

Halogenation of N-Substituted *p*-Quinone Monoimines and *p*-Quinone Monooxime Esters: XI.* Synthesis and Halogenation of 4-[Aryl(alkyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-ones

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Abstract—4-[Aryl(alkyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-ones were synthesized by treatment of various substituted *p*-quinone monooximes with aryl isocyanates. The selectivity in the halogenation of the obtained *p*-quinone monooxime esters depended on the substrate structure and was either completely (*syn* addition) or partly regioselective (*syn* or *anti* addition). In all cases, the effect of steric factor was crucial, and the reaction was accompanied by halogenation of the aryl fragment.

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We previously synthesized *N*-alkyl(aryl)aminocarbonyl-1,4-benzoquinone monoimines by reaction of alkyl and aryl isocyanates with various aminophenols and subsequent oxidation [2]. *N*-Alkyl(aryl)aminocarbonyl-3,5-dimethyl-1,4-benzoquinone monoimines reacted with alcohols to give 1-aryl-4,7a-dimethyl-7,7a-dihydro-1*H*-benzimidazole-2,6-diones [3] due to the presence of NH group in the initial quinone imine. Isocyanates are capable of reacting with both amines and alcohols [4]; therefore, reactions of aryl isocyanates with *p*-quinone monooximes were expected to afford compounds belonging to a new class of *para*-quinone monooxime esters, 4-(arylamino-carbonyloxyimino)cyclohexa-2,5-dien-1-ones. *O*-Arylsulfonyl [5, 6] and *O*-aroyl [6, 7] *para*-quinone monooximes were synthesized previously. It was found that the direction of their halogenation is determined by electronic (difference in the polarities of the quinoid C=C bonds) and steric factors (size and position of substituents in the quinoid ring). Here, the effect of substituent on the oxime oxygen atom on the reactivity ratio of the quinoid C=C bonds in *O*-aroyl derivatives was stronger than in their *O*-arylsulfonyl analogs [8].

4-(Arylamino-carbonyloxyimino)cyclohexa-2,5-dien-1-ones are analogs of 4-(aroyloxyimino)cyclohexa-

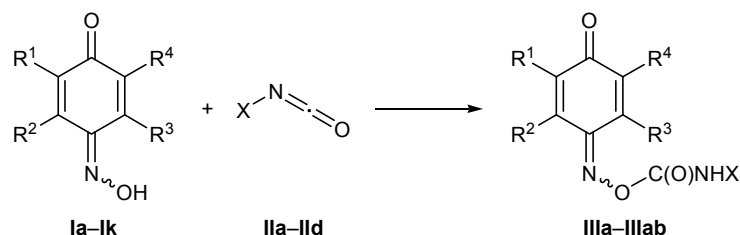
2,5-dien-1-ones; the difference is that an NH group is present between the aryl fragment and carbonyl group in the former. A similar difference in the structures of *N*-aroyl- and *N*-alkyl(aryl)aminocarbonyl-3,5-dimethyl-1,4-benzoquinone monoimines gave rise to considerable difference in their reactivity [3].

The goal of the present work was to synthesize new 4-[aryl(alkyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-ones and study their reactions with halogens. 4-[Aryl(alkyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-ones **IIIa–IIIab** were obtained by reaction of *p*-quinone monooximes **Ia–Ik** with aryl and alkyl isocyanates **IIa–IIc** on heating in dioxane (Scheme 1). The structure of compounds **IIIa–IIIab** was confirmed by the ¹H NMR and IR spectra and elemental analyses. We also did not rule out the possibility for aryl (alkyl) isocyanates to react with another tautomeric form of *p*-quinone monooximes, the corresponding *p*-nitroso-phenols. However, the ¹H NMR and IR data showed the absence of isocyanate addition products at the hydroxy group of *p*-nitrosophenol.

It was found previously that 4-(aroyloxyimino)-cyclohexa-2,5-dien-1-ones are characterized by a higher energy barrier to *Z*–*E* isomerization about the C=N bond ($\Delta G^\ddagger > 100$ kJ/mol) [9], as compared to the corresponding *p*-quinone monoimines ($\Delta G^\ddagger = 44$ –

* For communication X, see [1].

Scheme 1.



I, R¹ = R² = R³ = R⁴ = H (**a**); R¹ = Me, R² = R³ = R⁴ = H (**b**); R¹ = R³ = R⁴ = H, R² = Me (**c**); R¹ = R² = H, R³ = R⁴ = Me (**d**); R¹ = R³ = Me, R² = R⁴ = H (**e**); R¹ = *i*-Pr, R² = R⁴ = H, R³ = Me (**f**); R¹ = Me, R² = R⁴ = H, R³ = *i*-Pr (**g**); R¹ = R⁴ = H, R² = R³ = Me (**h**); R¹ = R⁴ = Me, R² = R³ = H (**i**); R¹ = R⁴ = *i*-Pr, R² = R³ = H (**j**); R¹ = R⁴ = *t*-Bu, R² = R³ = H (**k**); **II**, X = Ph (**a**), 4-MeC₆H₄ (**b**), Bu (**c**), *t*-Bu (**d**); **III**, R¹ = R² = R³ = R⁴ = H (**a**, **b**); R¹ = Me, R² = R³ = R⁴ = H (**c**, **d**); R¹ = R³ = R⁴ = H, R² = Me (**e**, **f**); R¹ = R² = H, R³ = R⁴ = Me (**g**, **h**, **i**); R¹ = R³ = Me, R² = R⁴ = H (**j**, **k**, **l**, **aa**); R¹ = *i*-Pr, R² = R⁴ = H, R³ = Me (**m**, **n**); R¹ = Me, R² = R⁴ = H, R³ = *i*-Pr (**o**, **p**); R¹ = R⁴ = H, R² = R³ = Me (**q-s**); R¹ = R⁴ = Me, R² = R³ = H (**t-v**, **ab**); R¹ = R⁴ = *i*-Pr, R² = R³ = H (**w**, **x**); R¹ = R⁴ = *t*-Bu, R² = R³ = H (**y**, **z**); X = Ph (**a**, **c**, **e**, **g**, **j**, **m**, **o**, **q**, **t**, **w**, **y**), 4-MeC₆H₄ (**b**, **d**, **f**, **h**, **k**, **n**, **p**, **r**, **u**, **x**, **z**), 3-ClC₆H₄ (**i**, **l**, **s**, **v**), Bu (**aa**), *t*-Bu (**ab**).

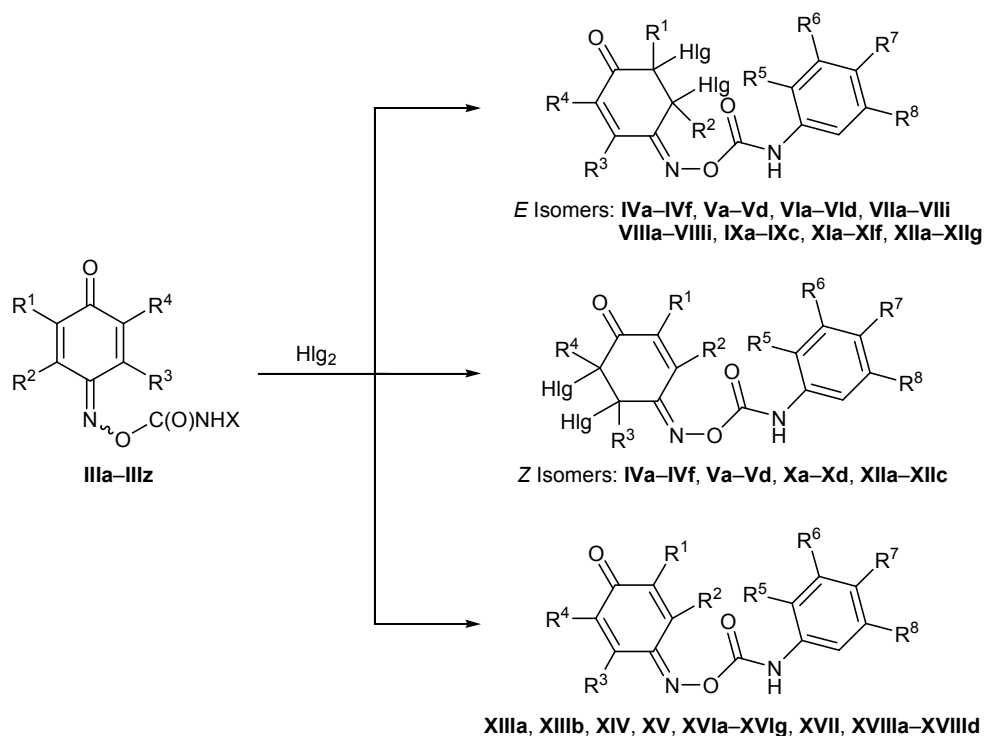
46 kJ/mol) [10]. Therefore, their *Z-E* isomerization becomes improbable, and particular isomers of unsymmetrically substituted *p*-quinone monooxime esters can be isolated as individual substances. It was also shown that halogenation of these compounds is not accompanied by *Z-E* isomerization [8]. According to the ¹H NMR data, 4-arylamino-carbonyloxyimino-2-methylcyclohexa-2,5-dien-1-ones **IIIc** and **IIId** isolated by recrystallization exist in solution as mixtures of *Z* and *E* isomers at a ratio of 60 : 40 (**IIIc**) or 15 : 85 (**IIId**). The observed difference in the *Z/E* isomer ratios is explained by the fact that the *Z* and *E* isomers of 4-tolyl derivative **IIId** are separated more readily by recrystallization. The ratio of the *Z* and *E* isomers of both phenyl derivative **IIIc** and 4-tolyl derivative **IIId** in the crude product (before recrystallization) was ~60:40. While studying halogenation of 4-(arylsulfonyloxyimino)cyclohexa-2,5-dien-1-ones we succeeded in isolating individual *E* isomer only for the 4-tolyl derivative [8].

p-Quinone monooximes **Ia-Ik** reacted with alkyl isocyanates **IIc** and **IId** under relatively severe conditions, and the yield of 4-alkylaminocarbonyloxyimino-cyclohexa-2,5-dien-1-ones was poor even on prolonged heating in dioxane at 100°C; the conversion of the initial *p*-quinone monooxime was incomplete, and a number of by-products were formed. We succeeded in isolating only two individual 4-alkylaminocarbonyloxyiminocyclohexa-2,5-dien-1-ones **IIIaa** and **IIIab** (yield 8 and 15%, respectively); therefore, the reactivity of these compounds toward halogens was not studied. The poor yields of **IIIaa** and **IIIab** are likely to result from lower reactivity of aliphatic isocyanates compared to aryl isocyanates toward compounds having a hydroxy group.

4-(Arylamino-carbonyloxyimino)cyclohexa-2,5-dien-1-ones **IIIa-IIIz** were subjected to chlorination with gaseous chlorine which was passed until complete saturation of the reaction mixture. The bromination of these compounds was carried out using molecular bromine in acetic acid or chloroform, the substrate-to-bromine ratio being 1:5. Crystalline products isolated as a result of halogenation were analyzed ¹H NMR spectroscopy before recrystallization with a view to reveal all possible isomers. Many compounds were isolated as individual substances by recrystallization, so that we were able to determine the composition of almost all product mixtures. The results are shown in Scheme 2.

Halogenation of *p*-quinone monooxime esters **IIIa** and **IIIb** having no substituents in the quinoid ring led to the formation of several isomers. The chlorination of **IIIa** and **IIIb** gave products of addition of one halogen molecule at the double C=C bond in the quinoid ring (compounds **IVa** and **IVd**), as well as 2,5,6-trichlorocyclohex-2-en-1-ones **IVb** and **IVe**, the latter being formed via successive halogenation-dehydrohalogenation. Among bromination products, we detected only 2,5,6-tribromocyclohex-2-en-1-ones **IVc** and **IVf** having a bromine atom at the quinoid C=C bond. Obviously, compounds **IVc** and **IVf** were formed via addition of bromine molecule to *p*-quinone monooxime esters resulting from successive bromination-dehydrobromination. Analysis of the composition of the reaction mixtures showed that the addition of first halogen molecule to *p*-quinone monooxime esters **IIIa** and **IIIb** is regioselective: it involves preferentially the quinoid C=C bond located *syn* with respect to the oxime fragment (the ratio of the *syn*- and *anti*-addition products is 57 : 43 in the chlorination and

Scheme 2.



