C$^6$), 140.5 (C$^{4'}$), 147.6 (C$^3$), 157.7 (C$^4$), 178.7 (C=O), 186.4 (C$^1$). Found, %: C 64.51, 64.78; H 3.82, 3.99; Cl 13.40, 13.65; N 5.18, 5.42. $C_{14}H_{10}ClNO_2$. Calculated, %: C 64.75; H 3.88; Cl 13.65; N 5.39.

**3-Methyl-*N*-(4-nitrobenzoyl)-1,4-benzoquinone monoimine (Xf).** Yield 92%, mp 172–173°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.32 d (3H, 3-Me, *J* 0.9 Hz), 6.52–6.55 d.d (1H, H$^6$, *J* 9.0 Hz), 6.65 q (1H, H$^2$, *J* 1.2 Hz), 6.89 d (1H, H$^5$, $J_{5,6}$ 10.2 Hz), 8.10–8.35 d.d (4H, 4-$NO_2C_6H_4$, *J* 2.4 Hz). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 17.7 (3-Me), 124.0 (C$^{3'}$, C$^{5'}$), 130.5 (C$^{2'}$, C$^{6'}$), 130.8(C$^5$), 133.2 (C$^2$), 134.9 (C$^6$), 137.1 (C$^{1'}$), 147.4 (C$^3$), 150.8 (C$^{4'}$), 158.6 (C$^4$), 177.6 (C=O), 186.3 (C$^1$). Found, %: C 62.21, 62.45; H 3.68, 3.91; N 10.44, 10.68. $C_{14}H_{10}N_2O_4$. Calculated, %: C 62.22; H 3.73; N 10.37.

***N*-Acetyl-2,5-dimethyl-1,4-benzoquinone monoimine (XXIa).** Yield 65%, mp 64–65°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.00 d (3H, 2-Me, *J* 1.2 Hz), 2.13 d (3H, 5-Me, *J* 1.5 Hz), 2.31 s (3H, MeCO), 6.53 q (1H, H$^3$, *J* 1.2 Hz), 6.66 q (1H, H$^5$, *J* 1.5 Hz). Found, %: C 67.43, 67.70; H 6.09, 6.35; N 7.98, 8.22. $C_{10}H_{11}NO_2$. Calculated, %: C 67.78; H 6.26; N 7.90.

***N*-Acetyl-6-isopropyl-3-methyl-1,4-benzoquinone monoimine (XXIb).** Yield 80%, mp 26–27°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.10 d (6H, 6-CH<u>Me</u>$_2$, *J* 5.7 Hz), 2.13 br.s (3H, 3-Me), 2.32 br.s (3H, MeCO), 3.01–3.09 m (1H, 6-C<u>H</u>Me$_2$), 6.51 s (1H, H$^2$), 6.54 s (1H, H$^5$). Found, %: C 70.09, 70.25; H 7.34, 7.62; N 6.89, 7.16. $C_{12}H_{15}NO_2$. Calculated, %: C 70.22; H 7.37; N 6.82.

***N*-Acetyl-5-isopropyl-2-methyl-1,4-benzoquinone monoimine (XXIc).** Yield 95%, mp 72–73°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.19 d (6H, 5-CH<u>Me</u>$_2$, *J* 7.2 Hz), 2.01 d (3H, 2-Me, *J* 1.5 Hz), 2.31 s (3H, MeCO), 3.14–3.23 m (1H, 5-C<u>H</u>Me$_2$), 6.49 br.s (1H, H$^6$), 6.67 q (1H, H$^3$, *J* 1.2 Hz). Found, %: C 70.04, 70.35; H 7.42, 7.61; N 6.99, 7.36. $C_{12}H_{15}NO_2$. Calculated, %: C 70.22; H 7.37; N 6.82.

**Hydrochlorination of *N*-acetyl(aroyl)-1,4-benzoquinone monoimines IIa–IIf, VIIIa–VIIIf, Xa–Xf, XXIa–XXIc.** Through a solution of 0.01 mol of quinone monoimine **IIa–IIf, VIIIa–VIIIf, Xa–Xf, XXIa–XXIc** in 5 ml of dry chloroform a flow of dry gaseous hydrogen chloride was passed over 20 min, the reaction solution got lighter, a colorless precipitate separated that was filtered off and analyzed by $^1$H NMR without additional purification. In order to characterize pure compounds and for their further use in oxidation the precipitate was subjected to recrystallization from benzene.

**4-Amino-*N*-acetyl-2-chlorophenol (IIIa).** Yield 47%, mp 140–141°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 1.99 s (3H, Me), 6.89 d (1H, H$^6$, $J_{5,6}$ 8.7 Hz), 7.20–7.23 d.d (1H, H$^5$, $J_{3,5}$ 1.2 Hz), 7.68 d (1H, H$^3$, *J* 2.7 Hz), 9.82 s (1H, OH), 9.85 s (1H, NH). Found, %: C 51.63, 51.84; H 4.32, 4.60; Cl 19.11, 19.45; N 7.69, 7.92. $C_8H_8ClNO_2$. Calculated, %: C 51.77; H 4.34; Cl 19.10; N 7.55.

**4-Amino-*N*-(4-methoxybenzoyl)-2-chlorophenol (IIIb).** Yield 78%, mp 228–229°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 3.84 s (3H, MeO), 6.95 d (1H, H$^6$, $J_{5,6}$ 8.7 Hz), 7.03–7.96 d.d (4H, 4-$MeOC_6$<u>H</u>$_4$, *J* 9.0 Hz), 7.48–7.51 d.d (1H, H$^5$, $J_{3,5}$ 2.1 Hz), 7.83 d (1H, H$^3$, *J* 2.4 Hz), 9.94 br.s (1H, OH), 9.99 br.s (1H, NH). $^{13}$C NMR spectrum, δ, ppm: 55.4 (OMe), 113.6 (C$^{3'}$, C$^{5'}$), 116.4 (C$^6$), 119.1 (C$^2$), 120.6 (C$^5$), 122.1 (C$^3$), 126.9 (C$^{1'}$), 129.6 (C$^{2'}$, C$^{6'}$), 131.9 (C$^4$), 149.3 (C$^1$), 161.9 (C$^{4'}$), 164.7 (C=O). Found, %: C 60.21, 60.49; H 4.42, 4.75; Cl 12.62, 12.94; N 5.10, 5.48. $C_{14}H_{12}ClNO_3$. Calculated, %: C 60.55; H 4.36; Cl 12.77; N 5.04.

