

Halogenation of N-Substituted *p*-Quinone Monoimines and *p*-Quinone Monooxime Esters: VIII.* Halogenation of *N*-Aroyl(arylsulfonyl)-2,6-di-*tert*-butyl-1,4-benzoquinone Monoimines and Their Reduced Forms

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Abstract—Chlorination of *N*-aroyl(arylsulfonyl)-2,6-di-*tert*-butyl-1,4-benzoquinone imines gave *Z* and *E* isomers of 4-arylsulfonylimino-2,6-di-*tert*-butyl-5,6-dichlorocyclohex-2-en-1-ones and *Z* isomers of 4-aroyl(arylsulfonyl)imino-2,6-di-*tert*-butyl-5,5,6-trichlorocyclohex-2-en-1-ones, in which the *tert*-butyl group on the *sp*³-hybridized carbon atom occupies exclusively the axial position. The formation of *Z/E*-isomeric structures is related to configurational stability of the chlorination products. The chlorination of 4-aroylamino-2,6-di-*tert*-butylphenols was found to be accompanied by replacement of one *tert*-butyl group by chlorine atom with formation of 4-aroylimino-6-*tert*-butyl-2,3,5,6-tetrachlorocyclohex-2-en-1-ones.

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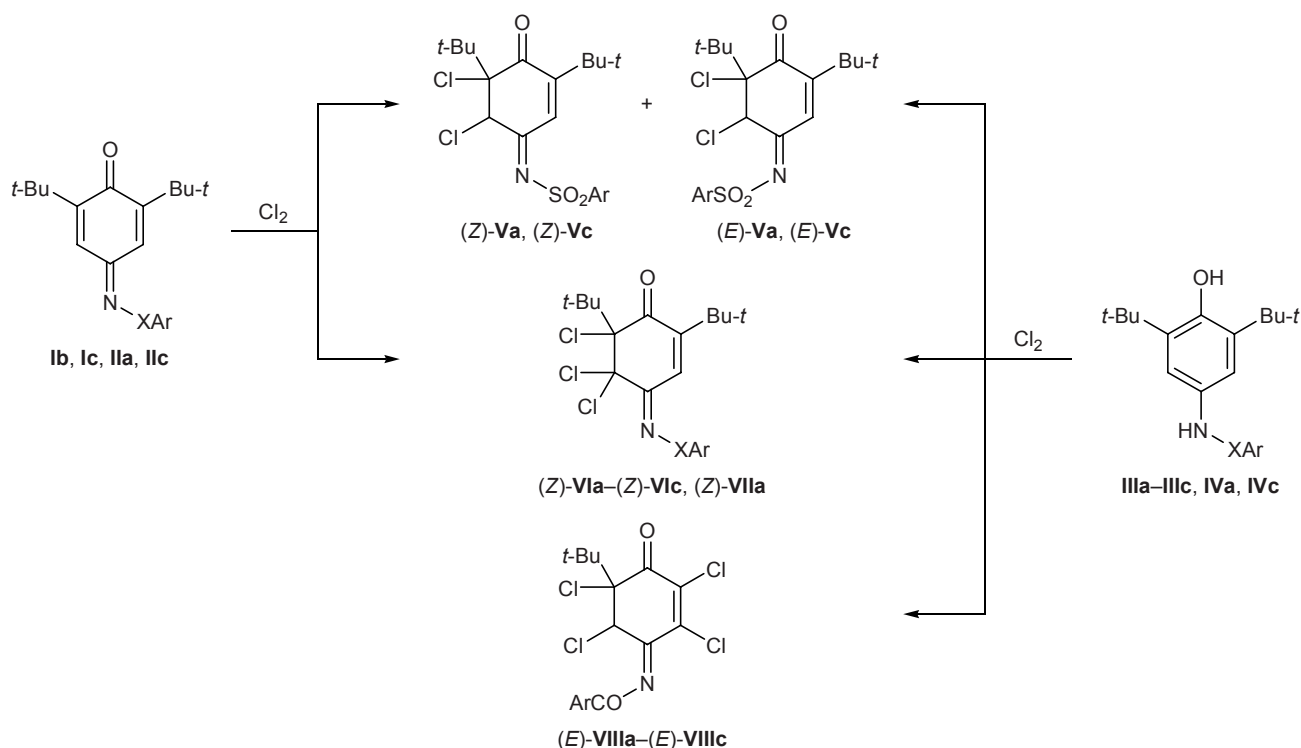
The presence of donor isopropyl groups in positions 2 and 6 of 1,4-benzoquinone monoimines was shown to favor formation of carbocationic intermediate in the halogenation of these compounds, making both *trans* and *cis* addition of the second halogen atom possible [1]. As a result, cyclohexene structures were obtained, in which the isopropyl group at the *sp*³-hybridized carbon atom occupies equatorial (*trans* addition) or axial position (*cis* addition); such a behavior was not reported previously for these compounds. Addition of a halogen molecule at the double C=C bond in the quinoid ring usually gives products with *trans*-diaxial orientation of the halogen atoms. It might be expected that introduction of a stronger electron-donating and bulkier *tert*-butyl group into positions 2 and 6 of the quinoid ring will favor formation of intermediate carbocation to even greater extent, so that the *tert*-butyl group in the adduct will occupy only the axial position.