IV, $R^2 = R^3 = R^6 = R^8 = H$; $R^1 = R^4 = H$, $\text{Hlg} = R^5 = R^7 = \text{Cl}$ (**a**); $R^1 = H$, $\text{Hlg} = R^4 = R^5 = R^7 = \text{Cl}$ (**b**); $R^1 = R^5 = H$, $\text{Hlg} = R^4 = R^7 = \text{Br}$ (**c**); $R^1 = R^4 = H$, $\text{Hlg} = R^5 = \text{Cl}$, $R^7 = \text{Me}$ (**d**); $R^1 = H$, $\text{Hlg} = R^4 = R^5 = \text{Cl}$, $R^7 = \text{Me}$ (**e**); $R^1 = H$, $\text{Hlg} = R^4 = R^5 = \text{Br}$, $R^7 = \text{Me}$ (**f**); **V**, $R^1 = R^2 = R^3 = R^6 = R^8 = H$, $R^4 = \text{Me}$; $\text{Hlg} = R^7 = \text{Cl}$, $R^5 = H$ (**a**); $\text{Hlg} = R^7 = \text{Br}$, $R^5 = H$ (**b**); $\text{Hlg} = R^5 = \text{Cl}$, $R^7 = \text{Me}$ (**c**); $\text{Hlg} = R^5 = \text{Br}$, $R^7 = \text{Me}$ (**d**); **VI**, $R^1 = R^2 = R^4 = R^6 = R^8 = H$, $R^3 = \text{Me}$; $\text{Hlg} = R^5 = R^7 = \text{Cl}$ (**a**); $\text{Hlg} = R^7 = \text{Br}$, $R^5 = H$ (**b**); $\text{Hlg} = R^5 = \text{Cl}$, $R^7 = \text{Me}$ (**c**); $\text{Hlg} = R^5 = \text{Br}$, $R^7 = \text{Me}$ (**d**); **VII**, $R^1 = R^2 = H$, $R^3 = R^4 = \text{Me}$; $\text{Hlg} = R^7 = \text{Cl}$, $R^5 = R^6 = R^8 = H$ (**a**); $\text{Hlg} = R^5 = R^7 = \text{Cl}$, $R^6 = R^8 = H$ (**b**); $\text{Hlg} = R^7 = \text{Br}$, $R^5 = R^6 = R^8 = H$ (**c**); $\text{Hlg} = R^5 = \text{Cl}$, $R^6 = R^8 = H$, $R^7 = \text{Me}$ (**d**); $\text{Hlg} = R^5 = \text{Br}$, $R^6 = R^8 = H$, $R^7 = \text{Me}$ (**e**); $\text{Hlg} = R^5 = R^8 = \text{Cl}$, $R^6 = R^7 = H$ (**f**); $\text{Hlg} = R^5 = R^7 = R^8 = \text{Cl}$, $R^6 = H$ (**g**); $\text{Hlg} = R^5 = R^6 = R^8 = \text{Cl}$, $R^7 = H$ (**h**); $\text{Hlg} = R^5 = \text{Br}$, $R^6 = R^7 = H$, $R^8 = \text{Cl}$ (**i**); **VIII**, $R^1 = R^3 = \text{Me}$, $R^2 = R^4 = H$; $\text{Hlg} = R^7 = \text{Cl}$, $R^5 = R^6 = R^8 = H$ (**a**); $\text{Hlg} = R^5 = R^7 = \text{Cl}$, $R^6 = R^8 = H$ (**b**); $\text{Hlg} = R^7 = \text{Br}$, $R^5 = R^6 = R^8 = H$ (**c**); $\text{Hlg} = R^5 = \text{Cl}$, $R^6 = R^8 = H$, $R^7 = \text{Me}$ (**d**); $\text{Hlg} = R^5 = \text{Br}$, $R^6 = R^8 = H$, $R^7 = \text{Me}$ (**e**); $\text{Hlg} = R^5 = R^8 = \text{Cl}$, $R^6 = R^7 = H$ (**f**); $\text{Hlg} = R^5 = R^7 = R^8 = \text{Cl}$, $R^6 = H$ (**g**); $\text{Hlg} = R^5 = R^6 = R^8 = \text{Cl}$, $R^7 = H$ (**h**); $\text{Hlg} = R^5 = \text{Br}$, $R^6 = R^7 = H$, $R^8 = \text{Cl}$ (**i**); **IX**, $R^1 = i\text{-Pr}$, $R^2 = R^4 = H$, $R^3 = \text{Me}$; $\text{Hlg} = R^5 = R^7 = \text{Cl}$, $R^6 = R^8 = H$ (**a**); $\text{Hlg} = R^7 = \text{Br}$, $R^5 = R^6 = R^8 = H$ (**b**); $\text{Hlg} = R^5 = R^8 = \text{Cl}$, $R^6 = H$, $R^7 = \text{Me}$ (**c**); **X**, $R^1 = R^2 = H$, $R^3 = \text{Me}$, $R^4 = i\text{-Pr}$; $\text{Hlg} = R^5 = R^7 = \text{Cl}$, $R^6 = R^8 = H$ (**a**); $\text{Hlg} = R^7 = \text{Br}$, $R^5 = R^6 = R^8 = H$ (**b**); $\text{Hlg} = R^5 = R^8 = \text{Cl}$, $R^6 = H$, $R^7 = \text{Me}$ (**c**); $\text{Hlg} = R^5 = \text{Br}$, $R^6 = R^8 = H$, $R^7 = \text{Me}$ (**d**); **XI**, $R^1 = \text{Me}$, $R^2 = R^4 = H$, $R^3 = i\text{-Pr}$; $\text{Hlg} = R^7 = \text{Cl}$, $R^5 = R^6 = R^8 = H$ (**a**); $\text{Hlg} = R^5 = R^7 = \text{Cl}$, $R^6 = R^8 = H$ (**b**); $\text{Hlg} = R^7 = \text{Br}$, $R^5 = R^6 = R^8 = H$ (**c**); $\text{Hlg} = R^5 = \text{Cl}$, $R^6 = R^8 = H$, $R^7 = \text{Me}$ (**d**); $\text{Hlg} = \text{Br}$, $R^5 = R^6 = R^8 = H$, $R^7 = \text{Me}$ (**e**); $\text{Hlg} = R^5 = \text{Br}$, $R^6 = R^8 = H$, $R^7 = \text{Me}$ (**f**); **XII**, $R^1 = R^4 = H$, $R^2 = R^3 = \text{Me}$; $\text{Hlg} = R^5 = R^7 = \text{Cl}$, $R^6 = R^8 = H$ (**a**); $\text{Hlg} = R^7 = \text{Br}$, $R^5 = R^6 = R^8 = H$ (**b**); $\text{Hlg} = R^5 = \text{Cl}$, $R^6 = R^8 = H$, $R^7 = \text{Me}$ (**c**); $\text{Hlg} = R^5 = R^8 = \text{Cl}$, $R^6 = R^7 = H$ (**d**); $\text{Hlg} = R^5 = R^6 = R^7 = \text{Cl}$, $R^8 = H$ (**e**); $\text{Hlg} = R^5 = R^7 = R^8 = \text{Cl}$, $R^6 = H$ (**f**); $\text{Hlg} = R^5 = \text{Br}$, $R^6 = R^7 = H$, $R^8 = \text{Cl}$ (**g**); **XIII**, $R^1 = R^3 = R^7 = \text{Me}$, $R^2 = R^4 = R^6 = R^8 = H$, $R^5 = \text{Cl}$ (**a**); Br (**b**); **XIV**, $R^1 = i\text{-Pr}$, $R^2 = R^4 = R^6 = R^8 = H$, $R^3 = R^7 = \text{Me}$, $R^5 = \text{Br}$; **XV**, $R^1 = R^4 = R^6 = R^8 = H$, $R^2 = R^3 = R^7 = \text{Me}$, $R^5 = \text{Cl}$; **XVI**, $R^1 = R^4 = \text{Me}$, $R^2 = R^3 = H$; $R^5 = R^6 = R^8 = H$, $R^7 = \text{Cl}$ (**a**); $R^5 = R^7 = \text{Cl}$, $R^6 = R^8 = H$ (**b**); $R^5 = R^6 = R^8 = H$, $R^7 = \text{Br}$ (**c**); $R^5 = \text{Cl}$, $R^6 = R^8 = H$, $R^7 = \text{Me}$ (**d**); $R^5 = R^8 = \text{Cl}$, $R^6 = R^7 = H$ (**e**); $R^5 = R^6 = R^8 = \text{Cl}$, $R^7 = H$ (**f**); $R^5 = R^7 = R^8 = \text{Cl}$, $R^6 = H$ (**g**); **XVII**, $R^1 = R^4 = i\text{-Pr}$, $R^2 = R^3 = R^5 = R^6 = R^8 = H$, $R^7 = \text{Cl}$; **XVIII**, $R^1 = R^4 = i\text{-Bu}$, $R^2 = R^3 = H$; $R^5 = R^7 = \text{Cl}$, $R^6 = R^8 = H$ (**a**); $R^7 = \text{Br}$, $R^5 = R^6 = R^8 = H$ (**b**); $R^5 = \text{Cl}$, $R^6 = R^8 = H$, $R^7 = \text{Me}$ (**c**); $R^5 = \text{Br}$, $R^6 = R^8 = H$, $R^7 = \text{Me}$ (**d**).

63:37 in the bromination). Thus the effect of electronic factor in the halogenation of *p*-quinone monooxime esters **IIIa** and **IIIb** is considerably weaker than in the halogenation of 4-[aroyl(arylsulfonyl)oxyimino]-cyclohexa-2,5-dien-1-ones [11, 12] studied previously, where the isomer ratio was 85:15.

4-Arylamino carbonyloxyimino-2-methyl(3-methyl, 2,3-dimethyl)cyclohexa-2,5-dien-1-ones **IIIc-IIIi** took

up halogen molecule exclusively at the unsubstituted C=C bond in the quinoid ring. In the halogenation of 2-methyl derivatives **IIIc** and **IIId**, as in the reactions with 4-aroyl- and 4-arylsulfonylimino derivatives [8], the *Z/E*-isomer ratio did not change during the process within the experimental error and was 58:42 (**Va**) and 57:43 (**Vb**) for **IIIc** and 21:79 (**Vc**) and 18:82 (**Vd**) for **IIId**. These data indicate that in the halogenation of

4-arylamino-carbonyloxyimino derivatives **IIIc** and **IIIe** steric factor is more significant than in the reactions with 4-arylimino and 4-arylsulfonylimino analogs [8], i.e., the effect of the ArNHCO substituent on the reactivity of C=C bonds in the quinoid ring (in the *syn* and *anti* positions) of *p*-quinone monooxime esters **IIIa–IIIz** is weaker than in aroyl- and arylsulfonylimino derivatives. In the halogenation of **IIIe–IIIi**, both steric and electronic factors act in one direction; therefore, only addition products at the *syn*-C=C bond were obtained.

The halogenation of compounds **IIIj–IIIl**, **IIIo**, and **IIIp** gave only the corresponding *syn*-addition products, *E* isomers **VIIIa–VIIIi** and **XIa–XIf**. The halogenation of **IIIm** and **IIIn** was regioselective with predominant formation of *anti*-addition products (the ratio of the *Z* and *E* isomers was about 58:42), indicating stronger effect of steric factor, as compared to 4-arylimino- and 4-(arylsulfonyloxyimino)cyclohexa-2,5-dien-1-ones. The *E/Z*-isomer ratio for the halogenation products of compounds **IIIq–IIIs** was ~63:37 (predominant *syn* addition), but the selectivity was lower than in the halogenation of *N*-aroyl and *N*-arylsulfonyl analogs [13].

The halogenation of 4-(arylamino-carbonyloxyimino)cyclohexa-2,5-dien-1-ones **IIIa–IIIz** was accompanied by electrophilic replacement in the *N*-aryl fragment due to the presence of electron-donating NH group. As might be expected, halogen atom entered mainly *ortho* and *para* positions with respect to the NH group. On the one hand, the NH group activates the benzene ring toward electrophilic substitution by halogen; on the other hand, the presence of the neighboring carbonyl group weakens the activating effects. Therefore, compounds having one to three halogen atoms in the aryl fragment were obtained.

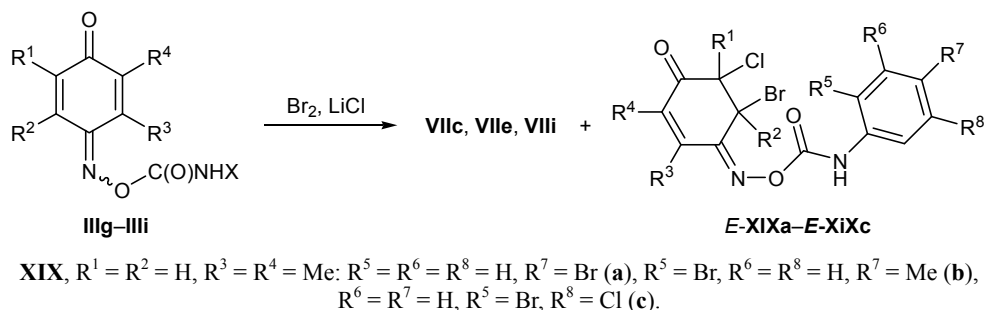
Among halogenation products of *p*-quinone monooxime esters having two alkyl groups in the quinoid ring we also detected compounds **XIII–XVIII** with

halogen atoms only in the *N*-aryl fragment, the quinoid fragment remaining intact. This means that introduction of alkyl groups deactivates the quinoid ring toward halogens. In the reactions with 2,6-dialkyl derivatives **IIIt–IIIz** no halogenation of the quinoid ring occurred at all, and the products were only haloaryl derivatives **XVIa–XVIg**, **XVII**, and **XVIIIa–XVIIId**.

In order to elucidate the mechanism of halogenation of *p*-quinone monooxime esters we previously examined the bromination of 4-[aroyl(arylsulfonyl)oxyimino]-2,3-dimethylcyclohexa-2,5-dien-1-ones in the presence of LiCl [8]. In the present work we also examined the bromination of compounds **IIIg–IIIi** in the presence of LiCl. As a result, we obtained mixtures consisting of two compounds. One of these was the product of addition of one bromine molecule at the unsubstituted double C=C bond in the quinoid ring (compounds **VIIc**, **VIIe**, and **VIIIi**), while the second contained one bromine and one chlorine atom. As with 4-(arylsulfonyloxyimino)cyclohexa-2,5-dien-1-ones, the chlorine atom was attached to the carbon atom in the *ortho* position with respect to the carbonyl group (compounds **XIXa–XIXc**, Scheme 3). The product structure suggests that the halogenation of 4-arylimino-, 4-arylsulfonylimino-, and 4-(arylamino-carbonyloxyimino)cyclohexa-2,5-dien-1-ones follows a common mechanism involving addition of the first halogen atom at the quinoid C=C bond through intermediate halonium ion and exclusive *trans*-addition of the second halogen atom [8].

Thus the results of the present study showed that, unlike previously studied 4-[aroyl(arylsulfonyl)imino]-cyclohexa-2,5-dien-1-ones, the halogenation of 4-(arylamino-carbonyloxyimino)cyclohexa-2,5-dien-1-ones is affected more strongly by steric rather than electronic factor due to the presence of NH group between the aryl fragment and carbonyl group. Introduction of two alkyl groups into the quinoid ring of

Scheme 3.



4-(arylamino-carbonyloxyimino)cyclohexa-2,5-dien-1-ones, especially into positions 2 and 6, deactivates the quinoid ring toward halogens, whereas the *N*-aryl group becomes more reactive than the quinoid fragment due to the presence of NH group.

EXPERIMENTAL

The ^1H NMR spectra were recorded from solutions in CDCl_3 on a Varian VXR-300 spectrometer operating at 300 MHz; the chemical shifts were determined relative to tetramethylsilane. The purity of the initial *p*-quinone monooxime esters and their halogenation products was checked by TLC on Silufol UV-254 plates; samples were applied from solutions in chloroform, ethanol–chloroform (1:10) was used as eluent, and spots were visualized under UV light.

Alkyl and aryl isocyanates **IIa–IIId** were synthesized according to the procedure described in [2].

4-[Aryl(alkyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-ones IIIa–IIIab (general procedure). A suspension of 0.01 mol of *p*-quinone monooxime **Ia–Ik** in 50–55 ml of dioxane was heated to 100°C, and an equimolar amount of the corresponding alkyl or aryl isocyanate **IIa–IIId** was slowly added under stirring. After cooling, crystalline solid separated and was filtered off and recrystallized from ethanol.

