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Halogenation of *N*-Substituted *p*-Quinone Monoimines and *p*-Quinone Monooxime Ethers: XV.[1] Synthesis and Bromination of 4-(Cinnamoyloxyimino)-cyclohexa-2,5-dienones

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Abstract—New 4-(cinnamoyloxyimino)cyclohexa-2,5-dien-1-ones were synthesized, and their bromination afforded bromine addition products to the *syn*- and *anti*-C=C bonds of the quinoid ring. In all cases, bromine addition to the C=C double bond of the cinnamoyl fragment was observed.

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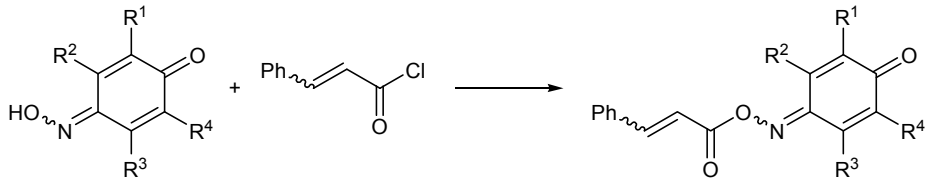
We previously synthesized new *N*-benzylideneacetyl-substituted 1,4-benzoquinone imines by reactions of the corresponding 4-aminophenols with benzylideneacetyl chloride (3-phenylacryloyl chloride) [2]. Carboxylic acid chlorides are capable of reacting not only with aminophenols but also with *p*-quinone monooximes to give *p*-quinone monooxime *O*-ethers [3]; the latter were found to undergo regioselective halogenation of the double bonds in the quinoid ring [4].

The goal of the present work was to synthesize new 4-(cinnamoyloxyimino)cyclohexa-2,5-dien-1-ones and study their halogenation. By reaction of 4-(hydroxyimino)cyclohexa-2,5-dien-1-ones **1a**–**1h** with 3-phenylacryloyl chloride (**2**) in diethyl ether in the presence of triethylamine on cooling we obtained 4-(cinnamoyloxyimino)cyclohexa-2,5-dien-1-ones **3a**–**3h** (Scheme 1) whose structure was confirmed by elemental analyses and ^{1}H NMR and IR spectra. The IR spectra of **3a**–**3h** contained absorption bands at 1620–1660 (C=O, quinone), 1680–1730 (C=O, ester), and 1550–1620 cm^{-1} (C=N). In the ^{1}H NMR spectra of **3a**–**3h** we observed two doublets in the δ range from 6.88 to 7.53 ppm due to protons of the exocyclic CH=CH fragment, and the positions and multiplicities of signals from protons of the quinoid ring were fully consistent with the proposed structures. The ^{1}H NMR spectrum of 2-methyl derivative **3b** displayed a double set of signals due to the presence of *Z* and *E* isomers with respect to the C=N bond at a ratio of 60:40; the Gibbs free energy of activation for the *Z*/*E* isomerization of 4-(hydroxyimino)cyclohexa-2,5-dien-1-ones about the C=N bond was estimated at $\Delta G^{\neq} > 100$ kJ×

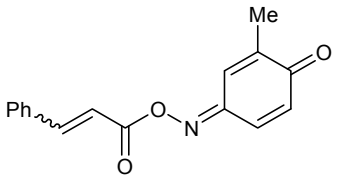
Scheme 1.



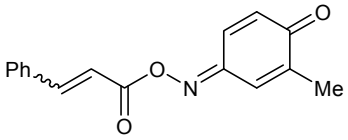
1a–1h **2** **3a–3h**

$R^1 = R^2 = R^3 = R^4 = H$ (**a**); R^1 = Me, $R^2 = R^3 = R^4 = H$ (**b**); $R^1 = R^3 = R^4 = H$, R^2 = Me (**c**); $R^1 = R^2$ = Me, $R^3 = R^4 = H$ (**d**); $R^1 = R^3$ = Me, $R^2 = R^4 = H$ (**e**); $R^1 = R^4$ = Me, $R^2 = R^3 = H$ (**f**); $R^1 = R^4 = H$, $R^2 = R^3$ = Me (**g**); R^1 = Me, $R^2 = R^4 = H$, R^3 = *i*-Pr (**h**).

[1] For communication XIV, see [1].



Z-**3b**



E-**3b**

mol^{-1} [5]. The 3-H proton in **3b** resonated as a quartet at δ 7.44 (*Z*) or 7.26 ppm (*E*), the 5-H signal was a doublet of doublets at δ 7.37–7.40 (*Z*) or 7.73–7.77 ppm (*E*), and the 6-H proton gave a doublet (vicinal coupling) at δ 6.68 (*Z*) or 6.59 ppm (*E*).