In order to verify this assumption, we examined halogenation of *N*-aroyl(arylsulfonyl)-2,6-di-*tert*-

butyl-1,4-benzoquinone imines **I** and **II** and their reduction products **III** and **IV**. It should be noted that both *N*-aroyl- and *N*-arylsulfonyl-2,6-di-*tert*-butyl-1,4-benzoquinone imines **I** and **II** in solution undergo *Z/E* isomerization and that the corresponding activation barriers are considerably different. For example, the Gibbs energy of activation $\Delta G_{298}^\ddagger$ for the isomerization of *N*-aroyl-1,4-benzoquinone imines ranges from 44 to 46 kJ/mol [2], while the $\Delta G_{298}^\ddagger$ value for *N*-arylsulfonyl-1,4-benzoquinone imines varies from 65 to 80 kJ/mol [3]. This is also reflected in the ¹H NMR spectra of these compounds: the 3-H and 5-H signals in the spectra of **Ib** and **Ic** give one broadened singlet in a strong field, while signals from analogous protons in arylsulfonyl derivatives **IIa** and **IIc** appear as doublets, and the difference in their chemical shifts $\Delta\delta$ is about 1.2 ppm. Taking into account that *Z/E* isomerization could essentially affect the halogenation of *N*-arylsulfonyl-1,4-benzoquinone imines [4], some differences in the behavior of compounds **I** and **II** under halogenation conditions might be expected.

* For communication VII, see [1].

Scheme 1.



Ar = Ph (a), 4-MeC₆H₄ (b), 4-O₂NC₆H₄ (c); **I**, **III**, **VI**, X = CO; **II**, **IV**, **VII**, X = SO₂.

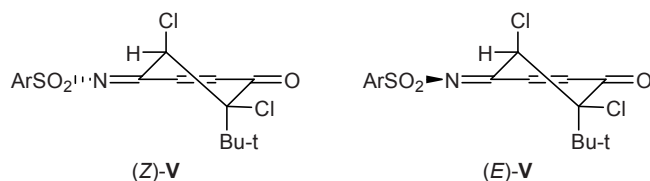
We found that compounds **I–IV** do not undergo bromination with molecular bromine. A probable reason is the large size of both *tert*-butyl group and bromine atom. In the reactions with **I** and **IV** we isolated from the reaction mixture 2,6-di-*tert*-butyl-1,4-benzoquinone, whereas compounds **II** and **III** remained intact.

The chlorination of compounds **I–IV** with gaseous chlorine was performed in acetic acid and acetic acid–dimethylformamide mixture (5:1) at different substrate-to-reagent ratios. Products of addition of one chlorine molecule, 4-arylsulfonylimino-2,6-di-*tert*-butyl-5,6-dichlorocyclohex-2-en-1-ones **Va** and **Vc** were obtained only from arylsulfonyl derivatives **IIa** and **IIc** (Scheme 1). As noted above, *N*-aroyl derivatives are characterized by considerably lower barrier to *Z/E* isomerization, whereas the ability of cyclohexene structures to undergo dehydrochlorination is strongly related to their isomer composition: dehydrochlorination of the *Z* isomers occurs more readily [4]. Therefore, we failed to isolate products of addition of one chlorine molecule to quinone imines **Ib** and **Ic**. Obviously, their fast dehydrochlorination is followed by addition of the second chlorine molecule. Compound **Vc** was isolated as individual substance, and com-

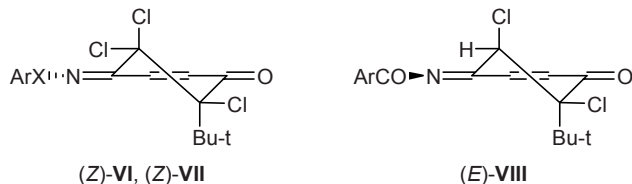
pound **Va** was isolated only as a mixture with **VIIa**. These data indicate high reactivity of the corresponding cyclohexene structures.