4-(Phenylaminocarbonyloxyimino)cyclohexa-2,5-dien-1-one (IIIa). Yield 40%, mp 166–168°C. ^1H NMR spectrum, δ , ppm: 6.59–6.62 d.d (1H, 6-H, $J_{2,6} = 1.8$, $J_{6,5} = 10.5$ Hz), 6.62–6.66 d.d (1H, 2-H, $J_{2,6} = 1.8$, $J_{2,3} = 10.5$ Hz), 7.16–7.54 m (5H, Ph), 7.31–7.35 d.d (1H, 5-H, $J_{3,5} = 2.7$, $J_{5,6} = 10.5$ Hz), 7.80–7.83 d.d (1H, 3-H, $J_{3,5} = 2.7$, $J_{2,3} = 10.5$ Hz), 8.04 br.s (1H, NH). Found, %: N 11.47, 11.53. $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_3$. Calculated, %: N 11.56.

4-[(4-Methylphenyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-one (IIIb). Yield 48%, mp 153–154°C. ^1H NMR spectrum, δ , ppm: 2.34 s (3H, $\text{CH}_3\text{C}_6\text{H}_4$), 6.55–6.59 d.d (1H, 6-H, $J_{2,6} = 1.8$, $J_{5,6} = 12$ Hz), 6.60–6.63 d.d (1H, 2-H, $J_{2,6} = 1.8$, $J_{2,3} = 9$ Hz), 7.17–7.40 d.d (4H, $\text{CH}_3\text{C}_6\text{H}_4$, $J = 8.4$ Hz), 7.31–7.35 d.d (1H, 5-H, $J_{3,5} = 2.7$, $J_{5,6} = 12$ Hz), 7.78–7.80 d.d (1H, 3-H, $J_{3,5} = 2.7$, $J_{2,3} = 9$ Hz), 8.07 br.s (1H, NH). Found, %: N 10.80, 10.98. $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3$. Calculated, %: N 10.93.

2-Methyl-4-(phenylaminocarbonyloxyimino)cyclohexa-2,5-dien-1-one (IIIc). Yield 36%, mp 141–142°C. ^1H NMR spectrum, δ , ppm: *E* isomer: 2.09 br.s (3H, CH_3), 6.57 d (1H, 6-H, $J_{5,6} = 12$ Hz), 7.12 q (1H,

3-H), 7.15–7.54 m (5H, Ph), 7.73–7.77 d.d (1H, 5-H, $J_{3,5} = 2.1$, $J_{5,6} = 12$ Hz), 8.15 br.s (1H, NH); *Z* isomer: 2.09 br.s (3H, CH_3), 6.61 d (1H, 6-H, $J_{5,6} = 12$ Hz), 7.15–7.54 m (5H, Ph), 7.22–7.26 d.d (1H, 5-H, $J_{3,5} = 2.4$, $J_{5,6} = 12$ Hz), 7.65 br.s (1H, 3-H), 8.15 br.s (1H, NH). Found, %: N 10.95, 11.10. $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3$. Calculated, %: N 10.93.

2-Methyl-4-[(4-methylphenyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-one (IIId). Yield 47%, mp 177–178°C. ^1H NMR spectrum, δ , ppm: *E* isomer: 2.07 d (3H, 2- CH_3 , $J = 1.5$ Hz), 2.34 s (3H, $\text{CH}_3\text{C}_6\text{H}_4$), 6.55 d (1H, 6-H, $J_{5,6} = 10.2$ Hz), 7.11 q (1H, 3-H), 7.17–7.40 d.d (4H, $\text{CH}_3\text{C}_6\text{H}_4$, $J = 8.4$ Hz), 7.72–7.75 d.d (1H, 5-H, $J_{3,5} = 1.5$, $J_{5,6} = 10.2$ Hz), 8.10 br.s (1H, NH); *Z* isomer: 2.08 d (3H, 2- CH_3 , $J = 1.5$ Hz), 2.34 s (3H, $\text{CH}_3\text{C}_6\text{H}_4$), 6.61 d (1H, 6-H, $J_{5,6} = 9.9$ Hz), 7.17–7.40 d.d (4H, $\text{CH}_3\text{C}_6\text{H}_4$, $J = 8.4$ Hz), 7.21–7.24 d.d (1H, 5-H, $J_{3,5} = 1.8$, $J_{5,6} = 9.9$ Hz), 7.64 br.s (1H, 3-H), 8.10 br.s (1H, NH). Found, %: N 10.35, 10.50. $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_3$. Calculated, %: N 10.36.

3-Methyl-4-(phenylaminocarbonyloxyimino)cyclohexa-2,5-dien-1-one (IIIe). Yield 64%, mp 168–169°C. ^1H NMR spectrum, δ , ppm: 2.34 d (3H, 3- CH_3 , $J = 1.5$ Hz), 6.46 q (1H, 2-H), 6.52–6.56 d.d (1H, 6-H, $J_{2,6} = 1.5$, $J_{5,6} = 12$ Hz), 7.16–7.52 m (5H, Ph), 7.82 d (1H, 5-H, $J_{5,6} = 12$ Hz), 8.02 br.s (1H, NH). Found, %: N 10.80, 10.98. $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3$. Calculated, %: N 10.93.

3-Methyl-4-[(4-methylphenyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-one (IIIff). Yield 55%, mp 200–201°C. ^1H NMR spectrum, δ , ppm: 2.33 br.s (3H, 3- CH_3), 2.35 s (3H, $\text{CH}_3\text{C}_6\text{H}_4$), 6.45 q (1H, 2-H), 6.51–6.55 d.d (1H, 6-H, $J_{2,6} = 1.5$, $J_{5,6} = 10.5$ Hz), 7.16–7.38 d.d (4H, $\text{CH}_3\text{C}_6\text{H}_4$, $J = 8.7$ Hz), 7.81 d (1H, 5-H, $J_{5,6} = 10.5$ Hz), 7.94 br.s (1H, NH). Found, %: N 10.29, 10.43. $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_3$. Calculated, %: N 10.36.

2,3-Dimethyl-4-(phenylaminocarbonyloxyimino)cyclohexa-2,5-dien-1-one (IIIg). Yield 61%, mp 191–192°C. ^1H NMR spectrum, δ , ppm: 2.07 s (3H, 2- CH_3), 2.30 s (3H, 3- CH_3), 6.54 d (1H, 6-H, $J_{5,6} = 10.2$ Hz), 7.16–7.53 m (5H, Ph), 7.79 d (1H, 5-H, $J_{5,6} = 10.2$ Hz), 8.10 br.s (1H, NH). $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_3$. Found, %: N 10.20, 10.32. Calculated, %: N 10.36.

2,3-Dimethyl-4-[(4-methylphenyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-one (IIIh). Yield 49%, mp 223–224°C. ^1H NMR spectrum, δ , ppm: 2.06 s (3H, 2- CH_3), 2.30 s (3H, 3- CH_3), 2.34 s (3H, $\text{CH}_3\text{C}_6\text{H}_4$), 6.54 d (1H, 6-H, $J_{5,6} = 10.2$ Hz), 7.19–7.39 d.d (4H, $\text{CH}_3\text{C}_6\text{H}_4$, $J = 8.4$ Hz), 7.80 d (1H, 5-H,

$J_{5,6} = 10.2$ Hz), 8.02 br.s (1H, NH). Found, %: N 9.72, 9.92. $C_{16}H_{16}N_2O_3$. Calculated, %: N 9.85.

4-[(3-Chlorophenyl)aminocarbonyloxyimino]-2,3-dimethylcyclohexa-2,5-dien-1-one (IIIi). Yield 39%, mp 211–212°C. 1H NMR spectrum, δ , ppm: 2.07 s (3H, 2-CH₃), 2.30 s (3H, 3-CH₃), 6.55 d (1H, 6-H, $J_{5,6} = 10.2$ Hz), 7.15–7.17 d.d (1H, 4'-H, $J_{4',2'} = 1.2$, $J_{4',5'} = 7.5$ Hz), 7.28–7.34 t (1H, 5'-H, $J = 7.8$ Hz), 7.38–7.41 d.d (1H, 6'-H, $J_{6',2'} = 1.5$, $J_{6',5'} = 8.1$ Hz), 7.60 q (1H, 2'-H), 7.78 d (1H, 5-H, $J_{5,6} = 10.2$ Hz), 8.12 br.s (1H, NH). Found, %: N 9.09, 9.25. $C_{15}H_{13}ClN_2O_3$. Calculated, %: N 9.19.

2,5-Dimethyl-4-(phenylaminocarbonyloxyimino)cyclohexa-2,5-dien-1-one (IIIj). Yield 52%, mp 148–150°C. 1H NMR spectrum, δ , ppm: 2.07 d (3H, 2-CH₃, $^4J = 1.5$ Hz), 2.30 d (3H, 5-CH₃, $^4J = 1.5$ Hz), 6.43 q (1H, 6-H, $^4J = 1.5$ Hz), 7.15–7.52 m (5H, Ph), 7.65 q (1H, 3-H, $^4J = 1.5$ Hz), 8.12 br.s (1H, NH). Found, %: N 10.22, 10.46. $C_{15}H_{14}N_2O_3$. Calculated, %: N 10.36.

2,5-Dimethyl-4-[(4-methylphenyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-one (IIIk). Yield 68%, mp 138–140°C. 1H NMR spectrum, δ , ppm: 2.06 d (3H, 2-CH₃, $^4J = 1.5$ Hz), 2.29 d (3H, 5-CH₃, $^4J = 1.2$ Hz), 2.34 s (3H, CH₃C₆H₄), 6.42 q (1H, 6-H, $^4J = 1.5$ Hz), 7.18–7.39 d.d (4H, CH₃C₆H₄, $J = 8.4$ Hz), 7.63 br.s (1H, 3-H), 8.06 br.s (1H, NH). Found, %: N 9.77, 9.89. $C_{16}H_{16}N_2O_3$. Calculated, %: N 9.85.

4-[(3-Chlorophenyl)aminocarbonyloxyimino]-2,5-dimethylcyclohexa-2,5-dien-1-one (IIIl). Yield 62%, mp 193–194°C. 1H NMR spectrum, δ , ppm: 2.07 d (3H, 2-CH₃, $^4J = 1.2$ Hz), 2.30 d (3H, 5-CH₃, $^4J = 1.2$ Hz), 6.43 q (1H, 3-H, $^4J = 1.5$ Hz), 7.13–7.16 d.d (1H, 4'-H, $J_{4',2'} = 1.2$, $J_{4',5'} = 7.5$ Hz), 7.28–7.33 t (1H, 5'-H, $J = 7.8$ Hz), 7.37–7.40 d.d (1H, 6'-H, $J_{6',2'} = 1.5$, $J_{6',5'} = 8.1$ Hz), 7.60 q (1H, 2'-H), 7.62 br.s (1H, 3-H), 8.17 br.s (1H, NH). Found, %: N 9.15, 9.28. $C_{15}H_{13}ClN_2O_3$. Calculated, %: N 9.19.

2-Isopropyl-5-methyl-4-(phenylaminocarbonyloxyimino)cyclohexa-2,5-dien-1-one (IIIIm). Yield 69%, mp 113–114°C. 1H NMR spectrum, δ , ppm: 1.15 d (6H, *i*-Pr, $J = 6.9$ Hz), 2.30 d (3H, 5-CH₃, $^4J = 1.2$ Hz), 3.06–3.15 m (1H, *i*-Pr), 6.43 q (1H, 6-H, $^4J = 1.2$ Hz), 7.16–7.53 m (5H, Ph), 7.54 br.s (1H, 3-H), 8.19 br.s (1H, NH). Found, %: N 9.18, 9.28. $C_{17}H_{18}N_2O_3$. Calculated, %: N 9.39.

2-Isopropyl-5-methyl-4-[(4-methylphenyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-one (IIIn). Yield 57%, mp 105–107°C. 1H NMR spectrum, δ , ppm: 1.15 d (6H, *i*-Pr, $J = 6.9$ Hz), 2.29 d (3H, 5-CH₃,

$^4J = 1.2$ Hz), 2.34 s (3H, CH₃C₆H₄), 3.06–3.14 m (1H, *i*-Pr), 6.42 q (1H, 6-H, $^4J = 1.2$ Hz), 7.18–7.39 d.d (4H, CH₃C₆H₄, $J = 8.1$ Hz), 7.54 br.s (1H, 3-H), 8.13 br.s (1H, NH). Found, %: N 8.88, 9.01. $C_{18}H_{20}N_2O_3$. Calculated, %: N 8.97.

5-Isopropyl-2-methyl-4-(phenylaminocarbonyloxyimino)cyclohexa-2,5-dien-1-one (IIIo). Yield 59%, mp 121–123°C. 1H NMR spectrum, δ , ppm: 1.28 d (6H, *i*-Pr, $J = 6.9$ Hz), 2.07 d (3H, 2-CH₃, $^4J = 1.2$ Hz), 3.27–3.36 m (1H, *i*-Pr), 6.44 s (1H, 6-H), 7.16–7.53 m (5H, Ph), 7.68 br.s (1H, 3-H), 8.11 br.s (1H, NH). Found, %: N 9.42, 9.50. $C_{17}H_{18}N_2O_3$. Calculated, %: N 9.39.

5-Isopropyl-2-methyl-4-[(4-methylphenyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-one (IIIp). Yield 43%, mp 109–110°C. 1H NMR spectrum, δ , ppm: 1.27 d (6H, *i*-Pr, $J = 6.9$ Hz), 2.06 br.s (3H, 2-CH₃), 2.34 s (3H, CH₃C₆H₄), 3.27–3.36 m (1H, *i*-Pr), 6.44 s (1H, 6-H), 7.18–7.38 d.d (4H, CH₃C₆H₄, $J = 8.1$ Hz), 7.67 br.s (1H, 3-H), 8.06 br.s (1H, NH). Found, %: N 8.91, 9.08. $C_{18}H_{20}N_2O_3$. Calculated, %: N 8.97.

3,5-Dimethyl-4-(phenylaminocarbonyloxyimino)cyclohexa-2,5-dien-1-one (IIIq). Yield 64%, mp 125–126°C. 1H NMR spectrum, δ , ppm: 2.33 br.s (3H, 5-CH₃), 2.57 br.s (3H, 3-CH₃), 6.31 br.s (1H, 6-H), 6.43 br.s (1H, 2-H), 7.14–7.54 m (5H, Ph), 8.11 br.s (1H, NH). Found, %: N 10.25, 10.38. $C_{15}H_{14}N_2O_3$. Calculated, %: N 10.36.

3,5-Dimethyl-4-[(4-methylphenyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-one (IIIr). Yield 35%, mp 199–200°C. 1H NMR spectrum, δ , ppm: 2.32 d (3H, 5-CH₃, $^4J = 1.2$ Hz), 2.34 s (3H, CH₃C₆H₄), 2.56 br.s (3H, 3-CH₃), 6.30 q (1H, 6-H, $^4J = 1.2$ Hz), 6.41 q (1H, 2-H), $^4J = 1.2$ Hz), 7.18–7.38 d.d (4H, CH₃C₆H₄, $J = 8.1$ Hz), 8.08 br.s (1H, NH). Found, %: N 9.79, 9.87. $C_{16}H_{16}N_2O_3$. Calculated, %: N 9.85.