The chlorination of **3a**–**3h** was carried out by saturation with gaseous chlorine. As a result, complex non-crystallizable mixtures of products were formed, which we failed to isolate and identify. The bromination of **3a**–**3h** was performed in acetic acid using 5 equiv of bromine. Crystalline bromination products were analyzed by ^{1}H NMR before recrystallization in order to detect all components of the product mixtures.

The regioselectivity of halogen addition to the double bonds of the quinoid ring was studied for unsubstituted and 2,6(3,5)-dimethyl-substituted derivatives with a symmetric structure of the quinoid ring [4]. The bromination of **3a**, **3f**, and **3g** gave mixtures of *Z*- and *E*-isomeric products at ratios of 36 : 64 (**4a**), 42 : 58 (**4f**), and 36 : 64 (**4g**) as a result of bromine addition to the *syn*- or *anti*-C=C bond with respect to the substituent on the nitrogen (Scheme 2).

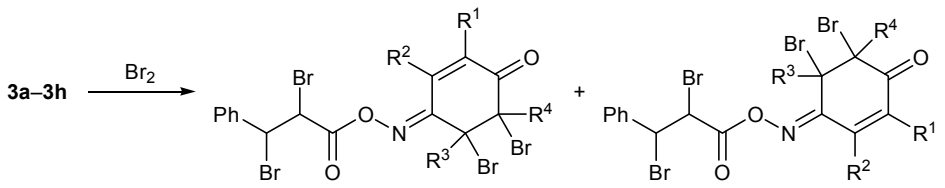
In the ^{1}H NMR spectrum of **4a**, the 5-H and 6-H signals were quartets at δ 4.68 and 5.73 ppm (*E*) and 4.81 and 5.40 ppm (*Z*), respectively; the 2-H and 3-H protons resonated as doublets of doublets at δ 6.49–6.53 (2-H, *E*), 6.43–6.47 (2-H, *Z*), 7.23–7.26 (3-H, *E*), and 7.57–7.61 ppm (3-H, *Z*). The doublet signal from the 2-Me protons of **4f** was located at δ 2.17 (*Z*) and 2.14 (*E*), and from the 6-Me group, at δ 2.14 (*Z*) and 2.12 ppm (*E*). The 5-Me signal of both isomers of **4g** was a singlet at δ 2.34 ppm, the 3-Me group gave rise to doublets at δ 2.61 (*E*) and 2.59 ppm (*Z*), and the 6-H and 2-H signals were doublets of doublets at δ 4.73 and 6.19 (*E*) and 4.58 and 6.34 ppm (*Z*), respectively.

According to the data of [5], no *Z*,*E*-isomerization of *p*-quinone monooxime *O*-ethers is observed at room temperature, and the *Z* and *E* isomers are converted into each other neither in initial solution nor during halogenation [4]. Therefore, the isomer ratio of the halogenation products should be the same as that of initial *O*-substituted *p*-quinone monooximes.

As shown previously, the ratio of the halogen addition products to the *syn*- and *anti*-C=C bonds of the quinoid ring is determined by two factors, electronic (acceptor properties of the substituent on the nitrogen atom) and steric (size of substituents in the quinoid ring) [4, 6, 7]. The *syn*-C^2=C^3 bond in *O*-arenesulfonyl-substituted *p*-quinone monooximes is more reactive due to its lower polarity (the conjugation along the N=C–C^2=C^3–C=O bond sequence is weaker than that along the N=C–C^5=C^6–C=O sequence) [4], while reduction of the acceptor power of the ArNHCO substituent on the oxygen atom in *O*-arylaminocarbonyl derivatives leads to leveling of the reactivities of the quinoid C=C bonds toward halogens [8].

The results of bromination of compounds **3a**, **3f**, and **3g** showed that the fraction of the *E* isomer (Scheme 2) arising from the addition of bromine to the *syn*-C=C bond is considerably smaller than in the halogenation of 4-(arenesulfonyloxyimino)cyclohexa-2,5-dien-1-ones (80–85% of the *E* isomer) [9] and is comparable with that in the halogenation of 4-(carbamoyloxyimino)cyclohexa-2,5-dien-1-ones (58–64% of the *E* isomer) [8]. Therefore, we can conclude that the PhCH=CHCO substituent on the oxime oxygen

Scheme 2.



Z-**4a**, *Z*-**4b**, *Z*-**4f**, *Z*-**4g** *E*-**4a**–*E*-**4h**

$R^1 = R^2 = R^3 = R^4 = H$ (**a**); R^1 = Me, $R^2 = R^3 = R^4 = H$ (**b**); $R^1 = R^3 = R^4 = H$, R^2 = Me (**c**); $R^1 = R^2$ = Me, $R^3 = R^4 = H$ (**d**); $R^1 = R^3$ = Me, $R^2 = R^4 = H$ (**e**); $R^1 = R^4$ = Me, $R^2 = R^3 = H$ (**f**); $R^1 = R^4 = H$, $R^2 = R^3$ = Me (**g**); R^1 = Me, $R^2 = R^4 = H$, R^3 = *i*-Pr (**h**).

atom of **3a**, **3f**, and **3g**, as well as ArNHCO group, exerts a weaker acceptor effect on the quinoid double bonds than does arenesulfonyl group.