According to the ¹H NMR data, 4-arylsulfonylimino-2,6-di-*tert*-butyl-5,6-dichlorocyclohex-2-en-1-ones **Va** and **Vc** in solution exist as mixtures of *Z* and *E* isomers at a ratio of 1:1. Their spectra contain double sets of signals from 3-H and 5-H and protons in the *tert*-butyl groups. The ¹³C NMR spectra of **Va** and **Vc** also displayed double sets of signals. The chemical shift of C⁵ strongly depends on the orientation of the substituent on the nitrogen atom. *E* Isomers of **V** (*trans* orientation of the arylsulfonyl group with respect to the double C=C bond) are characterized by more upfield position of the C⁵ signal (δ_C 58.97 ppm), while the C⁵ signal of the *Z* isomers is located at δ_C 67.16 ppm. The signal from the *sp*³-hybridized C⁶ carbon atom appears in a fairly weak field, at δ_C 86.48 and 86.90 ppm for the *E* and *Z* isomers, respectively. We previously revealed a relation between the chemical shift of the *sp*³-C⁶ atom and orientation of the substituent attached thereto in 4-aroyl(arylsulfonyl)imino-3,5,6-trichloro-2,6-diisopropylcyclohex-2-en-1-ones (the C⁶ signal is displaced considerably downfield if the isopropyl group occupies the axial position) [1]. Therefore, axial

orientation of the *tert*-butyl group in molecules **V** was assumed.



By chlorination of quinone imines **IIb** and **IIc** and aminophenols **IIIa**, **IIIc**, and **IVa** at a substrate-to-chlorine ratio of 1:3 to 1:4.5 we obtained 4-arylsulfonylimino-2,6-di-*tert*-butyl-5,5,6-trichlorocyclohex-2-en-1-ones **VIa–VIc** and **VIIa** whose structure was confirmed by analysis of their ^1H NMR spectra. Compounds **VIa–VIc** displayed the 3-H signal at δ 6.83–6.84 ppm, while the chemical shift of 3-H in **VIIa** was 8.17 ppm. These data unambiguously indicate location of the 3-H proton at the double $\text{C}=\text{C}$ bond. In the ^{13}C NMR spectra of the products, the sp^3 -hybridized C^5 carbon atom resonated at δ_{C} 92.85–93.19 ppm, and the C^6 signal was located in the region δ_{C} 94.34–95.07 ppm. We believe that the downfield position of the C^6 signal indicates axial orientation of the *tert*-butyl group attached thereto.



The chlorination of aminophenols **IIIa–IIIc** in acetic acid led to the formation of anomalous products, 4-arylimino-6-*tert*-butyl-2,3,5,6-tetrachlorocyclohex-2-en-1-ones **VIIIa–VIIIc**, i.e., the reaction involved replacement of one *tert*-butyl group by chlorine atom. The chemical shifts of 5-H (δ 5.34–5.37 ppm) and C^6 (δ_{C} 84.25 ppm) in the ^1H and ^{13}C NMR spectra indicated axial orientation of the *tert*-butyl group in molecules **VIII** [1]. Presumably, compounds **VIII** are formed through intermediate 4-arylimino-2,6-di-*tert*-butyl-5,6-dichlorocyclohex-2-en-1-ones that are analogous to compounds **V**; the subsequent elimination of isobutane molecule gives *N*-aroyl-2-*tert*-butyl-5,6-dichloro-1,4-benzoquinone imine which takes up the second chlorine molecule at the double $\text{C}=\text{C}$ bond substituted by *tert*-butyl group. Polo et al. [5] previously reported on the replacement of the *tert*-butyl group in 2,6-di-*tert*-butyl-1,4-benzoquinone 4-oxime by chlorine in the reaction with S_2Cl_2 in the presence of

ethyl(diisopropyl)amine and *N*-chlorosuccinimide in tetrahydrofuran [5].