4-[(3-Chlorophenyl)aminocarbonyloxyimino]-3,5-dimethylcyclohexa-2,5-dien-1-one (IIIs). Yield 56%, mp 147–148°C. 1H NMR spectrum, δ , ppm: 2.33 d (3H, 5-CH₃, $^4J = 1.2$ Hz), 2.56 d (3H, 3-CH₃, $^4J = 0.9$ Hz), 6.32 q (1H, 6-H, $^4J = 1.2$ Hz), 6.43 q (1H, 2-H), $^4J = 0.9$ Hz), 7.15–7.17 d.d (1H, 4'-H, $J_{4',2'} = 1.2$, $J_{4',5'} = 7.5$ Hz), 7.28–7.34 t (1H, 5'-H, $J = 7.8$ Hz), 7.38–7.41 d.d (1H, 6'-H, $J_{6',2'} = 1.5$, $J_{6',5'} = 8.1$ Hz), 7.57 q (1H, 2'-H), 8.14 br.s (1H, NH). Found, %: N 9.15, 9.29. $C_{15}H_{13}ClN_2O_3$. Calculated, %: N 9.19.

2,6-Dimethyl-4-(phenylaminocarbonyloxyimino)cyclohexa-2,5-dien-1-one (IIIt). Yield 59%, mp 156–

157°C. ^1H NMR spectrum, δ , ppm: 2.09 br.s (6H, 2-CH₃, 6-CH₃), 7.05 br.s (1H, 5-H), 7.14–7.54 m (5H, Ph), 7.62 br.s (1H, 3-H), 8.19 br.s (1H, NH). Found, %: N 10.25, 10.42. C₁₅H₁₄N₂O₃. Calculated, %: N 10.36.

2,6-Dimethyl-4-[(4-methylphenyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-one (IIIu). Yield 38%, mp 169–170°C. ^1H NMR spectrum, δ , ppm: 2.08 br.s (6H, 2-CH₃, 6-CH₃), 2.34 s (3H, CH₃C₆H₄), 7.04 q (1H, 5-H), 7.17–7.40 d.d (4H, CH₃C₆H₄, $J = 8.1$ Hz), 7.61 br.s (1H, 3-H), 8.15 br.s (1H, NH). Found, %: N 9.75, 9.88. C₁₆H₁₆N₂O₃. Calculated, %: N 9.85.

4-[(3-Chlorophenyl)aminocarbonyloxyimino]-2,6-dimethylcyclohexa-2,5-dien-1-one (IIIv). Yield 34%, mp 168–169°C. ^1H NMR spectrum, δ , ppm: 2.10 d (3H, 2-CH₃, $^4J = 1.5$ Hz), 2.09 d (3H, 6-CH₃, $^4J = 1.5$ Hz), 7.03 br.s (1H, 5-H), 7.13–7.15 d.d (1H, 4'-H, $J_{4',2'} = 1.2$, $J_{4',5'} = 7.5$ Hz), 7.27–7.32 t (1H, 5'-H, $J = 7.8$ Hz), 7.39–7.41 d.d (1H, 6'-H, $J_{6',2'} = 1.5$, $J_{6',5'} = 8.1$ Hz), 7.61 q (1H, 2'-H), 7.62 br.s (1H, 3-H), 8.25 br.s (1H, NH). Found, %: N 9.22, 9.38. C₁₅H₁₃ClN₂O₃. Calculated, %: N 9.19.

2,6-Diisopropyl-4-(phenylaminocarbonyloxyimino)cyclohexa-2,5-dien-1-one (IIIw). Yield 61%, mp 168–169°C. ^1H NMR spectrum, δ , ppm: 1.16 d (12H, *i*-Pr), 3.08–3.20 m (2H, 2-CH, 6-CH), 6.98 br.s (1H, 5-H), 7.14–7.56 m (5H, Ph), 7.51 br.s (1H, 3-H), 8.25 br.s (1H, NH). Found, %: N 8.48, 9.62. C₁₉H₂₂N₂O₃. Calculated, %: N 8.58.

2,6-Diisopropyl-4-[(4-methylphenyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-one (IIIx). Yield 45%, mp 136–138°C. ^1H NMR spectrum, δ , ppm: 1.16 d (12H, *i*-Pr), 2.35 s (3H, CH₃C₆H₄), 3.08–3.20 m (2H, 2-CH, 6-CH), 6.98 br.s (1H, 5-H), 7.19–7.42 d.d (4H, CH₃C₆H₄, $J = 8.1$ Hz), 7.52 br.s (1H, 3-H), 8.18 br.s (1H, NH). Found, %: N 8.12, 8.20. C₂₀H₂₄N₂O₃. Calculated, %: N 8.23.

2,6-Di-*tert*-butyl-4-(phenylaminocarbonyloxyimino)cyclohexa-2,5-dien-1-one (IIIy). Yield 64%, mp 136–138°C. ^1H NMR spectrum, δ , ppm: 1.31 s (18H, *t*-Bu), 7.00 d (1H, 5-H, $J_{3,5} = 2.4$ Hz), 7.14–7.56 m (5H, Ph), 7.53 br.s (1H, 3-H), 8.24 br.s (1H, NH). Found, %: N 7.82, 7.98. C₂₁H₂₆N₂O₃. Calculated, %: N 7.90.

2,6-Di-*tert*-butyl-4-[(4-methylphenyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-one (IIIz). Yield 62%, mp 136–138°C. ^1H NMR spectrum, δ , ppm: 1.31 s (18H, *t*-Bu), 2.34 s (3H, CH₃C₆H₄), 7.00 d (1H, 5-H, $J_{3,5} = 2.1$ Hz), 7.18–7.42 d.d (4H, CH₃C₆H₄,

$J = 7.8$ Hz), 7.52 br.s (1H, 3-H), 8.17 br.s (1H, NH). Found, %: N 7.62, 7.78. C₂₂H₂₈N₂O₃. Calculated, %: N 7.60.

4-(Butylaminocarbonyloxyimino)-2,5-dimethylcyclohexa-2,5-dien-1-one (IIIaa). Yield 8%, mp 136–138°C. ^1H NMR spectrum, δ , ppm: 0.94–0.99 t (3H, CH₂CH₃), 1.34–1.47 m (2H, CH₂CH₃), 1.57–1.64 d.d (2H, NHCH₂CH₂), 2.04 d (3H, 2-CH₃, $^4J = 0.9$ Hz), 2.34 d (3H, 5-CH₃, $^4J = 0.9$ Hz), 3.36–3.40 d.d (2H, NHCH₂), 6.31 br.s (1H, NH), 6.40 q (1H, 6-H, $^4J = 0.9$ Hz), 7.61 q (1H, 3-H, $^4J = 0.9$ Hz). Found, %: N 11.10, 11.25. C₁₃H₁₈N₂O₃. Calculated, %: N 11.19.

4-(*tert*-Butylaminocarbonyloxyimino)-2,6-dimethylcyclohexa-2,5-dien-1-one (IIIab). Yield 15%, mp 136–138°C. ^1H NMR spectrum, δ , ppm: 1.43 s (9H, *t*-Bu), 2.06 d (3H, 2-CH₃, $^4J = 1.2$ Hz), 2.07 d (3H, 6-CH₃, $^4J = 1.2$ Hz), 6.15 br.s (1H, NH), 6.99 q (1H, 5-H), 7.57 q (1H, 3-H). Found, %: N 11.20, 11.35. C₁₃H₁₈N₂O₃. Calculated, %: N 11.19.

Chlorination of 4-(arylamino carbonyloxyimino)-cyclohexa-2,5-dien-1-ones IIIa–IIIz (general procedure). Gaseous chlorine was passed at a flow rate of 15–20 ml/min through a solution of 5 mmol of compound IIIa–IIIz in 3 ml of acetic acid or chloroform, heated to 50–60°C, until complete saturation. The chlorination products were isolated by removal of the solvent to dryness (chloroform) or precipitation with water (acetic acid) and were recrystallized from benzene–hexane (1:1). The yields, melting points, and elemental compositions are given below only for products isolated as individual substances.

5,6-Dichloro-4-[(2,4-dichlorophenyl)aminocarbonyloxyimino]cyclohex-2-en-1-one (IVa). ^1H NMR spectrum, δ , ppm: *E* isomer (36%): 4.47 d (1H, 6-H, $J_{5,6} = 2.4$ Hz), 5.69 br.s (1H, 5-H), 6.51 d (1H, 2-H), $J_{2,3} = 10.5$ Hz), 7.19–7.23 d.d (1H, 3-H, $J_{3,5} = 1.8$, $J_{2,3} = 10.5$ Hz), 7.32–7.35 d.d (1H, 5'-H, $J_{5',3'} = 1.8$, $J_{5',6'} = 9$ Hz), 7.45 d (1H, 3'-H, $J_{5',3'} = 1.8$ Hz), 8.18 d (1H, 6'-H, $J_{5',6'} = 9$ Hz), 8.56 br.s (1H, NH); *Z* isomer (28%): 4.77 d (1H, 6-H, $J_{5,6} = 3$ Hz), 5.18 q (1H, 5-H), 6.46 d (1H, 2-H), $J_{2,3} = 11.7$ Hz), 7.32–7.35 d.d (1H, 5'-H, $J_{5',3'} = 1.8$, $J_{5',6'} = 9$ Hz), 7.45 d (1H, 3'-H, $J_{5',3'} = 1.8$ Hz), 7.68–7.71 d.d (1H, 3-H, $J_{3,5} = 1.8$ Hz), 8.18 d (1H, 6'-H, $J_{5',6'} = 9$ Hz), 8.39 br.s (1H, NH).

2,5,6-Trichloro-4-[(2,4-dichlorophenyl)aminocarbonyloxyimino]cyclohex-2-en-1-one (IVb). ^1H NMR spectrum, δ , ppm: *E* isomer (25%): 4.47 d (1H, 6-H, $J_{5,6} = 3.3$ Hz), 5.62 q (1H, 5-H), 7.29 d (1H, 3-H, $J_{3,5} = 1.5$ Hz), 7.32–7.35 d.d (1H, 5'-H, $J_{5',3'} = 1.8$, $J_{5',6'} = 9$ Hz), 7.45 d (1H, 3'-H, $J_{5',3'} = 1.8$ Hz), 8.21 d (1H,

6'-H, $J_{5',6'} = 9$ Hz), 8.56 br.s (1H, NH); *Z* isomer (11%): 4.77 d (1H, 6-H, $J_{5,6} = 2.4$ Hz), 5.16 q (1H, 5-H), 7.32–7.35 d.d (1H, 5'-H, $J_{5',3'} = 1.8$, $J_{5',6'} = 9$ Hz), 7.45 d (1H, 3'-H, $J_{5',3'} = 1.8$ Hz), 7.90 d (1H, 3-H, $J_{3,5} = 1.5$ Hz), 8.21 d (1H, 6'-H, $J_{5',6'} = 9$ Hz), 8.49 br.s (1H, NH).

5,6-Dichloro-4-[(2-chloro-4-methylphenyl)-aminocarbonyloxyimino]cyclohex-2-en-1-one (IVd).

^1H NMR spectrum, δ , ppm: *E* isomer (38%): 2.34 s (3H, $\text{CH}_3\text{C}_6\text{H}_3$), 4.47 d (1H, 6-H, $J_{5,6} = 2.7$ Hz), 5.70 q (1H, 5-H), 6.50 d (1H, 2-H), $J_{2,3} = 10.5$ Hz), 7.17–7.20 d.d (1H, 3-H, $J_{3,5} = 2.7$ Hz), 7.13–7.15 d.d (1H, 5'-H, $J_{5',3'} = 1.8$, $J_{5',6'} = 9$ Hz), 7.24 d (1H, 3'-H, $J_{5',3'} = 1.8$ Hz), 8.08 d (1H, 6'-H, $J_{5',6'} = 9$ Hz), 8.47 br.s (1H, NH); *Z* isomer (19%): 2.34 s (3H, $\text{CH}_3\text{C}_6\text{H}_3$), 4.76 d (1H, 6-H, $J_{5,6} = 3$ Hz), 5.17 q (1H, 5-H), 6.45 d (1H, 2-H), $J_{2,3} = 10.5$ Hz), 7.13–7.15 d.d (1H, 5'-H, $J_{5',3'} = 1.8$, $J_{5',6'} = 9$ Hz), 7.24 d (1H, 3'-H, $J_{5',3'} = 1.8$ Hz), 8.08 d (1H, 6'-H, $J_{5',6'} = 9$ Hz), 7.68–7.72 d.d (1H, 3-H, $J_{3,5} = 1.5$ Hz), 8.47 br.s (1H, NH).

2,5,6-Trichloro-4-[(2-chloro-4-methylphenyl)-aminocarbonyloxyimino]cyclohex-2-en-1-one (IVe).

^1H NMR spectrum, δ , ppm: *E* isomer (24%): 2.34 s (3H, $\text{CH}_3\text{C}_6\text{H}_3$), 4.47 d (1H, 6-H, $J_{5,6} = 2.7$ Hz), 5.64 q (1H, 5-H), 7.13–7.15 d.d (1H, 5'-H, $J_{5',3'} = 1.8$, $J_{5',6'} = 9$ Hz), 7.28 d (1H, 3-H, $J_{3,5} = 1.8$ Hz), 7.24 d (1H, 3'-H, $J_{5',3'} = 1.8$ Hz), 8.08 d (1H, 6'-H, $J_{5',6'} = 9$ Hz), 8.48 br.s (1H, NH); *Z* isomer (19%): 2.34 s (3H, $\text{CH}_3\text{C}_6\text{H}_3$), 4.76 d (1H, 6-H, $J_{5,6} = 3$ Hz), 5.13 q (1H, 5-H), 7.13–7.15 d.d (1H, 5'-H, $J_{5',3'} = 1.8$, $J_{5',6'} = 9$ Hz), 7.24 d (1H, 3'-H, $J_{5',3'} = 1.8$ Hz), 7.91 d (1H, 3-H, $J_{3,5} = 1.2$ Hz), 8.08 d (1H, 6'-H, $J_{5',6'} = 9$ Hz), 8.48 br.s (1H, NH).

5,6-Dichloro-4-[(4-chlorophenyl)aminocarbonyloxyimino]-2-methylcyclohex-2-en-1-one (Va).

