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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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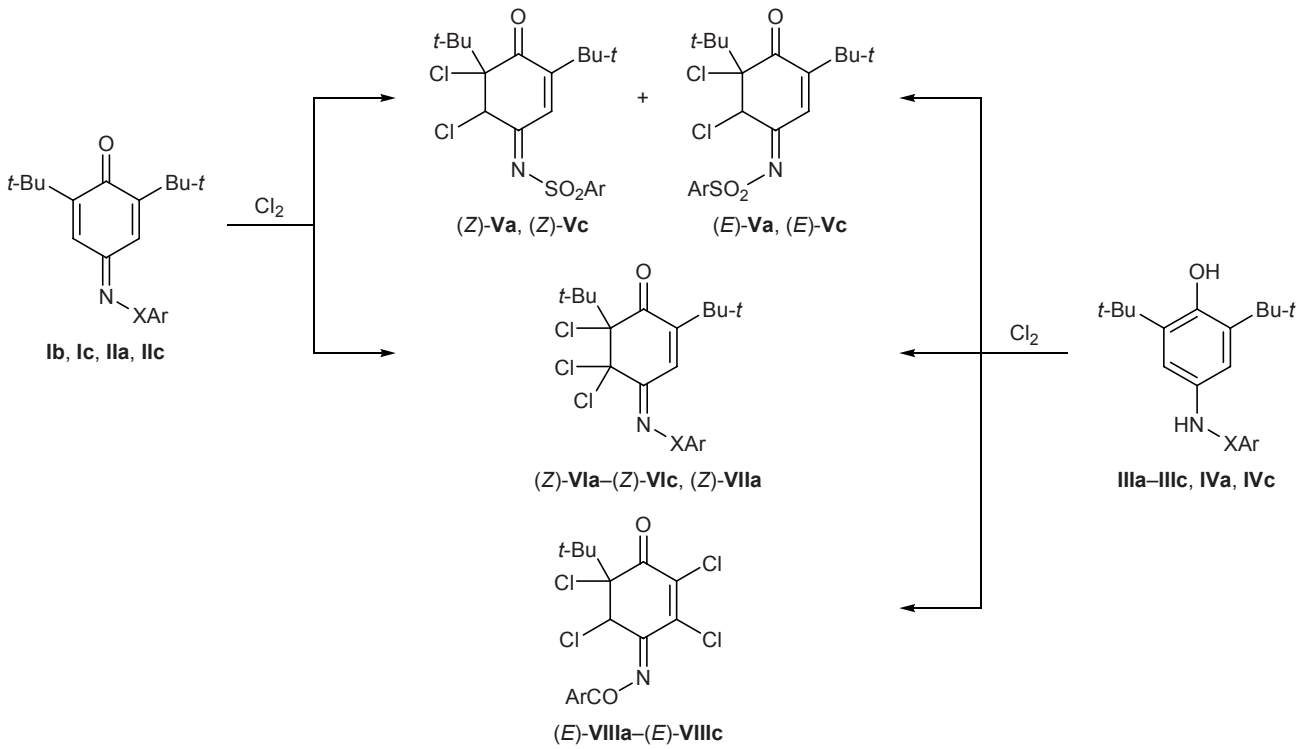
The presence of donor isopropyl groups in positions *2* and *6* of 1,4-benzoquinone monoimines was shown to favor formation of carbocationic intermediate in the halogenation of these compounds, making both *trans* and *cis* addition of the second halogen atom possible [1]. As a result, cyclohexene structures 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 $\Delta G^{\neq}_{298}$ for the isomerization of *N*-aroyl-1,4-benzoquinone imines ranges from 44 to 46 kJ/mol [2], while the $\Delta G^{\neq}_{298}$ value for *N*-arylsulfonyl-1,4-benzoquinone imines varies from 65 to 80 kJ/mol [3]. This is also reflected in the ^{1}H 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.



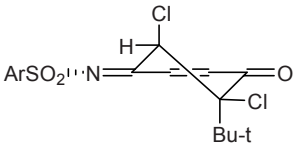
Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-$O_2NC_6H_4$ (**c**); **I**, **III**, **VI**, X = CO; **II**, **IV**, **VII**, X = SO_2.

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.

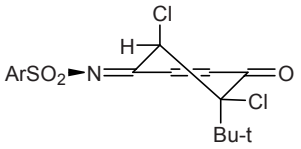
The chlorination of compounds **I**–**IV** with gaseous chlorine was performed in acetic acid and acetic acid–dimethylformamide mixture (5:1) at different substrate-to-reagent ratios. Products of addition of one chlorine molecule, 4-arylsulfonylimino-2,6-di-*tert*-butyl-5,6-dichlorocyclohex-2-en-1-ones **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 compound **Va** was isolated only as a mixture with **VIIa**. These data indicate high reactivity of the corresponding cyclohexene structures.

According to the ^{1}H 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 ^{13}C NMR spectra of **Va** and **Vc** also displayed double sets of signals. The chemical shift of C^5 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 C^5 signal (δ_C 58.97 ppm), while the C^5 signal of the *Z* isomers is located at δ_C 67.16 ppm. The signal from the sp^3-hybridized C^6 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-C^6 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 C^6 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.