**4-Amino-*N*-(4-methylbenzoyl)-2-chlorophenol (IIIc).** Yield 76%, mp 217–218°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.38 s (3H, Me), 6.95 d (1H, H$^6$, *J* 8.7 Hz), 7.31–7.87 d.d (4H, 4-$MeC_6$<u>H</u>$_4$, *J* 8.1 Hz), 7.48–7.52 d.d (1H, H$^5$, $J_{5,6}$ 9.0 Hz), 7.84 d (1H, H$^3$, $J_{3,5}$ 2.7 Hz), 9.97 s (1H, OH), 10.07 s (1H, NH). $^{13}$C NMR spectrum, δ, ppm: 21.0 (<u>Me</u>$C_6H_4$), 116.4 (C$^6$), 119.0 (C$^2$), 120.5 (C$^5$), 122.0 (C$^3$), 127.6 (C$^{3'}$, C$^{5'}$), 128.9 (C$^{2'}$, C$^{6'}$), 131.7 (C$^4$), 132.0 (C$^{1'}$), 141.5 (C$^{4'}$), 149.3 (C$^1$), 165.0 (C=O). Found, %: C 64.38, 6.51; H 4.07, 4.39; Cl 13.50, 13.72; N 5.31, 5.66. $C_{14}H_{12}ClNO_2$. Calculated, %: C 64.25; H 4.62; Cl 13.55; N 5.35.

**4-Amino-*N*-benzoyl-2-chlorophenol (IIId).** Yield 72%, mp 177–178°C. $^1$H NMR spectrum (DMSO-$d_6$),

δ, ppm: 6.95 d (1H, H$^6$, *J* 9.0 Hz), 7.48–7.52 d.d (1H, H$^5$, $J_{5,6}$ 8.7 Hz), 7.49–7.94 m (5H, Ph), 7.85 d (1H, H$^3$, $J_{3,5}$ 2.4 Hz), 9.95 s (1H, OH), 10.14 s (1H, NH). $^{13}$C NMR spectrum, δ, ppm: 116.4 (C$^6$), 119.1 (C$^2$), 120.6 (C$^5$), 122.0 (C$^3$), 127.6 (C$^{3'}$, C$^{5'}$), 128.4 (C$^{2'}$, C$^{6'}$), 131.5 (C$^4$), 131.6 (C$^{1'}$), 134.9 (C$^4$), 149.4 (C$^1$), 165.2 (C=O). Found, %: C 62.85, 63.04; H 4.15, 4.37; Cl 14.30, 14.58; N 5.69, 5.81. $C_{13}H_{10}ClNO_2$. Calculated, %: C 63.04; H 4.07; Cl 14.31; N 5.66.

**4-Amino-*N*-(4-chlorobenzoyl)-2-chlorophenol (IIIe).** Yield 59%, mp 190–191°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 6.96 d (1H, H$^6$, *J* 9.0 Hz), 7.30–7.97 d.d (4H, 4-Cl$C_6H_4$, *J* 8.7 Hz), 7.48–7.52 d.d (1H, H$^5$, $J_{5,6}$ 9.0 Hz), 7.84 d (1H, H$^3$, $J_{3,5}$ 2.4 Hz), 10.10 s (1H, OH), 10.24 s (1H, NH). Found, %: C 55.33, 55.61; H 3.20, 3.48; Cl 25.17, 25.39; N 4.95, 5.18. $C_{13}H_9Cl_2NO_2$. Calculated, %: C 55.34; H 3.22; Cl 25.13; N 4.96.

**4-Amino-*N*-(4-nitrobenzoyl)-2-chlorophenol (IIIf).** Yield 42%, mp 244–246°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 6.96 d (1H, H$^6$, *J* 8.4 Hz), 7.50–7.53 d.d (1H, H$^5$, $J_{5,6}$ 9.0 Hz), 7.86 d (1H, H$^3$, $J_{3,5}$ 2.7 Hz), 8.17–8.37 d.d (4H, 4-$NO_2C_6H_4$, *J* 9.0 Hz), 10.08 s (1H, OH), 10.47 s (1H, NH). Found, %: C 53.40, 53.71; H 3.02, 3.48; Cl 12.16, 12.57; N 9.62, 9.85. $C_{13}H_9ClN_2O_4$. Calculated, %: C 53.35; H 3.10; Cl 12.11; N 9.57.

**4-Amino-*N*-acetyl-2-methyl-6-chlorophenol (XIa).** Yield 69%, mp 98–100°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.00 s (3H, 2-Me), 2.17 s (3H, MeCO), 7.17 q (1H, H$^3$, *J* 2.1 Hz), 7.57 q (1H, H$^5$, *J* 2.1 Hz), 8.34 s (1H, NH), 9.91 s (1H, OH). Found, %: C 53.48, 53.79; H 4.88, 5.12; Cl 17.35, 17.66; N 7.09, 7.34. $C_9H_{10}ClNO_2$. Calculated, %: C 54.15; H 5.05; Cl 17.76; N 7.02.