^1H NMR spectrum, δ , ppm: *E* isomer (43%): 2.09 d (3H, 2- CH_3 , $^4J = 1.2$ Hz), 4.42 d (1H, 6-H, $J_{5,6} = 2.7$ Hz), 5.60 br.s (1H, 5-H), 6.99 q (1H, 3-H, $J_{5,3} = 1.5$ Hz), 7.35–7.47 d.d (4H, C_6H_4 , $J = 11.7$ Hz), 8.15 br.s (1H, NH); *Z* isomer (57%): 2.09 d (3H, 2- CH_3 , $^4J = 1.2$ Hz), 4.57 d (1H, 6-H, $J_{5,6} = 3.3$ Hz), 5.09 q (1H, 5-H, $J_{5,3} = 1.5$ Hz), 7.35–7.47 d.d (4H, C_6H_4 , $J = 11.7$ Hz), 7.50 br.s (1H, 3-H), 8.11 br.s (1H, NH).

5,6-Dichloro-4-[(2-chloro-4-methylphenyl)-aminocarbonyloxyimino]-2-methylcyclohex-2-en-1-one (Vc).

^1H NMR spectrum, δ , ppm: *E* isomer (79%): 2.12 br.s (3H, 2- CH_3), 2.33 s (3H, $\text{CH}_3\text{C}_6\text{H}_3$), 4.48 d (1H, 6-H, $J_{5,6} = 2.7$ Hz), 5.68 br.s (1H, 5-H), 6.96 q (1H, 3-H), 7.12–7.15 d.d (1H, 5'-H, $J_{5',3'} = 1.8$, $J_{5',6'} = 9$ Hz), 7.25 d (1H, 3'-H, $J_{5',3'} = 1.8$ Hz), 8.09 d (1H,

6'-H, $J_{5',6'} = 9$ Hz), 8.58 br.s (1H, NH); *Z* isomer (21%): 2.12 br.s (3H, 2- CH_3), 2.33 s (3H, $\text{CH}_3\text{C}_6\text{H}_3$), 4.59 br.s (1H, 6-H, $J_{5,6} = 3.3$ Hz), 5.07 q (1H, 5-H, $J_{5,3} = 1.5$ Hz), 7.12–7.15 d.d (1H, 5'-H, $J_{5',3'} = 1.8$, $J_{5',6'} = 9$ Hz), 7.25 d (1H, 3'-H, $J_{5',3'} = 1.8$ Hz), 7.48 q (1H, 3-H), 8.09 d (1H, 6'-H, $J_{5',6'} = 9$ Hz), 8.58 br.s (1H, NH).

5,6-Dichloro-4-[(2,4-dichlorophenyl)aminocarbonyloxyimino]-3-methylcyclohex-2-en-1-one (VIa).

Yield 91%, mp 156–157°C. ^1H NMR spectrum, δ , ppm: 2.33 br.s (3H, 3- CH_3), 4.45 q (1H, 6-H, $J_{5,6} = 3$, $J_{2,6} = 1.2$ Hz), 5.76 d (1H, 6-H, $J_{5,6} = 3$ Hz), 6.37 br.s (1H, 2-H), 7.32–7.35 d.d (1H, 5'-H, $J_{5',3'} = 2.1$, $J_{5',6'} = 9$ Hz), 7.45 d (1H, 3'-H, $J_{5',3'} = 2.1$ Hz), 8.26 d (1H, 6'-H, $J_{5',6'} = 9$ Hz), 8.88 br.s (1H, NH). Found, %: Cl 35.80, 35.92. $\text{C}_{14}\text{H}_{10}\text{Cl}_4\text{N}_2\text{O}_3$. Calculated, %: Cl 35.81.

5,6-Dichloro-4-[(2-chloro-4-methylphenyl)-aminocarbonyloxyimino]-3-methylcyclohex-2-en-1-one (VIc).

Yield 95%, mp 157–158°C. ^1H NMR spectrum, δ , ppm: 2.33 br.s (3H, 3- CH_3), 2.33 s (3H, $\text{CH}_3\text{C}_6\text{H}_3$), 4.44 q (1H, 6-H, $J_{2,6} = 0.9$ Hz), 5.76 d (1H, 6-H, $J_{5,6} = 2.7$ Hz), 6.36 br.s (1H, 2-H), 7.13–7.16 d.d (1H, 5'-H, $J_{5',3'} = 1.8$, $J_{5',6'} = 8.4$ Hz), 7.24 br.s (1H, 3'-H), 8.13 d (1H, 6'-H, $J_{5',6'} = 8.4$ Hz), 8.83 br.s (1H, NH). Found, %: Cl 28.34, 28.45. $\text{C}_{15}\text{H}_{13}\text{Cl}_3\text{N}_2\text{O}_3$. Calculated, %: Cl 28.31.

5,6-Dichloro-4-[(4-chlorophenyl)aminocarbonyloxyimino]-2,3-dimethylcyclohex-2-en-1-one (VIIa).

^1H NMR spectrum, δ , ppm: 2.09 br.s (3H, 2- CH_3), 2.29 br.s (3H, 3- CH_3), 4.46 d (1H, 6-H, $J_{5,6} = 2.7$ Hz), 5.72 d (1H, 6-H), 7.35–7.47 d.d (4H, C_6H_4 , $J = 9$ Hz), 9.00 br.s (1H, NH).

5,6-Dichloro-4-[(2,4-dichlorophenyl)aminocarbonyloxyimino]-2,3-dimethylcyclohex-2-en-1-one (VIIb).

^1H NMR spectrum, δ , ppm: 2.11 br.s (3H, 2- CH_3), 2.30 br.s (3H, 3- CH_3), 4.49 d (1H, 6-H, $J_{5,6} = 2.7$ Hz), 5.75 d (1H, 5-H), 7.31–7.34 d.d (1H, 5'-H, $J_{5',3'} = 2.4$, $J_{5',6'} = 12$ Hz), 7.45 d (1H, 3'-H, $J_{5',3'} = 2.4$ Hz), 8.27 d (1H, 6'-H, $J_{5',6'} = 12$ Hz), 8.96 br.s (1H, NH).

5,6-Dichloro-4-[(2-chloro-4-methylphenyl)-aminocarbonyloxyimino]-2,3-dimethylcyclohex-2-en-1-one (VIIId).

Yield 59%, mp 114–115°C. ^1H NMR spectrum, δ , ppm: 2.10 br.s (3H, 2- CH_3), 2.31 br.s (3H, 3- CH_3), 2.34 s (3H, $\text{CH}_3\text{C}_6\text{H}_3$), 4.49 d (1H, 6-H, $J_{5,6} = 2.7$ Hz), 5.77 d (1H, 5-H), 7.13–7.16 d.d (1H, 5'-H, $J_{5',3'} = 2.1$, $J_{5',6'} = 9$ Hz), 7.24 d (1H, 3'-H), 8.15 d (1H, 6'-H, $J_{5',6'} = 9$ Hz), 8.90 br.s (1H, NH). Found, %: Cl 27.26, 27.34. $\text{C}_{16}\text{H}_{15}\text{Cl}_3\text{N}_2\text{O}_3$. Calculated, %: Cl 27.29.

5,6-Dichloro-4-[(2,5-dichlorophenyl)aminocarbonyloxyimino]-2,3-dimethylcyclohex-2-en-1-one (VIIIf). ^1H NMR spectrum, δ , ppm: 2.11 s (3H, 2-CH₃), 2.31 s (3H, 3-CH₃), 4.50 d (1H, 6-H, $J_{5,6} = 3$ Hz), 5.76 d (1H, 5-H), 7.08–7.11 d.d (1H, 4'-H, $J_{4',6'} = 2.4$, $J_{4',3'} = 8.4$ Hz), 7.36 d (1H, 3'-H), 8.39 d (1H, 6'-H), 8.98 br.s (1H, NH).

5,6-Dichloro-2,3-dimethyl-4-[(2,4,5-trichlorophenyl)aminocarbonyloxyimino]cyclohex-2-en-1-one (VIIg). ^1H NMR spectrum, δ , ppm: 2.09 s (3H, 2-CH₃), 2.30 s (3H, 3-CH₃), 4.47 d (1H, 6-H, $J_{5,6} = 3$ Hz), 5.70 d (1H, 5-H), 7.54 s (1H, 3'-H), 8.51 s (1H, 6'-H), 9.04 br.s (1H, NH).

5,6-Dichloro-2,3-dimethyl-4-[(2,3,5-trichlorophenyl)aminocarbonyloxyimino]cyclohex-2-en-1-one (VIIh). ^1H NMR spectrum, δ , ppm: 2.10 s (3H, 2-CH₃), 2.30 s (3H, 3-CH₃), 4.49 d (1H, 6-H, $J_{5,6} = 2.4$ Hz), 5.74 d (1H, 5-H), 7.39 d (1H, 4'-H, $J_{4',6'} = 2.1$ Hz), 7.71 d (1H, 6'-H), 9.02 br.s (1H, NH).

5,6-Dichloro-4-[(4-chlorophenyl)aminocarbonyloxyimino]-3,6-dimethylcyclohex-2-en-1-one (VIIIa). Yield 87%, mp 188–189°C. ^1H NMR spectrum, δ , ppm: 1.87 s (3H, 6-CH₃), 2.30 d (3H, 3-CH₃, $^4J = 1.2$ Hz), 5.72 s (1H, 5-H), 6.35 q (1H, 2-H), $^4J = 1.2$ Hz), 7.35–7.46 d.d (4H, C₆H₄, $J = 8.7$ Hz), 7.97 br.s (1H, NH). Found, %: Cl 28.23, 28.31. C₁₅H₁₃Cl₃N₂O₃. Calculated, %: Cl 28.31.

5,6-Dichloro-4-[(2,4-dichlorophenyl)aminocarbonyloxyimino]-3,6-dimethylcyclohex-2-en-1-one (VIIIb). Yield 86%, mp 111–112°C. ^1H NMR spectrum, δ , ppm: 1.89 s (3H, 6-CH₃), 2.31 d (3H, 3-CH₃, $^4J = 1.2$ Hz), 5.75 s (1H, 5-H), 6.38 q (1H, 2-H), $^4J = 1.2$ Hz), 7.31–7.35 d.d (1H, 5'-H, $J_{5',3'} = 2.7$, $J_{5',6'} = 11.7$ Hz), 7.44 d (1H, 3'-H, $J_{5',3'} = 2.7$ Hz), 8.28 d (1H, 6'-H, $J_{5',6'} = 11.7$ Hz), 8.97 br.s (1H, NH). Found, %: Cl 34.55, 34.68. C₁₅H₁₂Cl₄N₂O₃. Calculated, %: Cl 34.58.

5,6-Dichloro-4-[(2-chloro-4-methylphenyl)aminocarbonyloxyimino]-3,6-dimethylcyclohex-2-en-1-one (VIIIc). ^1H NMR spectrum, δ , ppm: 1.89 s (3H, 6-CH₃), 2.31 d (3H, 3-CH₃, $^4J = 0.9$ Hz), 2.33 s (3H, CH₃C₆H₃), 5.77 s (1H, 5-H), 6.37 q (1H, 5-H), 7.13–7.16 d.d (1H, 5'-H, $J_{5',3'} = 2.1$, $J_{5',6'} = 9$ Hz), 7.23 br.s (1H, 3'-H), 8.15 d (1H, 6'-H, $J_{5',6'} = 9$ Hz), 8.92 br.s (1H, NH).

5,6-Dichloro-4-[(2,5-dichlorophenyl)aminocarbonyloxyimino]-3,6-dimethylcyclohex-2-en-1-one (VIIIf). ^1H NMR spectrum, δ , ppm: 1.89 s (3H, 6-CH₃), 2.30 br.s (3H, 3-CH₃), 5.75 s (1H, 5-H),

6.38 br.s (1H, 2-H), 7.08–7.11 d.d (1H, 4'-H, $J_{4',6'} = 2.4$, $J_{4',3'} = 8.4$ Hz), 7.34 d (1H, 3'-H, $J_{4',3'} = 8.4$ Hz), 8.39 d (1H, 6'-H, $J_{4',6'} = 2.4$ Hz), 9.02 br.s (1H, NH).

5,6-Dichloro-3,6-dimethyl-4-[(2,3,4-trichlorophenyl)aminocarbonyloxyimino]cyclohex-2-en-1-one (VIIIg). ^1H NMR spectrum, δ , ppm: 1.89 s (3H, 6-CH₃), 2.31 br.s (3H, 3-CH₃), 5.75 s (1H, 5-H), 6.38 br.s (1H, 2-H), 7.46 d (1H, 5'-H, $J_{5',6'} = 9$ Hz), 8.26 d (1H, 6'-H, $J_{5',6'} = 9$ Hz), 9.05 br.s (1H, NH).

5,6-Dichloro-3,6-dimethyl-4-[(2,4,5-trichlorophenyl)aminocarbonyloxyimino]cyclohex-2-en-1-one (VIIIh). ^1H NMR spectrum, δ , ppm: 1.89 s (3H, 6-CH₃), 2.31 br.s (3H, 3-CH₃), 5.75 s (1H, 5-H), 6.38 br.s (1H, 2-H), 7.54 s (1H, 3'-H), 8.51 s (1H, 6'-H), 8.98 br.s (1H, NH).

5,6-Dichloro-4-[(2,4-dichlorophenyl)aminocarbonyloxyimino]-6-isopropyl-3-methylcyclohex-2-en-1-one (IXa). ^1H NMR spectrum, δ , ppm: 1.22–1.24 d.d [6H, 6-CH(CH₃)₂, $J = 6.6$ Hz], 2.27 d (3H, 3-CH₃, $^4J = 1.5$ Hz), 2.67–2.74 m (1H, 6-CH), 5.72 s (1H, 5-H), 6.32 br.s (1H, 2-H), 7.31–7.34 d.d (1H, 5'-H, $J_{5',3'} = 2.1$, $J_{5',6'} = 8.7$ Hz), 7.44 d (1H, 3'-H, $J_{5',3'} = 2.1$ Hz), 8.28 d (1H, 6'-H, $J_{5',6'} = 8.7$ Hz), 9.06 br.s (1H, NH).

5,6-Dichloro-4-[(2,5-dichloro-4-methylphenyl)aminocarbonyloxyimino]-6-isopropyl-3-methylcyclohex-2-en-1-one (IXc). ^1H NMR spectrum, δ , ppm: 1.21–1.23 d.d [6H, 6-CH(CH₃)₂, $J = 8.4$ Hz], 2.09 s (3H, CH₃C₆H₂), 2.23 br.s (3H, 3-CH₃), 2.61–2.78 m (1H, 6-CH), 5.66 s (1H, 5-H), 6.31 br.s (1H, 2-H), 7.27 s (1H, 3'-H), 7.36 s (1H, 6'-H), 8.42 br.s (1H, NH).