The bromination of **3b** gave a mixture of *Z*-**4b** and *E*-**4b** at a ratio of 58:42 (Scheme 2). Bromine molecule adds exclusively to the unsubstituted C=C bond, and the isomer ratio *Z*-**4b**/*E*-**4b** is the same as *Z*-**3b**/*E*-**3b**; i.e., *E*-**3b** is converted to *E*-**4b**, and *Z*-**3b** to *Z*-**4b**. This is one more proof for the fact that the *Z* and *E* isomers of *p*-quinone monooxime *O*-ethers are not converted into each other during the halogenation process. The absence of addition products to the C^2=C^3 bond of **3b** containing a methyl group also indicates reduced acceptor effect of the PhCH=CHC(O) or PhC(Br)H–C(Br)HC(O) substituent on the oxygen atom as compared to arenesulfonyl group. The direction of halogen addition is determined mainly by steric factor, and the reaction becomes completely regioselective since the presence of a methyl group on C^2 hampers addition to the C^2=C^3 bond.

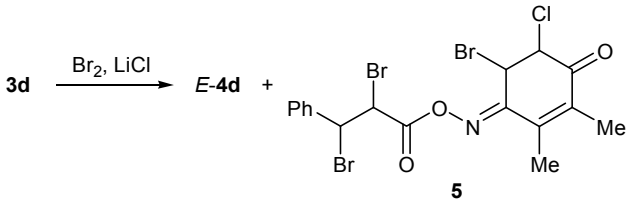
The structure of the *Z* and *E* isomers of **4b** was determined by comparing their ^{1}H NMR data with those of the halogenation products of 4-(aroyloxyimino)-2-methylcyclohexa-2,5-dien-1-ones [4, 10]. In the ^{1}H NMR spectrum of **4b**, the 3-H and 5-H protons resonated as quartets at δ 7.41 and 5.38 (*Z*) and 7.05 and 5.69 ppm (*E*), respectively, and the 2-Me and 6-H signals appeared as doublets (*meta* coupling) at δ 2.16 and 4.82 (*Z*) and 2.13 and 4.69 ppm (*E*).

The bromination of **3c**, **3d**, **3e**, and **3h**, which were obtained as a single isomer, afforded only the *syn*-addition products, *E* isomers **4c**, **4d**, **4e**, and **4h** (Scheme 2), whose structure was confirmed by ^{1}H NMR and elemental analyses. Analogous aroyl and arenesulfonyl derivatives reacted with bromine to give addition products to both *syn*- and *anti*-C=C bonds of the quinoid ring [4, 11].

In all cases, bromination of the quinoid ring of **3a**–**3h** was accompanied by bromine addition to the exocyclic double bond of the cinnamoyl fragment, and the reaction mixtures contained no dehydrobromination products like those obtained previously in the halogenation of aroyl, arenesulfonyl [4, 9–11], and carbamoyl derivatives [8].

While studying the mechanism of halogenation of *p*-quinone monooxime *O*-esters [4], the bromination of 4-aroyl(arenesulfonyl)oxyimino-2,3-dimethylcyclohexa-2,5-dien-1-ones was carried out in the presence of LiCl. In this work we also performed bromination of **3d** in acetic acid in the presence of LiCl, which led to the formation of a mixture of compounds **4d** and **5** at a ratio of 47:53 (Scheme 3).

Scheme 3.

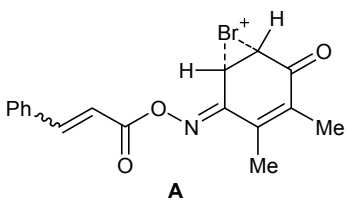


5

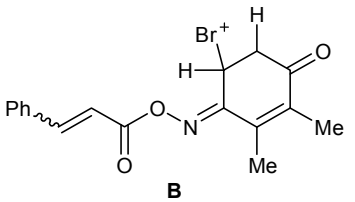
Comparison of the spectral data showed that the bromine and chlorine atoms in **5** are attached to C^5 and C^6, respectively. The 6-H and 5-H protons resonated as doublets at δ 4.69 and 5.77 (**4d**) and 4.57 and 5.76 ppm (**5**), respectively. The 6-H signal of **5** appeared in a stronger field relative to the corresponding signal of **4d**, indicating that the chlorine atom is located in the *ortho* position with respect to the carbonyl group. This is consistent with the results of halogenation of 4-aroyl- and 4-arenesulfonyloxyimino analogs [4].