**4-Amino-2-methyl-*N*-(4-methoxybenzoyl)-6-chlorophenol (XIb).** Yield 92%, mp 166–168°C. $^1$H NMR spectrum NMR spectrum (DMSO-$d_6$), δ, ppm: 2.21 s (3H, 2-Me), 3.84 s (3H, MeO), 7.05–7.94 d.d (4H, 4-MeO$C_6\underline{H}_4$, *J* 9.0 Hz), 7.43 d (1H, H$^3$, *J* 2.1 Hz), 7.72 d (1H, H$^5$, *J* 2.4 Hz), 8.33 s (1H, NH), 9.97 s (1H, OH). $^{13}$C NMR spectrum, δ, ppm: 17.1 (2-Me), 55.4 (OMe), 113.6 (C$^{3'}$, C$^{5'}$), 119.1 (C$^5$), 120.1 (C$^6$), 121.8 (C$^3$), 126.8 (C$^{1'}$), 126.9 (C$^2$), 129.5 (C$^{2'}$, C$^{6'}$), 131.8 (C$^4$), 146.9 (C$^1$), 161.9 (C$^{4'}$), 164.6 (C=O). Found, %: C 61.48, 61.59; H 4.80, 4.92; Cl 12.35, 12.67; N 4.88, 5.03. $C_{15}H_{14}ClNO_3$. Calculated, %: C 61.76; H 4.84; Cl 12.15; N 4.80.

**4-Amino-2-methyl-*N*-(4-methylbenzoyl)-6-chlorophenol (XIc).** Yield 69%, mp 156–158°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.21 s (3H, 2-Me), 2.38 s (3H, 4-Me$C_6\underline{H}_4$), 7.32–7.85 d.d (4H, 4-Me$C_6\underline{H}_4$, *J* 8.1 Hz), 7.43 d (1H, H$^3$, *J* 2.1 Hz), 7.71 d (1H, H$^5$, *J* 2.4 Hz), 8.33 s (1H, NH), 10.03 s (1H, OH). $^{13}$C NMR spectrum, δ, ppm: 17.1 (2-Me), 21.0 (Me$C_6H_4$), 119.2 (C$^3$), 120.2 (C$^6$), 121.8 (C$^5$), 126.9 (C$^2$), 127.6 (C$^{3'}$, C$^{5'}$), 128.9 (C$^{2'}$, C$^{6'}$), 131.7 (C$^4$), 132.0 (C$^{1'}$), 141.5 (C$^{4'}$), 147.0 (C$^1$), 165.0 (C=O). Found, %: C 65.58, 65.71; H 5.08, 5.49; Cl 12.94, 13.34; N 5.12, 5.60. $C_{15}H_{14}ClNO_2$. Calculated, %: C 65.34; H 5.12; Cl 12.86; N 5.08.

**4-Amino-*N*-benzoyl-2-methyl-6-chlorophenol (XId).** Yield 87%, mp 184–186°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.21 s (3H, 2-Me), 7.43 d (1H, H$^3$, *J* 2.4 Hz), 7.49–7.94 m (5H, Ph), 7.72 d (1H, H$^5$, *J* 2.7 Hz), 8.96 br.s (1H, NH), 10.11 s (1H, OH). $^{13}$C NMR spectrum, δ, ppm: 17.1 (2-Me), 119.2 (C$^3$), 120.2 (C$^6$), 121.8 (C$^5$), 127.0 (C$^2$), 127.6 (C$^{3'}$, C$^{5'}$), 128.4 (C$^{2'}$, C$^{6'}$), 131.5 (C$^{4'}$), 131.6 (C$^4$), 135.0 (C$^{1'}$), 147.1 (C$^1$), 165.3 (C=O). Found, %: C 64.08, 64.32; H 4.65, 4.79; Cl 13.50, 13.82; N 5.30, 5.66. $C_{14}H_{12}ClNO_2$. Calculated, %: C 64.25; H 4.62; Cl 13.55; N 5.35.

**4-Amino-*N*-(4-bromobenzoyl)-2-methyl-6-chlorophenol (XIf).** Yield 84%, mp 160–162°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.21 s (3H, 2-Me), 7.42 d (1H, H$^3$, *J* 1.8 Hz), 7.70 d (1H, H$^5$, *J* 2.4 Hz), 7.74–7.90 d.d (4H, 4-Br$C_6H_4$, *J* 8.4 Hz), 8.32 s (1H, NH), 10.18 s (1H, OH). Found, %: C 49.58, 49.72; H 3.22, 3.61; Cl 10.35, 10.76; N 4.08, 4.29. $C_{14}H_{11}BrClNO_2$. Calculated, %: C 49.37; H 3.26; Cl 10.41; N 4.11.

**4-Amino-2-methyl-*N*-(4-nitrobenzoyl)-6-chlorophenol (XIf).** Yield 51%, mp 256–258°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.22 s (3H, 2-Me), 7.42 d (1H, H$^3$, *J* 2.1 Hz), 7.72 d (1H, H$^5$, *J* 2.4 Hz), 8.16–8.37 d.d (4H, 4-$NO_2C_6H_4$, *J* 9.0 Hz), 9.07 s (1H, NH), 10.43 s (1H, OH). $^{13}$C NMR spectrum, δ, ppm: 17.1 (2-Me), 119.3 (C$^3$), 120.2 (C$^6$), 121.9 (C$^5$), 123.5 (C$^{3'}$, C$^{5'}$), 127.1 (C$^2$), 129.1 (C$^{2'}$, C$^{6'}$), 131.1 (C$^4$), 140.4 (C$^{1'}$), 147.5 (C$^1$), 149.1 (C$^{4'}$), 163.4 (C=O). Found, %: C 54.52, 54.73; H 3.58, 3.91; Cl 11.49, 11.62; N 9.06, 9.37. $C_{14}H_{11}ClN_2O_4$. Calculated, %: C 54.83; H 3.62; Cl 11.56; N 9.13.

**4-Amino-*N*-acetyl-3-methyl-6-chlorophenol (XVa).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.01 s (3H, 3-Me), 2.08 s (3H, MeO), 6.81 s (1H, H$^2$), 7.28 s (1H, H$^5$), 8.34 s (1H, NH), 9.25 s (1H, OH).