5,6-Dichloro-4-[(2,4-dichlorophenyl)aminocarbonyloxyimino]-2-isopropyl-5-methylcyclohex-2-en-1-one (Xa). ^1H NMR spectrum, δ , ppm: 1.12–1.15 d.d [6H, 2-CH(CH₃)₂, $J = 6.9$ Hz], 2.13 br.s (3H, 5-CH₃), 3.03–3.12 m (1H, 2-CH), 4.47 s (1H, 6-H), 7.31–7.34 d.d (1H, 5'-H, $J_{5',3'} = 2.1$, $J_{5',6'} = 8.7$ Hz), 7.42 br.s (1H, 3-H), 7.44 d (1H, 3'-H, $J_{5',3'} = 2.1$ Hz), 8.28 d (1H, 6'-H, $J_{5',6'} = 8.7$ Hz), 9.03 br.s (1H, NH).

5,6-Dichloro-4-[(2,5-dichloro-4-methylphenyl)aminocarbonyloxyimino]-2-isopropyl-5-methylcyclohex-2-en-1-one (Xc). ^1H NMR spectrum, δ , ppm: 1.11–1.14 d.d [6H, 2-CH(CH₃)₂, $J = 9$ Hz], 2.09 s (3H, 5-CH₃), 2.09 s (3H, CH₃C₆H₂), 3.01–3.12 m (1H, 2-CH), 4.45 s (1H, 6-H), 7.27 s (1H, 3'-H), 7.35 br.s (1H, 3-H), 7.36 s (1H, 6'-H), 8.42 br.s (1H, NH).

5,6-Dichloro-4-[(4-chlorophenyl)aminocarbonyloxyimino]-3-isopropyl-6-methylcyclohex-2-en-1-one (XIa). Yield 97%, mp 158–160°C. ^1H NMR spectrum,

δ , ppm: 1.25–1.31 d.d [6H, 3-CH(CH₃)₂, J = 8.4 Hz], 1.87 s (3H, 6-CH₃), 3.18–3.27 m (1H, 3-CH), 5.78 s (1H, 5-H), 6.32 s (1H, 2-H), 7.36–7.47 d.d (4H, C₆H₄, J = 9 Hz), 7.89 br.s (1H, NH). Found, %: Cl 26.38, 26.45. C₁₇H₁₇Cl₃N₂O₃. Calculated, %: Cl 26.35.

5,6-Dichloro-4-[(2,4-dichlorophenyl)aminocarbonyloxyimino]-3-isopropyl-6-methylcyclohex-2-en-1-one (XIb). Yield 92%, mp 161–162°C. ¹H NMR spectrum, δ , ppm: 1.26–1.32 d.d [6H, 3-CH(CH₃)₂, J = 7.8 Hz], 1.89 s (3H, 6-CH₃), 3.19–3.31 m (1H, 3-CH), 5.81 s (1H, 5-H), 6.35 s (1H, 2-H), 7.32–7.35 d.d (1H, 5'-H, $J_{5',3'} = 2.4$, $J_{5',6'} = 9$ Hz), 7.45 d (1H, 3'-H, $J_{5',3'} = 2.4$ Hz), 8.28 d (1H, 6'-H, $J_{5',6'} = 9$ Hz), 8.91 br.s (1H, NH). Found, %: Cl 32.29, 32.41. C₁₇H₁₆Cl₄N₂O₃. Calculated, %: Cl 32.37.

5,6-Dichloro-4-[(2-chloro-4-methylphenyl)aminocarbonyloxyimino]-3-isopropyl-6-methylcyclohex-2-en-1-one (XIc). Yield 55%, mp 184–185°C. ¹H NMR spectrum, δ , ppm: 1.26–1.32 d.d [6H, 3-CH(CH₃)₂, J = 7.8 Hz], 1.88 s (3H, 6-CH₃), 2.34 s (3H, CH₃C₆H₃), 3.21–3.33 m (1H, 3-CH), 5.82 s (1H, 5-H), 6.34 s (1H, 2-H), 7.13–7.16 d.d (1H, 5'-H, $J_{5',3'} = 2.1$, $J_{5',6'} = 8.1$ Hz), 7.24 br.s (1H, 3'-H), 8.15 d (1H, 6'-H, $J_{5',6'} = 8.1$ Hz), 8.85 br.s (1H, NH). Found, %: Cl 25.35, 25.49. C₁₈H₁₉Cl₃N₂O₃. Calculated, %: Cl 25.46.

5,6-Dichloro-4-[(2,4-dichlorophenyl)aminocarbonyloxyimino]-3,5-dimethylcyclohex-2-en-1-one (XIId). ¹H NMR spectrum, δ , ppm: *E* isomer (64%): 2.13 s (3H, 5-CH₃), 2.55 br.s (3H, 3-CH₃), 4.39 s (1H, 6-H), 6.23 br.s (1H, 2-H), 7.34–7.37 d.d (1H, 5'-H, $J_{5',3'} = 2.4$, $J_{5',6'} = 7.8$ Hz), 7.44 d (1H, 3'-H, $J_{5',3'} = 2.4$ Hz), 8.26 d (1H, 6'-H, $J_{5',6'} = 7.8$ Hz), 8.97 br.s (1H, NH); *Z* isomer (36%): 2.14 s (3H, 5-CH₃), 2.52 s (3H, 3-CH₃), 4.28 s (1H, 6-H), 6.39 br.s (1H, 2-H), 7.34–7.37 d.d (1H, 5'-H, $J_{5',3'} = 2.4$, $J_{5',6'} = 7.8$ Hz), 7.44 d (1H, 3'-H, $J_{5',3'} = 2.4$ Hz), 8.26 d (1H, 6'-H, $J_{5',6'} = 7.8$ Hz), 8.97 br.s (1H, NH).

5,6-Dichloro-3,5-dimethyl-4-[(2-chloro-4-methylphenyl)aminocarbonyloxyimino]cyclohex-2-en-1-one (XIId). ¹H NMR spectrum, δ , ppm: 2.13 s (3H, 5-CH₃), 2.34 s (3H, CH₃C₆H₃), 2.55 br.s (3H, 3-CH₃), 4.39 s (1H, 6-H), 6.22 br.s (1H, 2-H), 7.13–7.16 d.d (1H, 5'-H, $J_{5',3'} = 2.1$, $J_{5',6'} = 8.1$ Hz), 7.24 br.s (1H, 3'-H), 8.13 d (1H, 6'-H, $J_{5',6'} = 8.1$ Hz), 8.96 br.s (1H, NH).

5,6-Dichloro-4-[(2,5-dichlorophenyl)aminocarbonyloxyimino]-3,5-dimethylcyclohex-2-en-1-one (XIId). ¹H NMR spectrum, δ , ppm: 2.12 s (3H,

5-CH₃), 2.55 br.s (3H, 3-CH₃), 4.39 s (1H, 6-H), 6.24 br.s (1H, 2-H), 7.08–7.11 d.d (1H, 4'-H, $J_{4',6'} = 2.4$, $J_{4',3'} = 9$ Hz), 7.35 d (1H, 3'-H, $J_{4',3'} = 9$ Hz), 8.38 d (1H, 6'-H, $J_{4',6'} = 2.4$ Hz), 9.04 br.s (1H, NH).

5,6-Dichloro-3,5-dimethyl-4-[(2,3,4-trichlorophenyl)aminocarbonyloxyimino]cyclohex-2-en-1-one (XIId). ¹H NMR spectrum, δ , ppm: 2.13 s (3H, 5-CH₃), 2.55 br.s (3H, 3-CH₃), 4.39 s (1H, 6-H), 6.24 br.s (1H, 2-H), 7.46 d (1H, 5'-H, $J_{5',6'} = 9$ Hz), 8.24 d (1H, 6'-H, $J_{5',6'} = 9$ Hz), 9.00 br.s (1H, NH).

5,6-Dichloro-3,5-dimethyl-4-[(2,4,5-trichlorophenyl)aminocarbonyloxyimino]cyclohex-2-en-1-one (XIId). ¹H NMR spectrum, δ , ppm: 2.13 s (3H, 5-CH₃), 2.55 br.s (3H, 3-CH₃), 4.39 s (1H, 6-H), 6.24 br.s (1H, 2-H), 7.54 s (1H, 3'-H), 8.50 s (1H, 6'-H), 8.96 br.s (1H, NH).

4-[(2-Chloro-4-methylphenyl)aminocarbonyloxyimino]-2,5-dimethylcyclohexa-2,5-dien-1-one (XIIa). ¹H NMR spectrum, δ , ppm: 2.09 d (3H, 2-CH₃, 4J = 1.5 Hz), 2.33 br.s (3H, 5-CH₃), 2.33 s (3H, CH₃C₆H₃), 6.44 q (3H, 5-CH₃, 4J = 1.5 Hz), 7.13–7.16 d.d (1H, 5'-H, $J_{5',3'} = 2.1$, $J_{5',6'} = 9$ Hz), 7.23 br.s (1H, 3'-H), 7.66 d (1H, 3-H), 8.15 d (1H, 6'-H, $J_{5',6'} = 9$ Hz), 9.05 br.s (1H, NH).

4-[(2-Chloro-4-methylphenyl)-3,5-dimethylaminocarbonyloxyimino]cyclohexa-2,5-dien-1-one (XV). ¹NNMR spectrum, δ , ppm: 2.37 br.s (3H, 5-CH₃), 2.34 s (3H, CH₃C₆H₃), 2.55 br.s (3H, 3-CH₃), 6.47 br.s (1H, 6-H), 6.57 br.s (1H, 2-H), 7.13–7.16 d.d (1H, 5'-H, $J_{5',3'} = 2.1$, $J_{5',6'} = 8.1$ Hz), 7.24 br.s (1H, 3'-H), 8.13 d (1H, 6'-H, $J_{5',6'} = 8.1$ Hz), 8.87 br.s (1H, NH).

4-[(4-Chlorophenyl)aminocarbonyloxyimino]-2,6-dimethylcyclohexa-2,5-dien-1-one (XVIa). ¹H NMR spectrum, δ , ppm: 2.09 d (3H, 2-CH₃, 4J = 1.5 Hz), 2.10 d (3H, 6-CH₃, 4J = 1.5 Hz), 7.03 q (1H, 5-H, 4J = 1.5 Hz), 7.33–7.49 d.d (4H, C₆H₄, J = 9 Hz), 7.62 q (1H, 3-H), 8.20 br.s (1H, NH).

4-[(2,4-Dichlorophenyl)aminocarbonyloxyimino]-2,6-dimethylcyclohexa-2,5-dien-1-one (XVIb). ¹H NMR spectrum, δ , ppm: 2.10 d (3H, 2-CH₃, 4J = 1.5 Hz), 2.11 d (3H, 6-CH₃, 4J = 1.5 Hz), 7.03 q (1H, 5-H, 4J = 1.5 Hz), 7.30–7.33 d.d (1H, 5'-H, $J_{5',3'} = 2.4$, $J_{5',6'} = 9$ Hz), 7.43 d (1H, 3'-H, $J_{5',3'} = 2.4$ Hz), 7.62 q (1H, 3-H), 8.24 d (1H, 6'-H, $J_{5',6'} = 9$ Hz), 8.88 br.s (1H, NH).

4-[(2-Chloro-4-methylphenyl)aminocarbonyloxyimino]-2,6-dimethylcyclohexa-2,5-dien-1-one (XVIId). Yield 91%, mp 146–149°C. ¹H NMR spec-

trum, δ , ppm: 2.09 d (3H, 2-CH₃, $J = 1.5$ Hz), 2.11 d (3H, 6-CH₃, $^4J = 1.5$ Hz), 2.33 s (3H, CH₃C₆H₃), 7.05 q (1H, 5-H, $J_{3,5} = 1.2$ Hz), 7.12–7.15 d.d (1H, 5'-H, $J_{5',3'} = 1.5$, $J_{5',6'} = 9$ Hz), 7.23 br.s (1H, 3'-H), 7.63 q (1H, 3-H), 8.11 d (1H, 6'-H, $J_{5',6'} = 9$ Hz), 8.78 br.s (1H, NH). Found, %: Cl 11.06, 11.22. C₁₆H₁₅ClN₂O₃. Calculated, %: Cl 11.12.

4-[(2,5-Dichlorophenyl)aminocarbonyloxyimino]-2,6-dimethylcyclohexa-2,5-dien-1-one (XVIe). ¹H NMR spectrum, δ , ppm: 2.09 d (3H, 2-CH₃, $^4J = 1.2$ Hz), 2.10 d (3H, 6-CH₃, $^4J = 1.5$ Hz), 7.02 q (1H, 5-H, $J_{3,5} = 0.9$ Hz), 7.06–7.09 d.d (1H, 4'-H, $J_{4',6'} = 2.1$, $J_{4',3'} = 9$ Hz), 7.34 d (1H, 3'-H, $J_{4',3'} = 9$ Hz), 7.60 q (1H, 3-H), 8.36 d (1H, 6'-H, $J_{4',6'} = 2.1$ Hz), 8.28 br.s (1H, NH).

2,6-Dimethyl-4-[(2,3,5-trichlorophenyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-one (XVI f). ¹H NMR spectrum, δ , ppm: 2.10 d (3H, 2-CH₃, $^4J = 1.2$ Hz), 2.11 d (3H, 6-CH₃, $^4J = 1.5$ Hz), 7.02 q (1H, 5-H, $J_{3,5} = 0.9$ Hz), 7.40 d (1H, 4'-H, $J_{4',6'} = 2.4$ Hz), 7.60 q (1H, 3-H), 7.74 d (1H, 6'-H, $J_{4',6'} = 2.4$ Hz), 8.96 br.s (1H, NH).

2,6-Dimethyl-4-[(2,4,5-trichlorophenyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-one (XVI g). ¹H NMR spectrum, δ , ppm: 2.10 d (3H, 2-CH₃, $^4J = 1.2$ Hz), 2.11 d (3H, 6-CH₃, $^4J = 1.5$ Hz), 7.02 q (1H, 5-H, $J_{3,5} = 0.9$ Hz), 7.52 s (1H, 3'-H), 7.60 q (1H, 3-H), 8.48 s (1H, 6'-H), 8.94 br.s (1H, NH).

4-[(4-Chlorophenyl)aminocarbonyloxyimino]-2,6-diisopropylcyclohexa-2,5-dien-1-one (XVII). Yield 88%, mp 101–102°C. ¹H NMR spectrum, δ , ppm: 1.16–1.18 d.d (12H, CH₃, $J = 1.8$, 6.9 Hz), 3.06–3.21 m (2H, 2-CH, 6-CH), 6.97 br.s (1H, 5-H), 7.35–7.50 d.d (4H, C₆H₄, $J = 8.1$ Hz), 7.52 br.s (1H, 3-H), 8.87 br.s (1H, NH). Found, %: Cl 9.77, 9.90. C₁₉H₂₁ClN₂O₃. Calculated, %: Cl 9.83.