The structure of cyclohexenone derivatives **VIa** and **VIIa** was unambiguously proved by X-ray analysis of their single crystals (Figs. 1, 2). The results indicated considerable steric strain in their molecules due to the presence of bulky substituents. Structure **VIa** is characterized by the following short intramolecular contacts: $\text{Cl}^2 \cdots \text{C}^{12}$ 3.18, $\text{C}^4 \cdots \text{C}^{13}$ 2.99, $\text{C}^4 \cdots \text{H}^{13\text{c}}$ 2.48, $\text{C}^3 \cdots \text{H}^{10\text{a}}$ 2.73, $\text{C}^3 \cdots \text{H}^{10\text{c}}$ 2.74, $\text{C}^3 \cdots \text{H}^{13\text{c}}$ 2.69, $\text{C}^{10} \cdots \text{H}^3$ 2.41, $\text{H}^3 \cdots \text{H}^{10\text{a}}$ 2.25, and $\text{H}^3 \cdots \text{H}^{10\text{c}}$ 2.15 Å; the sums of the corresponding van der Waals radii [6] are $\text{Cl} \cdots \text{C}$ 3.61, $\text{C} \cdots \text{C}$ 3.42, $\text{C} \cdots \text{H}$ 2.87, and $\text{H} \cdots \text{H}$ 2.25 Å. As a result, some bond angles are distorted. The bond angles $\text{C}^3\text{C}^2\text{C}^7$ [$122.9(2)^\circ$] and $\text{C}^6\text{C}^5\text{Cl}^2$ [$114.3(2)^\circ$] are larger than $\text{C}^1\text{C}^2\text{C}^7$ [$118.6(2)^\circ$] and $\text{C}^4\text{C}^5\text{Cl}^2$ [$110.9(2)^\circ$]. In addition, the bond angles $\text{C}^6\text{C}^{11}\text{C}^{13}$ and $\text{C}^6\text{C}^{11}\text{C}^{12}$ are increased to $112.7(2)$ and $113.5(2)^\circ$, respectively, as compared to the other bond angles at the quaternary carbon atoms in the *tert*-butyl groups [$107.3(2)$ – $111.2(2)^\circ$]. Steric strain in molecule **VIa** also induces appreciable extension of the C^1 – C^6 [1.544(3) Å] and C^6 – C^{11} bonds [1.550(3) Å]; the corresponding average values are 1.51 [7] and 1.53 Å, respectively. Difference in the lengths of the chemically equivalent C^5 – Cl^2 [1.762(2) Å] and C^5 – Cl^3 bonds [1.800(2) Å] should also be noted. The C^6 – Cl^1 bond length is intermediate between the above values, 1.789(2) Å.

The axial orientation of the *tert*-butyl group in molecule **VIIIa** gives rise to short intramolecular contacts $\text{Cl}^4 \cdots \text{H}^{10\text{c}}$ 2.67 Å (the sum of the corresponding van der Waals radii is 3.06 Å) and $\text{Cl}^4 \cdots \text{H}^{8\text{c}}$ 2.76 Å (3.06 Å). Attractive interaction $\text{N}^1 \cdots \text{H}^{21\text{a}}$ 2.48 Å (2.67 Å) is observed between the H^1 atom and the aromatic ring; this interaction cannot be regarded as intramolecular hydrogen bond, for the $\text{C}^{13}\text{H}^{21\text{a}}\text{N}^1$ angle is 103° . Among structural features common for both molecules, shortening of the N^1 – C^4 bond to 1.263(2) Å in **VIa** and 1.267(2) Å in **VIIIa** against average bond length 1.279 Å should be noted.

The existence of compounds **V–VIII** as *Z* and *E* isomers is related to their configurational stability and is determined by steric effect of the substituents in positions 3 and 5. For example, the hydrogen atom at the sp^2 -hybridized C^3 carbon atom and chlorine and hydrogen atoms at the sp^3 -hybridized C^5 atom in cyclohexene structure **V** exert equivalent steric effects on the arylsulfonyl group, and compounds **V** in solution exist as equimolar mixtures of *Z* and *E* isomers. Steric



effect on the ArX group of two chlorine atoms at the sp^3 -hybridized C^5 atom in compounds **VI** and **VII** is much stronger than that of the chlorine atom at the sp^2 -hybridized C^3 atom; therefore, these compounds in solution exist only as *Z* isomers. By contrast, steric effect on the ArCO group of the Cl and H atoms on C^5 (sp^3) in structure **VIII** is considerably weaker than the effect of Cl on C^3 (sp^2), and compounds **VIII** exist only as *E* isomers.