**4-Amino-3-methyl-*N*-(4-methoxybenzoyl)-6-chlorophenol (XVb).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.12 s (3H, 3-Me), 3.83 s (3H, MeO), 6.86 s (1H, H$^2$), 7.03–7.92 d.d (4H, 4-MeO$C_6\underline{H}_4$, *J* 8.7 Hz), 7.25 s

(1H, H$^5$), 9.62 s (1H, NH), 10.06 s (1H, OH).

**4-Amino-3-methyl-*N*-(4-methylbenzoyl)-6-chlorophenol (XVc).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.12 s (3H, 3-Me), 2.38 s (3H, Me), 6.85 s (1H, H$^2$), 7.26 s (1H, H$^5$), 7.32–7.86 d.d (4H, 4-MeC$_6$H$_4$, *J* 7.8 Hz), 9.68 s (1H, NH), 10.04 s (1H, OH).

**4-Amino-*N*-benzoyl-3-methyl-6-chlorophenol (XVd).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.13 s (3H, 3-Me), 6.88 s (1H, H$^2$), 7.27 s (1H, H$^5$), 7.49–7.97 m (5H, Ph), 9.78 s (1H, NH), 10.08 s (1H, OH).

**4-Amino-3-methyl-6-chloro-*N*-(4-chlorobenzoyl)-phenol (XVe).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.13 s (3H, 3-Me), 6.87 s (1H, H$^2$), 7.28 s (1H, H$^5$), 7.60–7.98 d.d (4H, 4-ClC$_6$H$_4$, *J* 8.7 Hz), 9.86 s (1H, NH), 10.08 s (1H, OH).

**4-Amino-3-methyl-*N*-(4-nitrobenzoyl)-6-chlorophenol (XVf).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.15 s (3H, 3-Me), 6.88 s (1H, H$^2$), 7.32 s (1H, H$^5$), 8.18–8.37 d.d (4H, 4-NO$_2$C$_6$H$_4$, *J* 8.4 Hz), 10.11 s (1H, NH), 10.26 br.s (1H, OH).

**4-Amino-*N*-acetyl-3-methyl-2-chlorophenol (XVIIa).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.01 s (3H, 3-Me), 2.15 s (3H, MeO), 6.81 d (1H, H$^6$, *J* 7.8 Hz), 6.98 d (1H, H$^5$, *J* 8.4 Hz), 9.14 br.s (1H, NH), 9.41 br.s (1H, OH).

**4-Amino-3-methyl-*N*-(4-methoxybenzoyl)-2-chlorophenol (XVIIb).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.18 s (3H, 3-Me), 3.83 s (3H, MeO), 6.83 d (1H, H$^6$, *J* 9.0 Hz), 7.03–7.92 d.d (4H, 4-MeOC$_6$H$_4$, *J* 8.7 Hz), 7.04 d (1H, H$^5$, *J* 8.1 Hz), 9.78 s (1H, NH), 10.06 s (1H, OH).

**4-Amino-3-methyl-*N*-(4-methylbenzoyl)-2-chlorophenol (XVIIc).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.18 s (3H, 3-Me), 2.38 s (3H, Me), 6.83 d (1H, H$^6$, *J* 6.6 Hz), 7.04 d (1H, H$^5$, *J* 8.4 Hz), 7.32–7.86 d.d (4H, 4-MeC$_6$H$_4$, *J* 7.8 Hz), 9.84 s (1H, NH), 10.06 s (1H, OH).

**4-Amino-*N*-benzoyl-3-methyl-2-chlorophenol (XVIId).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.19 s (3H, 3-Me), 6.85 d (1H, H$^6$, *J* 6.6 Hz), 7.05 d (1H, H$^5$, *J* 8.4 Hz), 7.49–7.97 m (5H, Ph), 9.94 s (1H, NH), 10.11 s (1H, OH).

**4-Amino-3-methyl-2-chloro-*N*-(4-chlorobenzoyl)-phenol (XVIIe).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.19 s (3H, 3-Me), 6.85 d (1H, H$^6$, *J* 6.0 Hz), 7.05 d (1H, H$^5$, *J* 9.0 Hz), 7.60–7.98 d.d (4H, 4-ClC$_6$H$_4$, *J* 8.7 Hz), 10.01 s (1H, NH), 10.09 s (1H, OH).

**4-Amino-3-methyl-*N*-(4-nitrobenzoyl)-2-chlorophenol (XVIIf).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.21 s (3H, 3-Me), 6.86 d (1H, H$^6$, *J* 6.7 Hz), 7.09 d (1H, H$^5$, *J* 9.0 Hz), 8.18–8.37 d.d (4H, 4-NO$_2$C$_6$H$_4$, *J* 8.7 Hz), 10.12 s (1H, NH), 10.32 s (1H, OH).

**4-Amino-*N*-acetyl-2,5-dimethyl-6-chlorophenol (XXIIa).** Yield 70%, mp 213–215°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.12 s (3H, 2-Me), 2.14 s (3H, 5-Me), 2.41 s (3H, MeCO), 6.92 s (1H, H$^3$), 8.88 br.s (1H, NH), 9.32 c (1H, OH). Found, %: C 56.15, 56.43; H 5.62, 5.81; Cl 16.66, 16.98; N 6.58, 6.74. $C_{10}H_{12}ClNO_2$. Calculated, %: C 56.21; H 5.66; Cl 16.59; N 6.56.

**4-Amino-*N*-acetyl-6-isopropyl-3-methyl-2-chlorophenol (XXIIb).** Yield 75%, mp 196°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 1.14 d (6H, 6-CHMe$_2$, *J* 7.0 Hz), 1.99 s (3H, 3-Me), 2.11 s (3H, MeCO), 3.18–3.28 m (1H, 6-CHMe$_2$), 6.93 s (1H, H$^5$), 8.86 br.s (1H, NH), 9.39 s (1H, OH). Found, %: C 56.39, 56.66; H 6.14, 6.39; Cl 14.58, 14.72; N 5.66, 5.83. $C_{12}H_{16}ClNO_2$. Calculated, %: C 59.63; H 6.67; Cl 14.67; N 5.79.