In keeping with the classical theory, the addition of bromine to double C=C bond involves initial formation of a π-complex which is then converted to bromonium ion [12]. Depending on the conditions, the latter either reacts directly with bromide ion or is transformed to carbenium ion which in turn takes up bromide ion. As shown in [4], the formation of carbenium ion is possible only in the halogenation of 1,4-benzoquinone imines but is not typical of 1,4-quinone monooxime ethers [4].

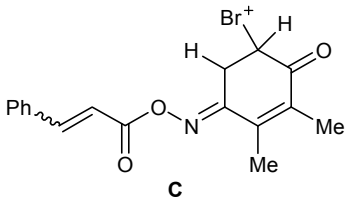
In order to get a deeper insight into the mechanism of bromination of compounds **3a**–**3h**, we performed quantum chemical calculations of possible intermediates **A**–**C** in the bromination of **3d**. All attempts to optimize the structures of carbocations **B** and **C** were unsuccessful; the optimization process resulted in



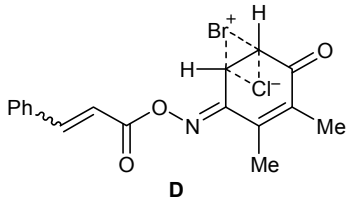
A



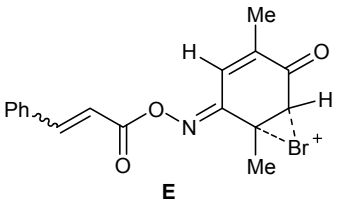
B



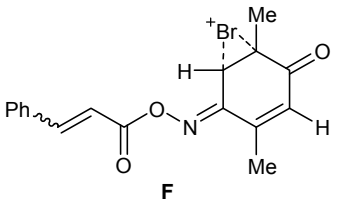
C



D



E



F

rupture of the C–O bond in the C=NOC=O fragment; therefore, we presumed that no carbocation is formed in the bromination of **3d**.

It may be concluded that the first step in the bromination of **3d** is addition of bromine cation to the quinoid C=C bond with formation of bromonium ion **A**. Next follows *trans*-addition of bromide ion (or chloride in the reaction in the presence of LiCl), which is confirmed by quantum chemical calculations (optimization of intermediate **D** led to a structure analogous to **5**) and is very consistent with the results of halogenation of 4-(aroyloxyimino)- and 4-(arenesulfonyloxyimino)cyclohexa-2,5-dien-1-ones [4].

The total energy of optimized structure **5** is lower by 15 kJ/mol than the energy of the alternative isomer with the chlorine atom attached to C^5 (i.e., in the *ortho* position with respect to the imino group) and the bromine atom on C^6. An additional evidence in support of the proposed mechanism is that the halogenation of *O*-substituted *p*-quinone monooximes gave only products with *trans* arrangement of the halogen atoms on the sp^3-carbon atoms of the cyclohexene ring.

In order to rationalize different reactivities of the C=C bonds in the quinoid ring, we performed quantum chemical calculations of possible intermediates, bromonium ions **E** and **F**, corresponding to the bromination of **3c**, **3e**, and **3h**. The energy of transition state **F** was estimated at –3508.658078 Ha, while attempted optimization of structure **E** led to rupture of the O–C bond in the C=NO–C=O fragment, which indicated its instability. Thus, the bromination of 2,5-dialkyl-substituted 4-(cinnamoyloxyimino)cyclohexa-2,5-dien-1-ones does not give addition products to the *anti*-C=C bond since the formation of the corresponding bromonium ion is impossible.

The results of our present study showed that the orientation (*syn* or *anti*) of the substituent on the nitrogen atom in 4-(cinnamoyloxyimino)cyclohexa-2,5-dien-1-ones affects the regioselectivity of halogen addition to the quinoid C=C bonds to a smaller extent than in 4-(arenesulfonyloxyimino)cyclohexa-2,5-dien-1-ones, which is related to weaker acceptor effect of the PhCH=CHC(O) substituent on the quinoid ring.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 MHz using $CDCl_3$ as solvent and tetramethylsilane as internal standard. The purity of compounds **3a**–**3h**, **4a**–**4h**, and **5** 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.

Quantum chemical calculations were performed in terms of the density functional theory with the B3LYP functional and 6-31+G(*d*) basis set using Firefly QC package [13] based in part on the GAMESS (US) code [14].

3-Phenylacryloyl chloride (**2**) was synthesized according to the procedure described in [15] and was recrystallized from hexane.

4-{[(Cinnamoyl)oxy]imino}cyclohexa-2,5-dien-1-ones 3a–3h (*general procedure*). Quinone oxime **1a**–**1h**, 0.01 mol, was dispersed in 30–35 mL of anhydrous diethyl ether, and an equimolar amount of 3-phenylacryloyl chloride (**2**) and 0.011 mol of triethylamine were slowly added with stirring and cooling. A crystalline solid separated from the mixture and was filtered off, washed with water, and recrystallized from glacial acetic acid or isopropyl alcohol.