Quinone oxime esters, 4-aryloxyimino- and 4-arylsulfonyloxyimino-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-ones **IXa–IXc** and **Xa–Xc** [Ar = Ph (**a**), 4-MeC₆H₄ (**b**), 4-O₂NC₆H₄ (**c**)] failed to undergo halogenation.

Thus chlorination of *N*-aroyl(arylsulfonyl)-2,6-di-*tert*-butyl-1,4-benzoquinone imines gives cyclohexenone derivatives in which the *tert*-butyl group at the sp^3 -hybridized carbon atom occupies exclusively the axial position, indicating that the process involves formation of intermediate carbocation and subsequent *syn*-addition of the second chlorine atom [8]. The *Z/E* isomer ratio of the addition products is determined by their configurational stability.

EXPERIMENTAL

The ¹H and ¹³C NMR spectra were recorded from solutions in CDCl₃ on a Varian VXR-300 spectrometer operating at 300 MHz; the chemical shifts were measured relative to tetramethylsilane. Thin-layer chromatography was performed on Silufol UV-254 plates; samples were applied as solutions in chloroform, and the chromatograms were eluted with benzene–hexane (10:1); spots were visualized under UV light.

The X-ray diffraction data for single crystals of compound **VIa** and **VIIIa** were acquired at 20°C using an Xcalibur-3 diffractometer (MoK_α irradiation, CCD detector, graphite monochromator, ω -scanning, $2\theta_{\max}$ = 50°). The structures were solved by the direct method and were refined with respect to F^2 by full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms using SHELXTL software package [9]. The positions of hydrogen atoms were determined by difference syntheses of electron density and were refined using the riding model with unfixed U_{iso} (**VIa**) or in isotropic approximation (**VIIIa**).

Compound **VIa**. Monoclinic crystals, C₂₁H₂₄Cl₃NO₂, with the following unit cell parameters (293 K): a = 26.151(4), b = 8.214(2), c = 20.897(3) Å; β = 108.294(13)°; V = 4261.8(1) Å³; M 428.76; Z = 8; space group $C2/c$; d_{calc} = 1.336 g/cm³; $\mu(\text{MoK}_{\alpha})$ =

0.45 mm^{−1}; $F(000)$ = 1792. Total of 10977 reflections were measured, 3677 of which were independent (R_{int} = 0.025). Absorption by the crystal was taken into account on a semiempirical level, $T_{\min}$ = 0.948, $T_{\max}$ = 0.956 [10]. The final divergence factors were wR_2 = 0.107 (for 3677 reflections) and R_1 = 0.040 [for 2623 reflections with $F > 4\sigma(F)$, S = 0.932].

Compound **VIIIa**. Monoclinic crystals, C₁₇H₁₅Cl₄NO₂, with the following unit cell parameters (100 K): a = 7.9010 (2), b = 20.2480 (4), c = 11.1500 (2) Å; β = 96.399 (2)°, V = 1772.66 (2) Å³; M 407.10; Z = 4; space group $P2_1/n$; d_{calc} = 1.525 g/cm³; $\mu(\text{MoK}_{\alpha})$ = 0.677 mm^{−1}; $F(000)$ = 832. Total of 12382 reflections were measured, 3064 of which were independent (R_{int} = 0.028). Absorption by the crystal was taken into account on a semiempirical level, $T_{\min}$ = 0.850, $T_{\max}$ = 0.940. The final divergence factors were wR_2 = 0.063 (for 3024 reflections) and R_1 = 0.028 [for 2938 reflections with $F > 4\sigma(F)$, S = 1.054].

The complete sets of crystallographic data for compounds **VIa** and **VIIIa**, including the final coordinates of atoms and geometric parameters of molecules, were deposited to the Cambridge Crystallographic Data Center, entry nos. CCDC 632049 and CCDC 632048, respectively.

Initial compounds **Ib**, **Ic**, and **IIIa–IIIc** were reported in [2], and **IIa**, **IIc**, **IVa**, and **IVc**, in [3, 11].