**4-Amino-*N*-acetyl-5-isopropyl-2-methyl-6-chlorophenol (XXIIc).** Yield 91%, mp 195–197°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 1.27 d (6H, 5-CHMe$_2$, *J* 6.9 Hz), 1.98 s (3H, 2-Me), 2.13 s (3H, MeCO), 3.26–3.37 m (1H, 5-CHMe$_2$), 6.77 s (1H, H$^3$), 8.87 br.s (1H, NH), 9.22 s (1H, OH). Found, %: C 59.70, 59.99; H 6.54, 6.82; Cl 14.66, 14.80; N 5.28, 5.53. $C_{12}H_{16}ClNO_2$. Calculated, %: C 59.63; H 6.67; Cl 14.67; N 5.79.

***N*-Acetyl-2-methyl(2,5-dialkyl)-6-chloro-1,4-benzoquinone monoimines XIIIb–XIIIf, XXIVa–XXIVc.** Into 10 ml of dry chloroform was added 0.01 mol of the corresponding *N*-acetylphenol **XIb–XIf, XXIIa–XXIIc**, and at stirring was added 0.012 mol of silver(I) oxide. The dispersion was heated to 40°C at vigorous stirring over 30 min, the solution turned yellow. The silver precipitate was filtered off from the reaction mixture, the solvent was distilled off in a vacuum. The residue was recrystallized from the mixture benzene–hexane.

**2-Methyl-*N*-(4-methoxybenzoyl)-6-chloro-1,4-benzoquinone monoimine (XIIIb).** Yield 69%, mp 124–126°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.10 d (3H, 2-Me, *J* 1.8 Hz), 3.89 s (3H, MeO), 6.90 q (1H, H$^3$, *J* 1.5 Hz), 6.97–7.87 d.d (4H, 4-MeOC$_6$H$_4$, *J* 9.3 Hz), 7.25 d (1H, H$^5$, *J* 2.7 Hz). Found, %: C 62.13, 62.47; H 4.18, 4.59; Cl 12.39, 12.70; N 4.68, 4.95. $C_{15}H_{12}ClNO_3$. Calculated, %: C 62.19; H 4.17; Cl 12.24; N 4.83.

**2-Methyl-*N*-(4-methylbenzoyl)-6-chloro-1,4-**

**benzoquinone monoimine (XIIIc).** Yield 63%, mp 110–112°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.09 d (3H, 2-Me, *J* 1.2 Hz), 2.44 c (3H, MeO), 6.89 q (1H, H$^3$, *J* 1.5 Hz), 7.24 d (1H, H$^5$, *J* 2.7 Hz), 7.29–7.79 d.d (4H, 4-Me$C_6\underline{H}_4$, *J* 8.7 Hz). Found, %: C 65.72, 66.09; H 4.38, 4.51; Cl 12.92, 13.40; N 5.06, 5.27. $C_{15}H_{12}ClNO_2$. Calculated, %: C 65.82; H 4.42; Cl 12.95; N 5.12.

***N*-Benzoyl-2-methyl-6-chloro-1,4-benzoquinone monoimine (XIIId).** Yield 76%, mp 112–114°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.10 d (3H, 2-Me, *J* 1.5 Hz), 6.90 q (1H, H$^3$, *J* 1.5 Hz), 7.25 d (1H, H$^5$, *J* 2.4 Hz), 7.42–7.92 m (5H, Ph). Found, %: C 64.52, 64.87; H 3.58, 3.91; Cl 13.79, 13.88; N 5.06, 5.47. $C_{14}H_{10}ClNO_2$. Calculated, %: C 64.75; H 3.88; Cl 13.65; N 5.39.

***N*-(4-Bromobenzoyl)-2-methyl-6-chloro-1,4-benzoquinone monoimine (XIIIe).** Yield 63%, mp 122–124°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.12 d (3H, 2-Me, *J* 1.5 Hz), 6.89 q (1H, H$^3$, *J* 1.2 Hz), 7.25 d (1H, H$^5$, *J* 2.1 Hz), 7.64–7.79 d.d (4H, 4-Br$C_6H_4$, *J* 9.0 Hz). Found, %: C 49.52, 49.81; H 2.57, 2.96; Cl 10.49, 10.75; N 4.06, 4.33. $C_{14}H_9BrClNO_2$. Calculated, %: C 49.66; H 2.68; Cl 10.47; N 4.14.

**2-Methyl-*N*-(4-nitrobenzoyl)-6-chloro-1,4-benzoquinone monoimine (XIIIf).** Yield 80%, mp 139–141°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.14 d (3H, 2-Me, *J* 1.5 Hz), 6.92 q (1H, H$^3$, *J* 1.5 Hz), 7.27 d (1H, H$^5$, *J* 3.0 Hz), 8.13–8.34 d.d (4H, 4-$NO_2C_6H_4$, *J* 9.3 Hz). Found, %: C 54.82, 55.17; H 2.58, 2.96; Cl 11.49, 11.70; N 9.06, 9.33. $C_{14}H_9ClN_2O_4$. Calculated, %: C 55.19; H 2.98; Cl 11.64; N 9.19.

***N*-Acetyl-2,5-dimethyl-6-chloro-1,4-benzoquinone monoimine (XXIVa).** Yield 63%, mp 122–124°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.08 d (3H, 2-Me, *J* 1.5 Hz), 2.30 s (3H, 5-Me), 2.32 s (3H, MeCO), 6.71 q (1H, H$^3$, *J* 1.2 Hz). Found, %: C 56.43, 56.77; H 4.80, 5.06; Cl 16.29, 16.49; N 6.40, 6.91. $C_{10}H_{10}ClNO_2$. Calculated, %: C 56.75; H 4.76; Cl 16.75; N 6.62.