4-{[(3-Phenylprop-2-enoyl)oxy]imino}cyclohexa-2,5-dien-1-one (3a). Yield 48%, mp 102–103°C. ^{1}H NMR spectrum, δ, ppm: 6.60 d.d (1H, 6-H, J = 1.8,

10.5 Hz), 6.63 d (1H, CH=CH, J = 15.9 Hz), 6.64 d.d (1H, 2-H, J = 1.8, 10.5 Hz), 7.46 d.d (1H, 5-H, J = 2.4, 10.5 Hz), 7.45–7.63 m (5H, Ph), 7.81 d.d (1H, 3-H, J = 2.4, 10.5 Hz), 7.96 d (1H, CH=CH, J = 15.9 Hz). Found, %: N 5.63, 5.41. $C_{15}H_{11}NO_3$. Calculated, %: N 5.53.

2-Methyl-4-{[(3-phenylprop-2-enoyl)oxy]imino}-cyclohexa-2,5-dien-1-one (3b). Yield 56%, mp 145–146°C. ^{1}H NMR spectrum, δ, ppm: *Z* isomer (60%): 2.13 d (3H, 2-Me, J = 1.5 Hz), 6.63 d (1H, CH=CH, J = 15.9 Hz), 6.68 d (1H, 6-H, $J_{5,6}$ = 9.9 Hz), 7.39 d.d (1H, 5-H, J = 2.7, 9.9 Hz), 7.44 q (1H, 3-H), 7.44–7.63 m (5H, Ph), 7.97 d (1H, CH=CH, J = 15.9 Hz); *E* isomer (40%): 2.08 d (3H, 2-Me, J = 1.5 Hz), 6.59 d (1H, 6-H, $J_{5,6}$ = 9.9 Hz), 6.63 d (1H, CH=CH, J = 15.9 Hz), 7.26 q (1H, 3-H), 7.44–7.63 m (5H, Ph), 7.75 d.d (1H, 5-H, J = 2.7, 9.9 Hz), 7.95 d (1H, CH=CH, J = 15.9 Hz). Found, %: N 5.30, 5.14. $C_{16}H_{13}NO_3$. Calculated, %: N 5.24.

3-Methyl-4-{[(3-phenylprop-2-enoyl)oxy]imino}-cyclohexa-2,5-dien-1-one (3c). Yield 64%, mp 177–178°C. ^{1}H NMR spectrum, δ, ppm: 2.37 s (3H, 3-Me), 6.44 q (1H, 2-H), 6.53 d.d (1H, 6-H, J = 1.8, 10.2 Hz), 6.65 d (1H, CH=CH, J = 16.2 Hz), 6.78 d (1H, 5-H, J = 10.2 Hz), 7.44–7.63 m (5H, Ph), 7.93 d (1H, CH=CH, J = 16.2 Hz). Found, %: N 5.34, 5.10. $C_{16}H_{13}NO_3$. Calculated, %: N 5.24.

2,3-Dimethyl-4-{[(3-phenylprop-2-enoyl)oxy]-imino}cyclohexa-2,5-dien-1-one (3d). Yield 70%, mp 185–186°C. ^{1}H NMR spectrum, δ, ppm: 2.06 s (3H, 2-Me), 2.35 s (3H, 3-Me), 6.53 d (1H, 6-H, J = 10.2 Hz), 6.65 d (1H, CH=CH, J = 15.9 Hz), 7.44–7.62 m (5H, Ph), 7.75 d (1H, 5-H, J = 10.2 Hz), 7.94 d (1H, CH=CH, J = 15.9 Hz). Found, %: N 5.00, 5.15. $C_{17}H_{15}NO_3$. Calculated, %: N 4.98.

2,5-Dimethyl-4-{[(3-phenylprop-2-enoyl)oxy]-imino}cyclohexa-2,5-dien-1-one (3e). Yield 82%, mp 195–196°C. ^{1}H NMR spectrum, δ, ppm: 2.08 d (3H, 2-Me, J = 1.5 Hz), 2.33 d (3H, 5-Me, J = 1.5 Hz), 6.41 q (1H, 6-H), 6.70 d (1H, CH=CH, J = 15.6 Hz), 7.43–7.63 m (5H, Ph), 7.57 q (1H, 3-H), 7.93 d (1H, CH=CH, J = 16.2 Hz). Found, %: N 5.05, 5.10. $C_{17}H_{15}NO_3$. Calculated, %: N 4.98.

2,6-Dimethyl-4-{[(3-phenylprop-2-enoyl)oxy]-imino}cyclohexa-2,5-dien-1-one (3f). Yield 76%, mp 139–140°C. ^{1}H NMR spectrum, δ, ppm: 2.07 d (1H, 2-Me, J = 1.2 Hz), 2.13 d (1H, 6-Me, J = 1.2 Hz), 6.65 d (1H, CH=CH, J = 16.2 Hz), 7.18 q (1H, 5-H), 7.57 q (1H, 3-H), 7.43–7.63 m (5H, Ph), 7.94 d (1H, CH=CH, J = 15.9 Hz). Found, %: N 5.00, 4.85. $C_{17}H_{15}NO_3$. Calculated, %: N 4.98.