2,6-Di-tert-butyl-4-[(2,4-dichlorophenyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-one (XVIIIa). Yield 85%, mp 134–136°C. ¹H NMR spectrum, δ , ppm: 1.32 d (18H, *t*-Bu, $J = 1.8$ Hz), 6.95 d (1H, 5-H, $J_{3,5} = 2.4$ Hz), 7.30–7.34 d.d (1H, 5'-H, $J_{5',3'} = 2.1$, $J_{5',6'} = 9$ Hz), 7.44 d (1H, 3'-H, $J_{5',3'} = 2.1$ Hz), 7.52 d (1H, 3-H, $J_{3,5} = 2.4$ Hz), 8.23 d (1H, 6'-H, $J_{5',6'} = 9$ Hz), 8.84 br.s (1H, NH). Found, %: Cl 16.71, 16.87. C₂₁H₂₄Cl₂N₂O₃. Calculated, %: Cl 16.75.

2,6-Di-tert-butyl-4-[(2-chloro-4-methylphenyl)aminocarbonyloxyimino]cyclohexa-2,5-dien-1-one (XVIIIc). Yield 82%, mp 161–162°C. ¹H NMR spectrum, δ , ppm: 1.32 s (18H, *t*-Bu), 2.33 s (3H,

CH₃C₆H₃), 6.97 d (1H, 5-H, $J_{3,5} = 1.8$ Hz), 7.12–7.15 d.d (1H, 5'-H, $J_{5',3'} = 1.5$, $J_{5',6'} = 8.4$ Hz), 7.24 br.s (1H, 3'-H), 7.53 br.s (1H, 3-H), 8.10 d (1H, 6'-H, $J_{5',6'} = 8.4$ Hz), 8.73 br.s (1H, NH). Found, %: Cl 8.73, 8.89. C₂₂H₂₇ClN₂O₃. Calculated, %: Cl 8.80.

Bromination of 4-(arylamino carbonyloxyimino)-cyclohexa-2,5-dien-1-ones Ia–Iz (general procedure). A solution of 5 mmol of compound IIIa–IIIz in 3 ml of acetic acid or chloroform was heated to the boiling point, a solution of 25 mmol of bromine in 2 ml of the same solvent, heated to 50–60°C, was added dropwise under vigorous stirring (the molar ratio III–Br₂ was 1:5), and the mixture was vigorously stirred on heating under reflux over a period of 5–10 min. The mixture was cooled, and the precipitate was filtered off and recrystallized from benzene–hexane (1:1). The yields, melting points, and elemental compositions are given only for products isolated as individual substances.

2,5,6-Tribromo-4-[(4-bromophenyl)aminocarbonyloxyimino]cyclohex-2-en-1-one (IVc). ¹H NMR spectrum, δ , ppm: *E* isomer (30%): 4.84 d (1H, 6-H, $J_{5,6} = 2.7$ Hz), 5.75 q (1H, 5-H, $J_{3,5} = 1.2$ Hz), 7.63 d (1H, 3-H), 7.42–7.51 d.d (4H, C₆H₄, $J = 8.7$ Hz), 8.45 br.s (1H, NH); *Z* isomer (70%): 4.98 d (1H, 6-H, $J_{5,6} = 3$ Hz), 5.31 q (1H, 5-H), 7.42–7.51 d.d (4H, C₆H₄, $J = 8.7$ Hz), 8.45 br.s (1H, NH), 8.15 d (1H, 3-H, $J_{3,5} = 1.5$ Hz).

2,5,6-Tribromo-4-[(2-bromo-4-methylphenyl)aminocarbonyloxyimino]cyclohex-2-en-1-one (IVf). ¹H NMR spectrum, δ , ppm: *E* isomer (60%): 2.34 s (3H, CH₃C₆H₃), 4.86 d (1H, 6-H, $J_{5,6} = 2.4$ Hz), 5.78 q (1H, 5-H), 7.17–7.19 d.d (1H, 5'-H, $J_{5',3'} = 1.8$ Hz), 7.41 d (1H, 3'-H, $J_{5',3'} = 1.8$ Hz), 7.61 d (1H, 3-H, $J_{3,5} = 1.8$ Hz), 8.06 d (1H, 6'-H, $J_{5',6'} = 9$ Hz), 8.55 br.s (1H, NH); *Z* isomer (40%): 2.34 s (3H, CH₃C₆H₃), 4.98 d (1H, 6-H, $J_{5,6} = 2.7$ Hz), 5.34 q (1H, 5-H), 7.17–7.19 d.d (1H, 5'-H, $J_{5',3'} = 1.8$ Hz), 7.41 d (1H, 3'-H, $J_{5',3'} = 1.8$ Hz), 8.06 d (1H, 6'-H, $J_{5',6'} = 8.1$ Hz), 8.16 d (1H, 3-H, $J_{3,5} = 0.9$ Hz), 8.36 br.s (1H, NH).

5,6-Dibromo-4-[(4-bromophenyl)aminocarbonyloxyimino]-2-methylcyclohex-2-en-1-one (Vb). ¹H NMR spectrum, δ , ppm: *E* isomer (43%): 2.12 d (3H, 2-CH₃, $^4J = 1.2$ Hz), 4.66 d (1H, 6-H, $J_{5,6} = 2.7$ Hz), 5.72 q (1H, 5-H, $J_{5,3} = 1.5$ Hz), 6.95 q (1H, 3-H), 7.43–7.50 d.d (4H, C₆H₄, $J = 8.7$ Hz), 8.00 br.s (1H, NH); *Z* isomer (57%): 2.12 d (3H, 2-CH₃, $^4J = 1.2$ Hz), 4.80 d (1H, 6-H, $J_{5,6} = 3.3$ Hz), 5.26 q (1H, 5-H, $J_{5,3} = 1.5$ Hz), 7.48 br.s (1H, 3-H), 7.43–7.50 d.d (4H, C₆H₄, $J = 8.7$ Hz), 8.03 br.s (1H, NH).

5,6-Dibromo-4-[(2-bromo-4-methylphenyl)-aminocarbonyloxyimino]-2-methylcyclohex-2-en-1-one (Vd). ¹H NMR spectrum, δ , ppm: *E* isomer (82%): 2.13 d (3H, 2-CH₃, ⁴*J* = 1.2 Hz), 2.33 s (3H, CH₃C₆H₃), 4.68 d (1H, 6-H, *J*_{5,6} = 2.7 Hz), 5.75 br.s (1H, 5-H), 6.95 q (1H, 3-H, *J*_{5,3} = 1.5 Hz), 7.16–7.19 d.d (1H, 5'-H, *J*_{5',3'} = 1.8 Hz), 7.40 br.s (1H, 3'-H), 8.08 d (1H, 6'-H, *J*_{5',6'} = 8.7 Hz), 8.63 br.s (1H, NH); *Z* isomer (18%): 2.13 d (3H, 2-CH₃, ⁴*J* = 1.2 Hz), 2.33 s (3H, CH₃C₆H₃), 4.81 d (1H, 6-H, *J*_{5,6} = 2.7 Hz), 5.28 q (1H, 5-H), 7.50 q (1H, 3-H, *J*_{5,3} = 1.5 Hz), 7.16–7.19 d.d (1H, 5'-H, *J*_{5',3'} = 1.8 Hz), 7.40 br.s (1H, 3'-H), 8.08 d (1H, 6'-H, *J*_{5',6'} = 8.1 Hz), 8.54 br.s (1H, NH).

5,6-Dibromo-4-[(4-bromophenyl)aminocarbonyloxyimino]-3-methylcyclohex-2-en-1-one (VIb). Yield 93%, mp 163–165°C. ¹H NMR spectrum, δ , ppm: 2.33 br.s (3H, 3-CH₃), 4.61 q (1H, 6-H, *J*_{2,6} = 1.2 Hz), 5.80 d (1H, 5-H, *J*_{5,6} = 2.4 Hz), 6.31 br.s (1H, 2-H), 7.41–7.50 d.d (4H, C₆H₄, *J* = 9 Hz), 8.00 br.s (1H, NH). Found, %: Br 48.38, 48.47. C₁₄H₁₁Br₃N₂O₃. Calculated, %: Br 48.43.

5,6-Dibromo-4-[(2-bromo-4-methylphenyl)-aminocarbonyloxyimino]-3-methylcyclohex-2-en-1-one (VId). Yield 98%, mp 142–143°C. ¹H NMR spectrum, δ , ppm: 2.34 s (3H, CH₃C₆H₃), 2.36 br.s (3H, 3-CH₃), 4.64 q (1H, 6-H, *J*_{2,6} = 1.5 Hz), 5.86 d (1H, 5-H, *J*_{5,6} = 2.7 Hz), 6.34 br.s (1H, 2-H), 7.18–7.21 d.d (1H, 5'-H, *J*_{5',3'} = 1.8 Hz), 7.41 br.s (1H, 3'-H), 8.15 d (1H, 6'-H, *J*_{5',6'} = 8.7 Hz), 8.92 br.s (1H, NH). Found, %: Br 47.12, 47.16. C₁₅H₁₃Br₃N₂O₃. Calculated, %: Br 47.10.

5,6-Dibromo-4-[(4-bromophenyl)aminocarbonyloxyimino]-2,3-dimethylcyclohex-2-en-1-one (VIIc). Yield 92%, mp 110–111°C. ¹H NMR spectrum, δ , ppm: 2.11 s (3H, 2-CH₃), 2.29 s (3H, 3-CH₃), 4.67 d (1H, 6-H, *J*_{5,6} = 2.7 Hz), 5.82 d (1H, 5-H), 7.41–7.50 d.d (4H, C₆H₄, *J* = 8.7 Hz), 7.95 br.s (1H, NH). Found, %: Br 47.01, 47.13. C₁₅H₁₃Br₃N₂O₃. Calculated, %: Br 47.10.

5,6-Dibromo-4-[(2-bromo-4-methylphenyl)-aminocarbonyloxyimino]-2,3-dimethylcyclohex-2-en-1-one (VIIe). Yield 97%, mp 91–94°C. ¹H NMR spectrum, δ , ppm: 2.12 s (3H, 2-CH₃), 2.33 s (3H, 3-CH₃), 2.33 s (3H, CH₃C₆H₃), 4.69 d (1H, 6-H, *J*_{5,6} = 2.4 Hz), 5.86 d (1H, 5-H), 7.17–7.20 d.d (1H, 5'-H, *J*_{5',3'} = 1.8 Hz), 7.40 br.s (1H, 3'-H), 8.15 d (1H, 6'-H, *J*_{5',6'} = 9 Hz), 8.96 br.s (1H, NH). Found, %: Br 45.80, 45.92. C₁₆H₁₅Br₃N₂O₃. Calculated, %: Br 45.83.

5,6-Dibromo-4-[(2-bromo-5-chlorophenyl)-aminocarbonyloxyimino]-2,3-dimethylcyclohex-2-

en-1-one (VIIi). Yield 91%, mp 157–158°C. ¹H NMR spectrum, δ , ppm: 2.11 s (3H, 2-CH₃), 2.29 s (3H, 3-CH₃), 4.67 d (1H, 6-H, *J*_{5,6} = 2.4 Hz), 5.79 d (1H, 5-H), 7.30–7.32 d.d (1H, 4'-H, *J*_{4',6'} = 2.7, *J*_{4',3'} = 9 Hz), 7.60 d (1H, 3'-H), 7.71 d (1H, 6'-H), 8.01 br.s (1H, NH). Found, %: Cl + Br 50.58, 50.67. C₁₅H₁₂Br₃ClN₂O₃. Calculated, %: Cl + Br 50.63.

5,6-Dibromo-4-[(4-bromophenyl)aminocarbonyloxyimino]-3,6-dimethylcyclohex-2-en-1-one (VIIIc). Yield 71%, mp 182–183°C. ¹H NMR spectrum, δ , ppm: 2.06 s (3H, 6-CH₃), 2.31 br.s (3H, 3-CH₃), 5.94 s (1H, 5-H), 6.33 br.s (1H, 2-H), 7.42–7.51 d.d (4H, C₆H₄, *J* = 9 Hz), 7.99 br.s (1H, NH). Found, %: Br 47.04, 47.16. C₁₅H₁₃Br₃N₂O₃. Calculated, %: Br 47.10.

5,6-Dibromo-4-[(2-bromo-4-methylphenyl)-aminocarbonyloxyimino]-3,6-dimethylcyclohex-2-en-1-one (VIIIe). Yield 77%, mp 123–124°C. ¹H NMR spectrum, δ , ppm: 2.08 s (3H, 6-CH₃), 2.34 br.s (3H, 3-CH₃), 2.34 s (3H, CH₃C₆H₃), 5.98 s (1H, 5-H), 6.35 br.s (1H, 2-H), 7.17–7.20 d.d (1H, 5'-H, *J*_{5',3'} = 1.8 Hz), 7.41 br.s (1H, 3'-H), 8.16 d (1H, 6'-H, *J*_{5',6'} = 9 Hz), 8.98 br.s (1H, NH). Found, %: Br 45.77, 45.89. C₁₆H₁₅Br₃N₂O₃. Calculated, %: Br 45.83.

5,6-Dibromo-4-[(2-bromo-5-chlorophenyl)-aminocarbonyloxyimino]-3,6-dimethylcyclohex-2-en-1-one (VIIIi). Yield 93%, mp 158–159°C. ¹H NMR spectrum, δ , ppm: 2.06 s (3H, 6-CH₃), 2.31 d (1H, 3-CH₃, ⁴*J* = 1.2 Hz), 5.92 s (1H, 5-H), 6.34 q (1H, 2-H, ⁴*J* = 1.2 Hz), 7.29–7.33 d.d (1H, 4'-H, *J*_{4',6'} = 2.4, *J*_{4',3'} = 8.7 Hz), 7.60 d (1H, 3'-H), 7.71 d (1H, 6'-H), 8.05 br.s (1H, NH). Found, %: Cl + Br 50.54, 50.70. C₁₅H₁₂Br₃ClN₂O₃. Calculated, %: Cl + Br 50.63.

5,6-Dibromo-4-[(4-bromophenyl)aminocarbonyloxyimino]-6-isopropyl-3-methylcyclohex-2-en-1-one (IXb). ¹H NMR spectrum, δ , ppm: 1.09–1.28 d.d [6H, 6-CH(CH₃)₂, *J* = 6.6 Hz], 2.27 d (3H, 3-CH₃, ⁴*J* = 1.2 Hz), 2.30–2.40 m (1H, 6-CH), 5.83 s (1H, 5-H), 6.28 q (1H, 2-H, ⁴*J* = 1.2 Hz), 7.38–7.51 d.d (4H, C₆H₄, *J* = 8.4 Hz), 8.02 br.s (1H, NH).