***N*-Acetyl-6-isopropyl-3-methyl-2-chloro-1,4-benzoquinone monoimine (XXIVb).** Yield 89%, mp 48–50°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.21 d (6H, 6-CH$\underline{Me}_2$, *J* 7.2 Hz), 2.17 s (3H, 3-Me), 2.23 s (3H, MeCO), 3.21–3.30 m (1H, 6-C$\underline{H}Me_2$), 6.52 d (1H, H$^5$, *J* 1.2 Hz). Found, %: C 59.84, 60.12; H 5.75, 5.93; Cl 14.80, 15.21; N 5.73, 5.92. $C_{12}H_{14}ClNO_2$. Calculated, %: C 60.13; H 5.89; Cl 14.79; N 5.84.

***N*-Acetyl-5-isopropyl-2-methyl-6-chloro-1,4-benzoquinone monoimine (XXIVc).** Yield 77%, mp 80–82°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.37 d (6H, 5-CH$\underline{Me}_2$, *J* 7.2 Hz), 2.05 d (3H, 2-Me, *J* 1.2 Hz), 2.31 s (3H, MeCO), 3.60–3.70 m (1H, 5-C$\underline{H}Me_2$), 6.66 q (1H, H$^3$, *J* 1.2 Hz). Found, %: C 60.11, 60.42; H 5.83, 6.01; Cl 14.57, 15.85; N 5.79, 5.98. $C_{12}H_{14}ClNO_2$. Calculated, %: C 60.13; H 5.89; Cl 14.79; N 5.84.

**Hydrobromination of *N*-acetyl(aroyl)-1,4-benzoquinone monoimines VIIIa–VIIIf, Xa–Xf, XXIa–XXIc.** Into a solution of 0.01 mol of quinone monoimine in 10 ml of AcOH was added by portions while stirring 2 ml of 40% HBr. The reaction mixture got lighter. On adding water a colorless precipitate formed. The obtained mixtures without further purification were analyzed by $^1$H NMR. In order to characterize pure compounds and for their further use in oxidation the precipitate was subjected to recrystallization from AcOH.

**4-Amino-6-bromo-2-methyl-*N*-(4-methoxybenzoyl) phenol (XIIb).** Yield 80%, mp 252°C. $^1$H NMR spectrum NMR spectrum (DMSO-$d_6$), δ, ppm: 2.23 s (3H, 2-Me), 3.84 s (3H, MeO), 7.05–7.94 d.d (4H, 4-Me$OC_6\underline{H}_4$, *J* 9.0 Hz), 7.47 d (1H, H$^3$, *J* 2.1 Hz), 7.85 d (1H, H$^5$, *J* 2.7 Hz), 9.79 br.s (1H, NH), 9.94 br.s (1H, OH). Found, %: C 53.49, 53.70; H 4.08, 4.29; Br 23.75, 24.18; N 4.07, 4.59. $C_{15}H_{14}BrNO_3$. Calculated, %: C 53.59; H 4.20; Br 23.77; N 4.17.

**4-Amino-6-bromo-2-methyl-*N*-(4-methylbenzoyl) phenol (XIIc).** Yield 79%, subl. temp. 244°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.23 s (3H, 2-Me), 2.38 s (3H, Me), 7.32–7.86 d.d (4H, 4-Me$C_6\underline{H}_4$, *J* 8.1 Hz), 7.48 d (1H, H$^3$, *J* 2.1 Hz), 7.83 d (1H, H$^5$, *J* 3.9 Hz), 9.86 br.s (1H, NH), 10.01 s (1H, OH). Found, %: C 56.38, 56.70; H 4.22, 4.42; Br 24.65, 24.89; N 4.18, 4.39. $C_{15}H_{14}BrNO_2$. Calculated, %: C 56.27; H 4.41; Br 24.96; N 4.37.

**4-Amino-*N*-benzoyl-6-bromo-2-methylphenol (XIId).** Yield 65%, subl. temp. 210°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.24 s (3H, 2-Me), 7.48 d (1H, H$^3$, *J* 2.1 Hz), 7.52–7.95 m (5H, Ph), 7.86 d (1H, H$^5$, *J* 2.7 Hz), 9.82 br.s (1H, NH), 10.09 br.s (1H, OH). Found, %: C 54.58, 54.71; H 3.22, 3.60; Br 26.11, 26.49; N 4.08, 4.37. $C_{14}H_{12}BrNO_2$. Calculated, %: C 54.92; H 3.95; Br 26.10; N 4.58.

**4-Amino-6-bromo-2-methyl-*N*-(4-bromobenzoyl) phenol (XIIe).** Yield 65%, mp 178–180°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.23 s (3H, 2-Me), 7.47 d (1H, H$^3$, *J* 1.8 Hz), 7.74–7.89 d.d (4H, 4-Cr$C_6H_4$, *J* 8.1 Hz), 7.85 d (1H, H$^5$, *J* 2.7 Hz), 10.02 br.s (1H, NH), 10.17 br.s (1H,OH). Found, %: C 43.58, 43.76; H 2.23, 2.59; Br 41.05, 41.27; N 3.80, 3.99. $C_{14}H_{11}Br_2NO_2$.

Calculated, %: C 43.67; H 2.88; Br 41.50; N 3.64.

**4-Amino-6-bromo-2-methyl-*N*-(4-nitrobenzoyl) phenol (XIIf).** Yield 67%, mp 204–206°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.24 s (3H, 2-Me), 7.48 d (1H, H$^3$, *J* 2.1 Hz), 7.86 s (1H, H$^5$, *J* 2.4 Hz), 8.19–8.37 d.d (4H, 4-$NO_2C_6H_4$, *J* 8.4 Hz), 10.29 br.s (1H, NH), 10.42 br.s (1H, OH). Found, %: C 47.55, 47.63; H 3.22, 3.58; Br 22.61, 22.97; N 7.68, 7.90. $C_{14}H_{11}BrN_2O_4$. Calculated, %: C 47.89; H 3.16; Br 22.75; N 7.98.