3,5-Dimethyl-4-{[(3-phenylprop-2-enoyl)oxy]-imino}cyclohexa-2,5-dien-1-one (3g). Yield 54%, mp 175–176°C. ^{1}H NMR spectrum, δ, ppm: 2.36 d (3H, 3-Me, J = 1.5 Hz), 2.56 d (3H, 5-Me, J = 1.5 Hz), 6.29 q (1H, 6-H), 6.40 q (1H, 2-H), 6.58 d (1H, CH=CH, J = 16.2 Hz), 7.44–7.63 m (5H, Ph), 7.93 d (1H, CH=CH, J = 15.9 Hz). Found, %: N 5.05, 4.79. $C_{17}H_{15}NO_3$. Calculated, %: N 4.98.

5-Isopropyl-2-methyl-4-{[(3-phenylprop-2-enoyl)oxy]imino}cyclohexa-2,5-dien-1-one (3h). Yield 73%, mp 104–105°C. ^{1}H NMR spectrum, δ, ppm: 1.25 d [6H, CH(C**H**$_3$)$_2$, J = 6.9 Hz], 2.09 br.s (3H, 2-Me), 3.44–3.53 m [1H, C**H**(CH$_3$)$_2$], 6.43 br.s (1H, 6-H), 6.68 d (1H, CH=CH, J = 15.6 Hz), 7.44–7.63 m (5H, Ph), 7.60 br.s (1H, 3-H), 7.93 d (1H, CH=CH, J = 16.5 Hz). Found, %: N 4.61, 4.38. $C_{19}H_{19}NO_3$. Calculated, %: N 4.53.

Bromination of 4-{[(cinnamoyl)oxy]imino}cyclohexa-2,5-dien-1-ones 3a–3h (*general procedure*). A solution of 5 mmol of compound **3a**–**3h** in 3 mL of acetic acid was heated to the boiling point, a solution of 25 mmol of bromine in 2 mL of acetic acid heated to 50–60°C was added dropwise under vigorous stirring, and the mixture was refluxed for 5–10 min under vigorous stirring. The mixture was cooled, and the precipitate was filtered off and recrystallized from acetic acid.

5,6-Dibromo-4-{[(2,3-dibromo-3-phenylpropanoyl)oxy]imino}cyclohex-2-en-1-one (4a). Yield 54%, mp 129–130°C. ^{1}H NMR spectrum, δ, ppm: *Z* isomer (36%): 4.81 q (1H, 6-H), 5.07 d (1H, CHBrCHBr, J = 11.7 Hz), 5.40 q (1H, 5-H), 5.42 d (1H, CHBrCHBr, J = 11.7 Hz), 6.45 d (1H, 2-H, J = 9.3 Hz), 7.42–7.52 m (5H, Ph), 7.59 d (1H, 3-H, J = 9.6 Hz); *E* isomer (64%): 4.68 q (1H, 6-H), 5.07 d and 5.47 d (1H each, CHBrCHBr, J = 11.7 Hz), 5.73 q (1H, 5-H), 6.50 d (1H, 2-H, J = 9.3 Hz), 7.24 d (1H, 3-H, J = 9.6 Hz), 7.42–7.52 m (5H, Ph). Found, %: Br 55.60, 55.52; N 2.35, 2.55. $C_{15}H_{11}Br_4NO_3$. Calculated, %: Br 55.79; N 2.45.

5,6-Dibromo-4-{[(2,3-dibromo-3-phenylpropanoyl)oxy]imino}-2-methylcyclohex-2-en-1-one (4b). Yield 62%, mp 163–164°C. ^{1}H NMR spectrum, δ, ppm: *Z* isomer (58%): 2.16 d (3H, 2-Me, J = 1.5 Hz), 4.82 d (1H, 6-H, J = 2.7 Hz), 5.06 d (1H, CHBrCHBr, J = 11.7 Hz), 5.38 q (1H, 5-H), 7.39–7.50 m (5H, Ph), 7.41 q (1H, 3-H), 5.43 d (1H,

CHBrCHBr, J = 11.7 Hz); *E* isomer (42%): 2.13 d (3H, 2-Me, J = 0.9 Hz), 4.69 d (1H, 6-H, J = 3.0 Hz), 5.06 d (1H, CHBrCHBr, J = 11.7 Hz), 7.39–7.50 m (5H, Ph), 5.43 d (1H, CHBrCHBr, J = 11.7 Hz), 5.69 q (1H, 5-H), 7.05 q (1H, 3-H). Found, %: Br 54.30, 54.55; N 2.47, 2.25. $C_{16}H_{13}Br_4NO_3$. Calculated, %: Br 54.46; N 2.39.