Quinone oxime ethers **IXa–IXc** and **Xa–Xc** were synthesized by acylation of 2,6-di-*tert*-butyl-4-nitrosophenol with the corresponding substituted benzoyl chlorides or arenesulfonyl chlorides in diethyl ether in the presence of triethylamine according to the procedure described in [12].

Chlorination of quinone imines Ia, Ib, IIa, and IIc and aminophenols IIIa–IIIc, IVa, and IVc. A stream of dry chlorine was passed at a flow rate of 15–20 ml/min at 35–75°C through a solution of 2 mmol of quinone imine **Ia**, **Ib**, **IIa**, or **IIc** or aminophenol **IIIa–IIIc**, **IVa**, or **IVc** in 3 ml of chloroform, acetic acid, or 1:5 DMF–AcOH mixture. The substrate-to-chlorine ratio was controlled by the gain in weight and was varied from 1:1 to 1:4.5. After 24 h, the precipitate was filtered off and recrystallized from acetic acid.

Insofar as compound **Va** was isolated in a mixture with **VIIa**, its melting point and elemental composition were not determined.

***N*-(3,5-Di-*tert*-butyl-5,6-dichloro-4-oxocyclohex-2-en-1-ylidene)benzenesulfonamide (Va).** ¹H NMR

spectrum, δ , ppm: *Z* isomer: 7.98 d (1H, 2-H, $^4J = 2.1$ Hz), 4.97 d (1H, 6-H, $^4J = 2.1$ Hz), 1.18 d and 1.31 d (9H each, *t*-Bu), 7.58–8.07 m (5H, Ph); *E* isomer: 6.80 d (1H, 2-H, $^4J = 2.1$ Hz), 6.32 d (1H, 6-H, $^4J = 2.1$ Hz), 1.18 d and 1.31 d (9H each, *t*-Bu), 7.58–8.07 m (5H, Ph).

***N*-(3,5-Di-*tert*-butyl-5,6-dichloro-4-oxocyclohex-2-en-1-ylidene)-4-nitrobenzenesulfonamide (Vc)** (a mixture of *Z* and *E* isomers at a ratio of 55:45). Yield 63%, mp 168–170°C. ^1H NMR spectrum, δ , ppm, *Z* isomer: 7.90 d (1H, 2-H, $^4J = 2.1$ Hz), 4.95 d (1H, 6-H, $^4J = 2.1$ Hz), 1.19 d and 1.33 d (9H each, *t*-Bu), 8.18–8.47 d.d (4H, H_{arom} , $J = 9.0$ Hz); *E* isomer: 6.79 d (1H, 2-H, $^4J = 2.1$ Hz), 6.19 d (1H, 6-H, $^4J = 2.1$ Hz), 1.19 d and 1.33 d (9H each, *t*-Bu), 8.18–8.47 d.d (4H, H_{arom} , $J = 9.0$ Hz). ^{13}C NMR spectrum, δ_{C} , ppm: 189.09, 188.94 (C^4); 171.98, 171.95 (C^1); 162.72, 159.75 (C^3); 150.61 (C^4); 145.07, 144.81 (C^1); 135.65, 127.91 (C^2); 128.96, 128.77 (C^2 , C^6); 124.41, 124.34 (C^3 , C^5); 86.90, 86.48 (C^5); 67.16, 58.97 (C^6); 41.71, 41.48, 37.35, 37.01 (CMe_3); 29.00, 28.22, 28.10 (Me_3C). Found, %: Cl 14.67, 15.01. $\text{C}_{20}\text{H}_{24}\text{Cl}_2\text{N}_2\text{O}_5$. Calculated, %: Cl 14.92.

***N*-(3,5-Di-*tert*-butyl-5,6,6-trichloro-4-oxocyclohex-2-en-1-ylidene)benzamide (VIa).** Yield 57%, mp 108–110°C. ^1H NMR spectrum, δ , ppm: 6.84 s (1H, 2-H), 1.26 s and 1.23 s (9H each, *t*-Bu), 7.51–8.02 m (5H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 187.52 (C^4), 178.02 ($\text{C}=\text{O}$, amide), 159.25 (C^1), 156.09 (C^3), 134.21 (C^4), 131.95 (C^1), 129.51 (C^2 , C^6), 128.95 (C^3 , C^5), 128.46 (C^2), 94.34 (C^5), 92.85 (C^6), 42.97 and 36.81 (Me_3C), 29.52 and 28.99 (Me_3C). Found, %: Cl 24.52, 24.77. $\text{C}_{21}\text{H}_{24}\text{Cl}_3\text{NO}_2$. Calculated, %: Cl 24.80.