**4-Amino-6-bromo-3-methyl-*N*-(4-methoxybenzoyl) phenol (XVIb).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.11 s (3H, 3-Me), 3.83 s (3H, MeO), 6.85 s (1H, H$^2$), 7.02–7.90 d.d (4H, 4-MeO$C_6\underline{H}_4$, *J* 9.0 Hz), 7.39 s (1H, H$^5$), 9.77 br.s (1H, NH), 10.05 br.s (1H, OH).

**4-Amino-6-bromo-3-methyl-*N*-(4-methylbenzoyl) phenol (XVIc).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.11 s (3H, 3-Me), 2.38 s (3H, Me), 6.85 s (1H, H$^2$), 7.32–7.86 d.d (4H, 4-Me$C_6\underline{H}_4$, *J* 8.7 Hz), 7.39 s (1H, H$^5$), 9.67 br.s (1H, NH), 9.96 br.s (1H, OH).

**4-Amino-*N*-benzoyl-6-bromo-3-methylphenol (XVId).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.13 s (3H, 3-Me), 6.86 s (1H, H$^2$), 7.41 s (1H, H$^5$), 7.49–7.97 m (5H, Ph), 9.73 br.s (1H, NH), 10.05 br.s (1H, OH).

**4-Amino-6-bromo-3-methyl-*N*-(4-chlorobenzoyl) phenol (XVIe).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.11 s (3H, 3-Me), 6.85 s (1H, H$^2$), 7.40 s (1H, H$^5$), 7.59–7.96 d.d (4H, 4-$ClC_6H_4$, *J* 8.7 Hz), 9.85 br.s (1H, NH), 10.14 br.s (1H, OH).

**4-Amino-6-bromo-3-methyl-*N*-(4-nitrobenzoyl) phenol (XVIf).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.14 s (3H, 3-Me), 6.88 s (1H, H$^2$), 7.45 s (1H, H$^5$), 8.19–8.36 d.d (4H, 4-$NO_2C_6H_4$, *J* 9.0 Hz), 10.10 br.s (1H, NH), 10.38 br.s (1H, OH).

**4-Amino-2-bromo-3-methyl-*N*-(4-methoxybenzoyl) phenol (XVIIIb).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.23 s (3H, 3-Me), 3.83 s (3H, MeO), 6.83 d (1H, H$^6$, *J* 8.7 Hz), 7.02–7.90 d.d (4H, 4-MeO$C_6\underline{H}_4$, *J* 8.7 Hz), 7.04 d (1H, H$^5$, *J* 8.7 Hz), 9.61 br.s (1H, NH), 9.89 s (1H, OH).

**4-Amino-2-bromo-3-methyl-*N*-(4-methylbenzoyl) phenol (XVIIIc).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.23 s (3H, 3-Me), 2.38 s (3H, Me), 6.83 d (1H, H$^6$, *J* 8.7 Hz), 7.07 d (1H, H$^5$, *J* 8.7 Hz), 7.32–7.86 d.d (4H, 4-Me$C_6\underline{H}_4$, *J* 7.5 Hz), 9.84 br.s (1H, NH), 9.96 br.s (1H, OH).

**4-Amino-*N*-benzoyl-2-bromo-3-methylphenol (XVIIId).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.24 s (3H, 3-Me), 6.84 d (1H, H$^6$, *J* 9.0 Hz), 7.09 d (1H, H$^5$, *J* 9.0 Hz), 7.49–7.97 m (5H, Ph), 9.90 br.s (1H, NH), 10.01 br.s (1H, OH).

**4-Amino-2-bromo-3-methyl-*N*-(4-chlorobenzoyl) phenol (XVIIIe).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.23 s (3H, 3-Me), 6.83 d (1H, H$^6$, *J* 8.1 Hz), 7.07 d (1H, H$^5$, *J* 8.1 Hz), 7.59–7.96 d.d (4H, 4-$ClC_6H_4$, *J* 8.7 Hz), 10.01 br.s (1H, NH), 10.19 br.s (1H, OH).

**4-Amino-2-bromo-3-methyl-*N*-(4-nitrobenzoyl) phenol (XVIIIf).** $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.26 s (3H, 3-Me), 6.87 d (1H, H$^6$, *J* 8.4 Hz), 7.13 d (1H, H$^5$, *J* 8.4 Hz), 8.19–8.36 d.d (4H, 4-$NO_2C_6H_4$, *J* 9.0 Hz), 9.86 br.s (1H, NH), 10.27 br.s (1H, OH).

**4-Amino-*N*-acetyl-2,6-dibromo-3-methylphenol (XIX).** Yield 31%, mp 243–245°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.02 s (3H, 3-Me), 2.19 s (3H, MeCO), 7.46 s (1H, H$^5$), 9.50 s (1H, NH), 9.71 br.s (1H, OH). Found, %: C 33.17, 33.48; H 2.59, 2.70; Br 49.32, 49.56; N 4.37, 4.60. $C_9H_9Br_2NO_2$. Calculated, %: C 33.47; H 2.81; Br 49.48; N 4.34.

**4-Amino-*N*-acetyl-6-bromo-2,5-dimethylphenol (XXIIIa).** Yield 84%, mp 230–232°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 1.99 s (3H, 2-Me), 2.16 s (3H, 5-Me), 2.17 s (3H, MeCO), 6.94 s (1H, H$^3$), 8.81 s (1H, NH), 9.32 br.s (1H, OH). Found, %: C 46.47, 46.78; H 4.59, 4.82; Br 40.31, 40.55; N 5.39, 5.60. $C_{10}H_{12}BrNO_2$. Calculated, %: C 46.53; H 4.69; Br 30.96; N 5.43.