5,6-Dibromo-4-{[(2,3-dibromo-3-phenylpropanoyl)oxy]imino}-3-methylcyclohex-2-en-1-one (4c). Yield 78%, mp 164–165°C. ^{1}H NMR spectrum, δ, ppm: 2.37 d (3H, 3-Me, J = 1.5 Hz), 4.64 q (1H, 6-H), 5.04 d and 5.43 d (1H each, CHBrCHBr, J = 9.9 Hz), 7.42–7.50 m (5H, Ph), 5.77 d (1H, 5-H, J = 2.4 Hz), 6.34 q (1H, 2-H). Found, %: Br 54.27, 54.64; N 2.45, 2.60. $C_{16}H_{13}Br_4NO_3$. Calculated, %: Br 54.46; N 2.39.

5,6-Dibromo-4-{[(2,3-dibromo-3-phenylpropanoyl)oxy]imino}-2,3-dimethylcyclohex-2-en-1-one (4d). Yield 70%, mp 186–187°C. ^{1}H NMR spectrum, δ, ppm: 2.11 s (3H, 2-Me), 2.34 s (3H, 3-Me), 4.69 d (1H, 6-H, J = 2.1 Hz), 5.07 d and 5.43 d (1H each, CHBrCHBr, J = 11.7 Hz), 7.41–7.46 m (5H, Ph), 5.77 d (1H, 5-H, J = 2.1 Hz). Found, %: Br 53.10, 53.28; N 2.53, 2.25. $C_{17}H_{15}Br_4NO_3$. Calculated, %: Br 53.19; N 2.33.

5,6-Dibromo-4-{[(2,3-dibromo-3-phenylpropanoyl)oxy]imino}-3,6-dimethylcyclohex-2-en-1-one (4e). Yield 50%, mp 91–92°C. ^{1}H NMR spectrum, δ, ppm: 2.10 s (3H, 6-Me), 2.34 d (3H, 3-Me, J = 1.2 Hz), 5.11 d and 5.43 d (1H each, CHBrCHBr, J = 11.7 Hz), 5.86 d (1H, 5-H, J = 2.7 Hz), 6.34 q (1H, 2-H), 7.42–7.49 m (5H, Ph). Found, %: Br 53.08, 53.31; N 2.40, 2.20. $C_{17}H_{15}Br_4NO_3$. Calculated, %: Br 53.19; N 2.33.

5,6-Dibromo-4-{[(2,3-dibromo-3-phenylpropanoyl)oxy]imino}-2,6-dimethylcyclohex-2-en-1-one (4f). Yield 69%, mp 139–140°C. ^{1}H NMR spectrum, δ, ppm: *Z* isomer (42%): 2.14 s (3H, 6-Me), 2.17 d (3H, 2-Me, J = 1.2 Hz), 5.05 d and 5.45 d (1H each, CHBrCHBr, J = 11.7 Hz), 5.45 q (1H, 5-H), 7.32 q (1H, 3-H) 7.42–7.46 m (5H, Ph); *E* isomer (58%): 2.12 s (6H, 6-Me), 2.14 d (3H, 2-Me, J = 1.2 Hz), 5.08 d and 5.44 d (1H each, CHBrCHBr, J = 11.7 Hz), 7.42–7.46 m (5H, Ph), 5.79 q (1H, 5-H), 6.98 q (1H, 3-H). Found, %: Br 53.12, 53.25; N 2.51, 2.42. $C_{17}H_{15}Br_4NO_3$. Calculated, %: Br 53.19; N 2.33.

5,6-Dibromo-4-{[(2,3-dibromo-3-phenylpropanoyl)oxy]imino}-3,5-dimethylcyclohex-2-en-1-one (4g). Yield 81%, mp 89–90°C. ^{1}H NMR spectrum, δ, ppm: *Z* isomer (36%): 2.34 s (3H, 5-Me), 2.59 d (3H, 3-Me, J = 0.9 Hz), 4.58 q (1H, 6-H), 4.96 d and 5.41 d (1H each, CHBrCHBr, J = 11.7 Hz), 6.34 q (1H, 2-H), 7.44–7.63 m (5H, Ph); *E* isomer (64%): 2.34 s (3H, 5-Me), 2.61 d (3H, 3-Me, J = 2.1 Hz), 4.73 q (1H, 6-H), 5.01 d and 5.41 d (1H each, CHBrCHBr, J = 11.7 Hz), 6.19 q (1H, 2-H), 7.44–7.63 m (5H, Ph). Found, %: Br 53.02, 53.27; N 2.41, 2.50. $C_{17}H_{15}Br_4NO_3$. Calculated, %: Br 53.19; N 2.33.