***N*-(3,5-Di-*tert*-butyl-5,6,6-trichloro-4-oxocyclohex-2-en-1-ylidene)-4-methylbenzamide (VIb).** Yield 56%, mp 110–112°C. ^1H NMR spectrum, δ , ppm: 6.83 s (1H, 2-H), 1.26 s and 1.22 s (9H each, *t*-Bu), 7.31–7.91 d.d (4H, H_{arom} , $J = 8.1$ Hz), 2.45 s (3H, MeC_6H_4). ^{13}C NMR spectrum, δ_{C} , ppm: 187.67 (C^4), 178.03 ($\text{C}=\text{O}$, amide), 159.02 (C^1), 155.95 (C^3), 145.32 (C^4), 129.68 (C^2 , C^6), 129.62 (C^3 , C^5), 129.52 (C^1), 128.58 (C^2), 94.40 (C^6), 93.04 (C^5), 43.01 and 38.81 (Me_3C), 29.56 and 29.02 (Me_3C), 21.86 (MeC_6H_4). Found, %: Cl 23.68, 23.90. $\text{C}_{22}\text{H}_{26}\text{Cl}_3\text{NO}_2$. Calculated, %: Cl 24.02.

***N*-(3,5-Di-*tert*-butyl-5,6,6-trichloro-4-oxocyclohex-2-en-1-ylidene)-4-nitrobenzamide (VIc).** Yield 67%, mp 180–182°C. ^1H NMR spectrum, δ , ppm: 6.84 s (1H, 2-H), 1.26 s and 1.25 s (9H each, *t*-Bu),

8.19–8.39 d.d (4H, H_{arom} , $J = 8.7$ Hz). Found, %: Cl 22.07, 22.35. $\text{C}_{21}\text{H}_{23}\text{Cl}_3\text{N}_2\text{O}_4$. Calculated, %: Cl 22.45.

***N*-(3,5-Di-*tert*-butyl-5,6,6-trichloro-4-oxocyclohex-2-en-1-ylidene)benzenesulfonamide (VIIa)** was synthesized from compound IVa. Yield 58%, mp 150–152°C. ^1H NMR spectrum, δ , ppm: 8.17 s (1H, 2-H), 1.36 s and 1.19 s (9H each, *t*-Bu), 7.58–8.07 m (5H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 187.16 (C^4), 167.25 (C^3), 158.33 (C^1), 139.77 (C^1), 133.68 (C^4), 129.15 (C^3 , C^5), 128.11 (C^2), 127.36 (C^2 , C^6), 94.63 (C^6), 93.21 (C^5), 42.82 and 37.47 (Me_3C), 29.48 and 29.07 (Me_3C). Found, %: Cl 22.81, 22.99. $\text{C}_{20}\text{H}_{24}\text{Cl}_3\text{NO}_3\text{S}$. Calculated, %: Cl 22.88.

***N*-(5-*tert*-Butyl-2,3,5,6-tetrachloro-4-oxocyclohex-2-en-1-ylidene)benzamide (VIIa).** Yield 60%, mp 104–106°C. ^1H NMR spectrum, δ , ppm: 5.35 s (1H, 6-H), 1.21 s (9H, *t*-Bu), 7.50–7.98 m (5H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 181.63 (C^4), 177.85 ($\text{C}=\text{O}$, amide), 155.64 (C^1), 144.08 and 141.50 (C^2 , C^3), 134.65 (C^4), 130.89 (C^1), 129.65 (C^2 , C^6), 128.93 (C^3 , C^5), 84.25 (C^5), 59.00 (C^6), 42.43 (Me_3C), 27.45 (Me_3C). Found, %: Cl 34.56, 34.78. $\text{C}_{17}\text{H}_{15}\text{Cl}_4\text{NO}_2$. Calculated, %: Cl 34.83.

***N*-(5-*tert*-Butyl-2,3,5,6-tetrachloro-4-oxocyclohex-2-en-1-ylidene)-4-methylbenzamide (VIIb).** Yield 42%, mp 158–160°C. ^1H NMR spectrum, δ , ppm: 5.34 s (1H, 6-H), 1.21 s (9H, *t*-Bu), 7.30–7.86 d.d (4H, H_{arom} , $J = 8.1$ Hz), 2.45 s (3H, MeC_6H_4). Found, %: Cl 33.57, 33.81. $\text{C}_{18}\text{H}_{17}\text{Cl}_4\text{NO}_2$. Calculated, %: Cl 33.67.