**4-Amino-*N*-acetyl-2-bromo-6-isopropyl-3-methyl-phenol (XXIIIb).** Yield 69%, mp 182°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 1.13 d (6H, 6-CH$\underline{Me}_2$, *J* 6.9 Hz), 1.99 s (3H, 3-Me), 2.15 s (3H, MeCO), 3.20–3.29 m (1H, 6-C$\underline{H}$Me$_2$), 6.96 s (1H, H$^5$), 8.86 br.s (1H, NH), 9.39 br.s (1H, OH). Found, %: C 50.29, 50.48; H 5.61, 5.83; Br 27.60, 27.91; N 4.70, 4.93. $C_{12}H_{16}BrNO_2$. Calculated, %: C 50.37; H 5.64; Br 27.92; N 4.89.

**4-Amino-*N*-acetyl-6-bromo-5-isopropyl-2-methylphenol (XXIIIc).** Yield 56%, mp 168–169°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 1.25 d (6H, 5-CH$\underline{Me}_2$, *J* 6.9 Hz), 1.98 s (3H, 2-Me), 2.15 s (3H, MeCO), 3.43–3.48 m (1H, 5-C$\underline{H}$Me$_2$), 6.79 s (1H, H$^3$), 8.81 s (1H, NH), 9.19 br.s (1H, OH). Found, %: C 50.41, 50.56; H 5.34, 5.62; Br 27.81, 27.99; N 4.66, 4.90. $C_{12}H_{16}BrNO_2$. Calculated, %: C 50.37; H 5.64; Br 27.92; N 4.89.

***N*-Aroyl-6-bromo-2-methyl-1,4-benzoquinone monoimines XIVe, XIVf and *N*-acetyl-6-bromo-2,5-dialkyl-1,4-benzoquinone monoimines XXVa–XXVc.**

Into 10 ml of dry chloroform was added 0.01 mol of the corresponding *N*-acetyl(aroyl)phenol **XIIe, XIIf**, **XXIIIa–XXIIIc** and at stirring was added 0.012 mol of silver(I) oxide. The dispersion was heated to 40°C at vigorous stirring over 30 min, the solution turned yellow. The silver precipitate was filtered off from the reaction mixture, the solvent was distilled off in a vacuum. The residue was recrystallized from the mixture benzene–hexane.

***N*-(4-Bromobenzoyl)-6-bromo-2-methyl-1,4-benzoquinone monoimine (XIVe).** Yield 79%, mp 118–120°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.11 s (3H, 2-Me), 6.89 q (1H, H$^3$, *J* 1.2 Hz), 7.52 d (1H, H$^5$, *J* 2.4 Hz), 7.64–7.78 d.d (4H, 4-Br$C_6H_4$, *J* 9.0 Hz). Found, %: C 43.71, 43.96; H 2.35, 2.51; Br 41.80, 42.07; N 3.55, 3.90. $C_{14}H_9Br_2NO_2$. Calculated, %: C 43.90; H 2.37; Br 41.72; N 3.66.

**2-Methyl-*N*-(4-nitrobenzoyl)-1,4-benzoquinone monoimine (XIVf).** Yield 79%, mp 118–120°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.14 s (3H, 2-Me), 6.92 q (1H, H$^3$, *J* 0.9 Hz), 6.87 d (1H, H$^5$, *J* 1.5 Hz), 8.12–8.35 d.d (4H, 4-Br$C_6H_4$, *J* 8.4 Hz). Found, %: C 47.81, 48.26; H 2.35, 2.44; Br 22.90, 23.18; N 7.85, 8.30. $C_{14}H_9BrN_2O_4$. Calculated, %: C 48.16; H 2.60; Br 22.89; N 8.02.

***N*-Acetyl-6-bromo-2,5-dimethyl-1,4-benzoquinone monoimine (XXVa).** Yield 92%, mp 127°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.09 d (3H, 2-Me, *J* 1.2 Hz), 2.32 s (3H, 5-Me), 2.34 s (3H, MeCO), 6.69 q (1H, H$^3$, *J* 1.8 Hz). Found, %: C 46.81, 46.98; H 3.57, 3.77; Br 31.19, 31.48; N 5.20, 5.45. $C_{10}H_{10}BrNO_2$. Calculated, %: C 46.90; H 3.94; Br 31.20; N 5.47.

***N*-Acetyl-2-bromo-6-isopropyl-3-methyl-1,4-benzoquinone monoimine (XXVb).** Yield 77%, mp 73°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.12 d (6H, 6-CH$\underline{Me}_2$, *J* 6.9 Hz), 2.32 s (3H, 3-Me), 2.34 s (3H, MeCO), 3.05–3.14 m (1H, 6-C$\underline{H}Me_2$), 6.58 d (1H, H$^5$, *J* 1.2 Hz). Found, %: C 50.51, 50.79; H 4.63, 4.82; Br 28.21, 28.46; N 5.17, 5.39. $C_{12}H_{14}BrNO_2$. Calculated, %: C 50.72; H 4.97; Br 28.12; N 4.93.

***N*-Acetyl-6-bromo-5-isopropyl-2-methyl-1,4-benzoquinone monoimine (XXVc).** Yield 78%, mp 81–83°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.38 d (6H, 5-CH$\underline{Me}_2$, *J* 7.2 Hz), 2.07 d (3H, 2-Me, *J* 1.5 Hz), 2.31 s (3H, MeCO), 3.61–3.70 m (1H, 5-C$\underline{H}Me_2$), 6.64 q (1H, H$^3$, *J* 1.2 Hz). Found, %: C 50.57, 50.72; H 4.63, 4.81; Br 28.07, 28.19; N 4.90, 5.16. $C_{12}H_{14}BrNO_2$. Calculated, %: C 50.72; H 4.97; Br 28.12; N 4.93.

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