5,6-Dibromo-4-{[(2,3-dibromo-3-phenylpropanoyl)oxy]imino}-3-isopropyl-6-methylcyclohex-2-en-1-one (4h). Yield 76%, mp 117–118°C. ^{1}H NMR spectrum, δ, ppm: 1.26 d [6H, CH(C**H**$_3$)$_2$, J = 6.9, 13.6 Hz], 2.09 s (3H, 6-Me), 3.30–3.41 m [1H, C**H**(CH$_3$)$_2$], 5.11 d and 5.42 d (1H each, CHBrCHBr, J = 12.0 Hz), 5.89 d (1H, 2-H, J = 2.7 Hz), 6.32 br.s (1H, 5-H), 7.41–7.50 m (5H, Ph). Found, %: Br 50.68, 50.75; N 2.15, 2.31. $C_{19}H_{19}Br_4NO_3$. Calculated, %: Br 50.82; N 2.23.

Bromination of 2,3-dimethyl-4-{[(3-phenylprop-2-enoyl)oxy]imino}cyclohexa-2,5-dien-1-one (3d) in the presence of LiCl. A solution of 5 mmol of compound **3d** in 3 mL of acetic acid was heated to the boiling point, an equimolar amount of lithium chloride was added in portions under stirring, and a solution of 25 mmol of bromine in 2 mL of acetic acid heated to 50–60°C was then added dropwise under vigorous stirring. The mixture was refluxed for 5–10 min with stirring. After cooling, the precipitate was filtered off and recrystallized from acetic acid.

5-Bromo-6-chloro-4-{[(2,3-dibromo-3-phenylpropanoyl)oxy]imino}-2,3-dimethylcyclohex-2-en-1-one (5). ^{1}H NMR spectrum, δ, ppm: 2.11 s (3H, 2-Me), 2.34 s (3H, 3-Me), 4.57 d (1H, 6-H, J = 2.1 Hz), 5.07 d and 5.42 d (1H each, CHBrCHBr, J = 11.7 Hz), 5.76 d (1H, 5-H, J = 2.4 Hz), 7.42–7.46 m (5H, Ph).

REFERENCES

1. Avdeenko, A.P., Konovalova, S.A., Ledeneva, O.P., Santalova, A.A., Pirozhenko, V.V., Palamarchuk, G.V., and Shishkin, O.V., *Russ. J. Org. Chem*., 2012, vol. 48, p. 928.
2. Avdeenko, A.P., Konovalova, S.A., Vasil'eva, V.M., Shishkin, O.V., Palamarchuk, G.V., and Baumer, V.N., *Russ. J. Org. Chem*., 2012, vol. 48, p. 1309.
3. Grandberg, I.I., *Organicheskaya khimiya* (Organic Chemistry), Moscow: Drofa, 2001.
4. Avdeenko, A.P., Konovalova, S.A., Il'chenko, A.Ya., and Glinyanaya, N.M., *Russ. J. Org. Chem*., 2006, vol. 42, p. 56.
5. Pirozhenko, V.V. and Egorov, Yu.P., *Ukr. Khim. Zh*., 1992, vol. 58, p. 567.
6. Baldvin, J.E. and Norris, R.K., *J. Org. Chem*., 1981, vol. 46, p. 693.

7. Perrin, C.L. and Engler, R.E., *J. Org. Chem*., 1997, vol. 62, p. 687.
8. Avdeenko, A.P., Konovalova, S.A., and Sergeeva, A.G., *Russ. J. Org. Chem*., 2010, vol. 46, p. 830.
9. Avdeenko, A.P., Zhukova, S.A., Glinyanaya, N.M., and Konovalova, S.A., *Russ. J. Org. Chem*., 1999, vol. 35, p. 560.
10. Avdeenko, A.P., Glinyanaya, N.M., Konovalova, S.A., and Goncharova, S.A., *Russ. J. Org. Chem*., 2002, vol. 38, p. 692.
11. Avdeenko, A.P., Shishkina, S.V., Shishkin, O.V., Glinyanaya, N.M., Konovalova, S.A., and Goncharova, S.A., *Russ. J. Org. Chem*., 2002, vol. 38, p. 683.
12. Sykes, P., *A Guidebook to Mechanism in Organic Chemistry*, Harlow, Essex, England: Longman, 1986, 6th ed., p. 179.
13. Granovsky, A.A., *Firefly version 8*. http://classic.chem.msu.su/gran/firefly/index.html
14. Schmidt, M.W., Baldridge, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.H., Koseki, S., Matsunaga, N., Nguyen, K.A., Su, Sh., Windus, T.L., Dupuis, M., and Montgomery, J.A., *J. Comput. Chem*., 1993, vol. 14, p. 1347.
15. *Preparatyka Organiczna*, Polaczkowa, W., Ed., Warszawa: Panstwowe Wydawnictwa Techniczne, 1954, p. 429.