5,6-Dibromo-4-[(4-bromophenyl)aminocarbonyloxyimino]-2-isopropyl-5-methylcyclohex-2-en-1-one (Xb). ¹H NMR spectrum, δ , ppm: 1.15–1.22 d.d [6H, 2-CH(CH₃)₂, *J* = 6.9 Hz], 2.33 s (3H, 5-CH₃), 3.05–3.13 m (1H, 2-CH), 4.79 s (1H, 6-H), 7.43 br.s (1H, 2-H), 7.38–7.51 d.d (4H, C₆H₄, *J* = 8.4 Hz), 8.02 br.s (1H, NH).

5,6-Dibromo-4-[(2-bromo-4-methylphenyl)-aminocarbonyloxyimino]-2-isopropyl-5-methylcyclohex-2-en-1-one (Xd). ¹H NMR spectrum, δ ,

ppm: 1.16–1.23 d.d [6H, 2-CH(CH₃)₂, *J* = 8.7 Hz], 2.33 s (3H, CH₃C₆H₃), 2.36 s (3H, 5-CH₃), 3.05–3.16 m (1H, 2-CH), 4.79 s (1H, 6-H), 7.17–7.20 d.d (1H, 5'-H, *J*_{5',3'} = 1.8, *J*_{5',6'} = 8.7 Hz), 7.41 br.s (1H, 3'-H), 7.56 br.s (1H, 3-H), 8.16 d (1H, 6'-H, *J*_{5',6'} = 8.7 Hz), 8.96 br.s (1H, NH).

5,6-Dibromo-4-[(4-bromophenyl)aminocarbonyloxyimino]-3-isopropyl-6-methylcyclohex-2-en-1-one (XIc). Yield 82%, mp 91–92°C. ¹H NMR spectrum, δ, ppm: 1.24–1.31 d.d [6H, 3-CH(CH₃)₂, *J* = 7.8 Hz], 2.05 s (3H, 6-CH₃), 3.16–3.29 m (1H, 3-CH), 5.98 s (1H, 5-H), 6.30 s (1H, 2-H), 7.42–7.51 d.d (4H, C₆H₄, *J* = 8.7 Hz), 7.93 br.s (1H, NH). Found, %: Br 44.57, 44.70. C₁₇H₁₇Br₃N₂O₃. Calculated, %: Br 44.64.

5,6-Dibromo-3-isopropyl-6-methyl-4-[(4-methylphenyl)aminocarbonyloxyimino]cyclohex-2-en-1-one (XIe). ¹H NMR spectrum, δ, ppm: 1.25–1.31 d.d [6H, 3-CH(CH₃)₂, *J* = 6.9 Hz], 2.06 s (3H, 6-CH₃), 2.35 s (3H, CH₃C₆H₄), 3.20–3.30 m (1H, 3-CH), 6.03 s (1H, 5-H), 6.29 s (1H, 2-H), 7.19–7.38 d.d (4H, CH₃C₆H₄, *J* = 7.8 Hz), 8.90 br.s (1H, NH).

5,6-Dibromo-4-[(2-bromo-4-methylphenyl)aminocarbonyloxyimino]-3-isopropyl-6-methylcyclohex-2-en-1-one (XI f). ¹H NMR spectrum, δ, ppm: 1.26–1.31 d.d [6H, 3-CH(CH₃)₂, *J* = 6.9 Hz], 2.07 s (3H, 6-CH₃), 2.34 s (3H, CH₃C₆H₃), 3.24–3.36 m (1H, 3-CH), 6.00 s (1H, 5-H), 6.31 s (1H, 2-H), 7.17–7.20 d.d (1H, 5'-H, *J*_{5',3'} = 1.8, *J*_{5',6'} = 8.1 Hz), 7.40 br.s (1H, 3'-H), 8.16 d (1H, 6'-H, *J*_{5',6'} = 8.1 Hz), 8.90 br.s (1H, NH).

5,6-Dibromo-4-[(4-bromophenyl)aminocarbonyloxyimino]-3,5-dimethylcyclohex-2-en-1-one (XIIfb). ¹H NMR spectrum, δ, ppm: *E* isomer (66%): 2.31 s (3H, 5-CH₃), 2.52 br.s (3H, 3-CH₃), 4.72 d (1H, 6-H, *J*_{2,6} = 1.2 Hz), 6.17 br.s (1H, 2-H), 7.39–7.49 d.d (4H, C₆H₄, *J* = 9 Hz), 7.93 br.s (1H, NH); *Z* isomer (34%): 2.27 s (3H, 5-CH₃), 2.60 s (3H, 3-CH₃), 4.57 d (1H, 6-H, *J*_{2,6} = 1.5 Hz), 6.33 br.s (1H, 2-H), 7.39–7.49 d.d (4H, C₆H₄, *J* = 9 Hz), 7.93 br.s (1H, NH).

5,6-Dibromo-4-[(2-bromo-5-chlorophenyl)aminocarbonyloxyimino]-3,5-dimethylcyclohex-2-en-1-one (XIIfg). Yield 89%, mp 105–107°C. ¹H NMR spectrum, δ, ppm: 2.32 s (3H, 5-CH₃), 2.52 br.s (3H, 3-CH₃), 4.72 s (1H, 6-H), 6.18 br.s (1H, 2-H), 7.28–7.31 d.d (1H, 4'-H, *J*_{4',6'} = 2.4, *J*_{4',3'} = 8.7 Hz), 7.60 d (1H, 3'-H), 7.69 d (1H, 6'-H), 7.95 br.s (1H, NH). Found, %: Cl + Br 50.57, 50.68. C₁₅H₁₂Br₃ClN₂O₃. Calculated, %: Cl + Br 50.63.

4-[(2-Bromo-4-methylphenyl)aminocarbonyloxyimino]-2,5-dimethylcyclohexa-2,5-dien-1-one

(XIIfb). Yield 85%, mp 182–183°C. ¹H NMR spectrum, δ, ppm: 2.08 d (3H, 2-CH₃, ⁴*J* = 1.5 Hz), 2.33 br.s (3H, 5-CH₃), 2.33 s (3H, CH₃C₆H₃), 6.44 q (1H, 6-H, ⁴*J* = 1.5 Hz), 7.17–7.20 d.d (1H, 5'-H, *J*_{5',3'} = 1.8, *J*_{5',6'} = 9 Hz), 7.40 br.s (1H, 3'-H), 7.66 d (1H, 3-H), 8.16 d (1H, 6'-H, *J*_{5',6'} = 9 Hz), 9.08 br.s (1H, NH). Found, %: Br 21.91, 22, 10. C₁₆H₁₅BrN₂O₃. Calculated, %: Br 22.00.

4-[(2-Bromo-4-methylphenyl)aminocarbonyloxyimino]-2-isopropyl-5-methylcyclohexa-2,5-dien-1-one (XIV). ¹H NMR spectrum, δ, ppm: 1.16 d [6H, 2-CH(CH₃)₂, *J* = 8.4 Hz], 2.32 br.s (3H, 5-CH₃), 2.33 s (3H, CH₃C₆H₃), 3.05–3.16 m (1H, 2-CH), 6.43 br.s (1H, 6-H), 7.17–7.20 d.d (1H, 5'-H, *J*_{5',3'} = 1.8, *J*_{5',6'} = 8.7 Hz), 7.41 br.s (1H, 3'-H), 7.43 br.s (1H, 5-H), 8.16 d (1H, 6'-H, *J*_{5',6'} = 8.7 Hz), 9.12 br.s (1H, NH).

4-[(4-Bromophenyl)aminocarbonyloxyimino]-2,6-dimethylcyclohexa-2,5-dien-1-one (XVIc). Yield 77%, mp 149–150°C. ¹H NMR spectrum, δ, ppm: 2.09 d (3H, 2-CH₃, ⁴*J* = 1.8 Hz), 2.10 d (3H, 6-CH₃, ⁴*J* = 1.5 Hz), 7.04 q (1H, 5-H, ⁴*J* = 1.5 Hz), 7.43–7.55 d.d (4H, C₆H₄, *J* = 8.1 Hz), 7.62 q (1H, 3-H), 8.20 br.s (1H, NH). Found, %: Br 22.74, 22.93. C₁₅H₁₃BrN₂O₃. Calculated, %: Br 22.88.

4-[(4-Bromophenyl)aminocarbonyloxyimino]-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one (XVIIIb). Yield 86%, mp 172–174°C. ¹H NMR spectrum, δ, ppm: 1.31 s (18H, *t*-Bu), 6.97 d (1H, 5-H, *J*_{3,5} = 2.7 Hz), 7.45–7.51 d.d (4H, C₆H₄, *J* = 8.7 Hz), 7.51 br.s (1H, 3-H), 8.23 br.s (1H, NH). Found, %: Br 18.32, 18.42. C₂₁H₂₅BrN₂O₃. Calculated, %: Br 18.44.

4-[(2-Bromo-4-methylphenyl)aminocarbonyloxyimino]-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one (XVIIIId). Yield 93%, mp 150–152°C. ¹H NMR spectrum, δ, ppm: 1.32 d (18H, *t*-Bu), 2.33 s (3H, CH₃), 6.96 d (1H, 5-H, *J*_{3,5} = 2.4 Hz), 7.16–7.19 d.d (1H, 5'-H, *J*_{5',3'} = 1.8, *J*_{5',6'} = 8.7 Hz), 7.41 br.s (1H, 3'-H), 7.43 br.s (1H, 5-H), 7.54 br.s (1H, 3-H), 8.08 br.s (1H, 6'-H), 8.78 br.s (1H, NH). Found, %: Br 17.79, 17.94. C₂₂H₂₇BrN₂O₃. Calculated, %: Br 17.86.

Bromination of 4-(arylamino carbonyloxyimino)-cyclohexa-2,5-dien-1-ones IIIg–IIIi in the presence of LiCl (general procedure). A solution of 5 mmol of compound IIIg–IIIi in 3 ml of acetic acid or chloroform was heated to the boiling point, 5 mmol of lithium chloride was added in portions under stirring, and a solution of 25 mmol of bromine in 2 ml of the same solvent, heated to 50–60°C, was added dropwise under vigorous stirring, the ratio compound III–bro-

mine being 1:5. The mixture was heated for 5–10 min under reflux with vigorous stirring. After cooling, a crystalline solid precipitated and was filtered off and recrystallized from benzene–hexane (1:1).

5-Bromo-4-[(4-bromophenyl)aminocarbonyloxyimino]-6-chloro-2,3-dimethylcyclohex-2-en-1-one (XIXa). ^1H NMR spectrum, δ , ppm: 2.11 s (3H, 2-CH₃), 2.29 s (3H, 3-CH₃), 4.55 d (1H, 6-H, $J_{5,6}$ = 2.4 Hz), 5.80 d (1H, 5-H, $J_{5,6}$ = 2.4 Hz), 7.42–7.50 d.d (4H, C₆H₄, J = 6.9 Hz), 7.97 br.s (1H, NH).

5-Bromo-6-chloro-2,3-dimethyl-4-[(4-methylphenyl)aminocarbonyloxyimino]cyclohex-2-en-1-one (XIXb). ^1H NMR spectrum, δ , ppm: 2.13 s (3H, 2-CH₃), 2.30 s (3H, 3-CH₃), 2.34 s (3H, CH₃C₆H₄), 4.53 d (1H, 6-H, $J_{5,6}$ = 2.1 Hz), 5.81 d (1H, 5-H, $J_{5,6}$ = 2.1 Hz), 7.18–7.39 d.d (4H, CH₃C₆H₄, J = 8.1 Hz), 7.97 br.s (1H, NH).

5-Bromo-4-[(2-bromo-5-chlorophenyl)aminocarbonyloxyimino]-6-chloro-2,3-dimethylcyclohex-2-en-1-one (XIXc). ^1H NMR spectrum, δ , ppm: 2.10 s (3H, 2-CH₃), 2.30 s (3H, 3-CH₃), 4.56 d (1H, 6-H, $J_{5,6}$ = 2.7 Hz), 5.80 d (1H, 6-H, $J_{5,6}$ = 2.7 Hz), 7.30–7.33 d.d (1H, 4'-H, $J_{4',6'}$ = 2.4, $J_{4',3'}$ = 8.7 Hz), 7.60 d (1H, 3'-H), 7.72 d (1H, 6'-H), 7.99 br.s (1H, NH).

REFERENCES

1. Avdeenko, A.P., Konovalova, S.A., and Ludchenko, O.N., *Russ. J. Org. Chem.*, 2009, vol. 45, p. 1799.
2. Avdeenko, A.P., Konovalova, S.A., Sergeeva, A.G., Zubatyuk, R.I., Palamarchuk, G.V., and Shishkin, O.V., *Russ. J. Org. Chem.*, 2008, vol. 44, p. 1765.
3. Avdeenko, A.P., Konovalova, S.A., Sergeeva, A.G., Palamarchuk, G.V., and Shishkin, O.V., *Russ. J. Org. Chem.*, 2009, vol. 45, p. 674.
4. Tennant, J., *Comprehensive Organic Chemistry*, Barton, D. and Ollis, W.D., Eds., Oxford: Pergamon, 1979, vol. 2. Translated under the title *Obshchaya organicheskaya khimiya*, Moscow: Khimiya, 1982, vol. 3, p. 639.
5. Titov, E.A., Burmistrov, S.I., and Brazhnik, D.E., *Zh. Obshch. Khim.*, 1963, vol. 33, p. 2270.
6. Titov, E.A. and Burmistrov, S.I., *Ukr. Khim. Zh.*, 1960, vol. 26, p. 744.
7. Titov, E.A. and Sukhina, N.K., USSR Inventor's Certificate no. 255210 (1968), *Byull. Izobret.*, 1969, no. 33.
8. Avdeenko, A.P., Konovalova, S.A., Il'chenko, A.Ya., and Glinyanaya, N.M., *Russ. J. Org. Chem.*, 2006, vol. 42, p. 56.
9. Pirozhenko, V.V., *Cand. Sci. (Chem.) Dissertation*, Kiev, 1992.
10. Pirozhenko, V.V. and Avdeenko, A.P., *Russ. J. Org. Chem.*, 1995, vol. 31, p. 1514.
11. Avdeenko, A.P. and Glinyanaya, N.M., *Russ. J. Org. Chem.*, 1995, vol. 31, p. 1507.
12. Perrin, C.L. and Engler, R.E., *J. Org. Chem.*, 1997, vol. 62, p. 687.
13. Avdeenko, A.P., Zhukova, S.A., Glinyanaya, N.M., and Konovalova, S.A., *Russ. J. Org. Chem.*, 1999, vol. 35, p. 560.