***N*-(5-*tert*-Butyl-2,3,5,6-tetrachloro-4-oxocyclohex-2-en-1-ylidene)-4-nitrobenzamide (VIIc).** Yield 59%, mp 162–164°C. ^1H NMR spectrum, δ , ppm: 5.37 s (1H, 6-H), 1.23 s (9H, *t*-Bu), 8.14–8.39 d.d (4H, H_{arom} , $J = 9.0$ Hz). Found, %: Cl 31.15, 31.42. $\text{C}_{17}\text{H}_{14}\text{Cl}_4\text{N}_2\text{O}_4$. Calculated, %: Cl 31.37.

Bromination of quinone imines Ib, Ic, IIa, and IIc and aminophenols IIIc and IVc (general procedure). Compound Ib, Ic, IIa, IIc, IIIc, or IVc, 2 mmol, was dissolved in 3 ml of DMF–AcOH (1:5), a solution of bromine in the same solvent mixture was added dropwise under stirring to a substrate-to-bromine ratio of 1:5, and the mixture was heated at 70–80°C.

Chlorination of *p*-quinone oxime esters IXa–IXc and Xa–Xc (general procedure). A stream of dry chlorine was passed at a flow rate of 15–20 ml/min at 65–75°C through a solution of 2 mmol of quinone

oxime ether **IXa–IXc** or **Xa–Xc** in 3 ml of AcOH, DMF–AcOH (1 : 5), or MeOH until a substrate-to-chlorine ratio of 1 : 7 was attained. After 24 h, the precipitate was filtered off and recrystallized from acetic acid. We thus isolated unreacted initial compounds.

Bromination of *p*-quinone oxime esters IXc and Xc (general procedure). Compound **IXc** or **Xc**, 2 mmol, was dissolved in 3 ml of DMF, DMF–AcOH (1 : 5), or MeOH, and a solution of bromine in the same solvent was added dropwise under stirring to a substrate-to-bromine ratio of 1 : 5. The mixture was heated to 70°C and kept for several minutes at that temperature. After cooling, the precipitate was filtered off, washed with acetic acid, and recrystallized from acetic acid. Unchanged initial compounds were thus isolated.

REFERENCES

1. Avdeenko, A.P., Pirozhenko, V.V., Shishkin, O.V., Shishkina, S.V., Konovalova, S.A., and Ludchenko, O.N., *Russ. J. Org. Chem.*, 2008, vol. 44, p. 542.
2. Pirozhenko, V.V. and Avdeenko, A.P., *Russ. J. Org. Chem.*, 1995, vol. 31, p. 1514.
3. Belov, V.V., Loban', S.V., Burmistrov, K.S., and Prosyannik, A.V., *Zh. Org. Khim.*, 1983, vol. 19, p. 825.
4. Avdeenko, A.P. and Konovalova, S.A., *Russ. J. Org. Chem.*, 2006, vol. 42, p. 349.
5. Polo, C., Ramos, V., and Torroba, T., *Tetrahedron*, 1998, vol. 54, p. 223.
6. Zefirov, Yu.V. and Zorkii, P.M., *Usp. Khim.*, 1989, vol. 58, p. 713.
7. Burgi, H.-B. and Dunitz, J.D., *Structure Correlation*, Weinheim: VCH, 1994, vol. 2, p. 741.
8. Avdeenko, A.P., Konovalova, S.A., Il'chenko, A.Ya., and Glinyanaya, N.M., *Russ. J. Org. Chem.*, 2006, vol. 42, p. 64.
9. Sheldrick, G.M., *SHELXTL PLUS. PC Version. A System of Computer Programs for the Determination of Crystal Structure from X-ray Diffraction Data. Rev. 5.1*, 1998.
10. Blessing, R.H., *Acta Crystallogr., Sect. A*, 1995, vol. 51, p. 33.
11. Burmistrov, K.S., *Doctoral (Chem.) Dissertation*, Dnepropetrovsk, 1990.
12. Titov, E.A. and Burmistrov, S.I., *Ukr. Khim. Zh.*, 1960, vol. 26, p. 744.