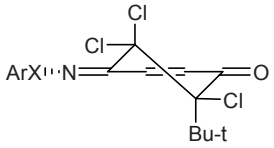


(*Z*)-**V**

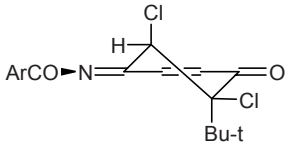


(*E*)-**V**

By chlorination of quinone imines **Ib** and **Ic** and aminophenols **IIIa**, **IIIc**, and **IVa** at a substrate-to-chlorine ratio of 1:3 to 1:4.5 we obtained 4-aroyl(arylsulfonyl)imino-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 ^{1}H 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 C=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.



(*Z*)-**VI**, (*Z*)-**VII**



(*E*)-**VIII**

The chlorination of aminophenols **IIIa**–**IIIc** in acetic acid led to the formation of anomalous products, 4-aroylimino-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 ^{1}H 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-aroylimino-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 C=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 **VIIIa** 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: $Cl^2\cdots C^{12}$ 3.18, $C^4\cdots C^{13}$ 2.99, $C^4\cdots H^{13c}$ 2.48, $C^3\cdots H^{10a}$ 2.73, $C^3\cdots H^{10c}$ 2.74, $C^3\cdots H^{13c}$ 2.69, $C^{10}\cdots H^3$ 2.41, $H^3\cdots H^{10a}$ 2.25, and $H^3\cdots H^{10c}$ 2.15 Å; the sums of the corresponding van der Waals radii [6] are Cl···C 3.61, C···C 3.42, C···H 2.87, and H···H 2.25 Å. As a result, some bond angles are distorted. The bond angles $C^3C^2C^7$ [122.9(2)°] and $C^6C^5Cl^2$ [114.3(2)°] are larger than $C^1C^2C^7$ [118.6(2)°] and $C^4C^5Cl^2$ [110.9(2)°]. In addition, the bond angles $C^6C^{11}C^{13}$ and $C^6C^{11}C^{12}$ are increased to 112.7(2) and 113.5(2)°. respectively, as compared to the other bond angles at the quaternary carbon atoms in the *tert*-butyl groups [107.3(2)–111.2(2)°]. 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 $Cl^4\cdots H^{10c}$ 2.67 Å (the sum of the corresponding van der Waals radii is 3.06 Å) and $Cl^4\cdots H^{8c}$ 2.76 Å (3.06 Å). Attractive interaction $N^1\cdots H^{21a}$ 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 $C^{13}H^{21a}N^1$ 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

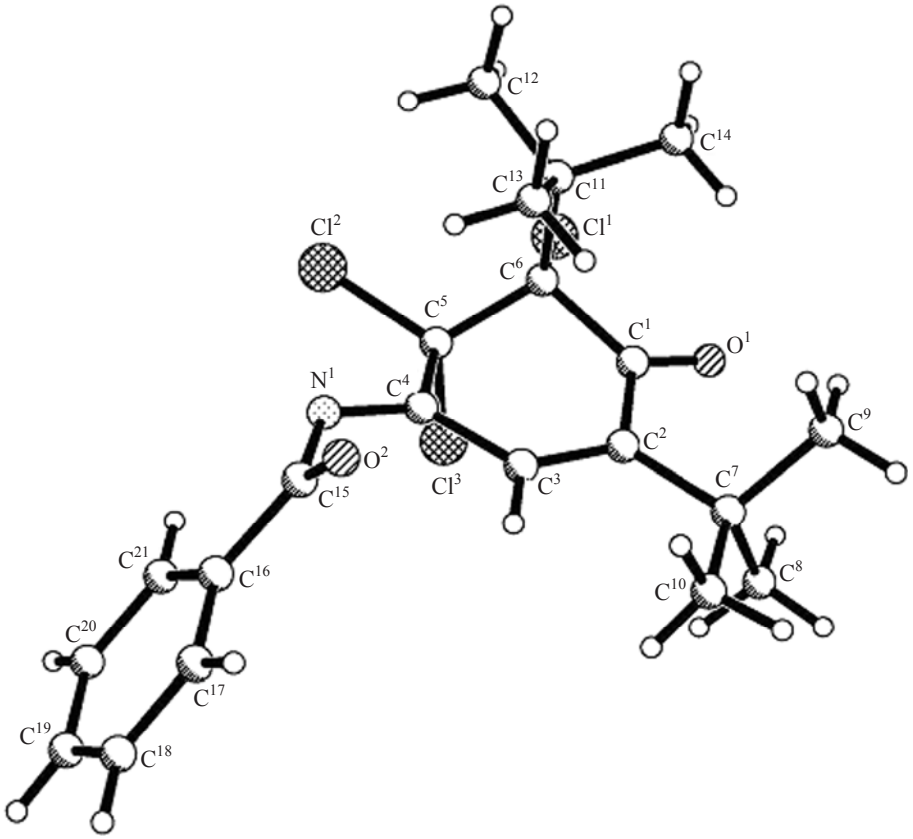


Fig. 1. Structure of the molecule of *N*-(3,5-di-*tert*-butyl-5,6,6-trichloro-4-oxocyclohex-2-en-1-ylidene)benzamide (**VIa**) according to the X-ray diffraction data.

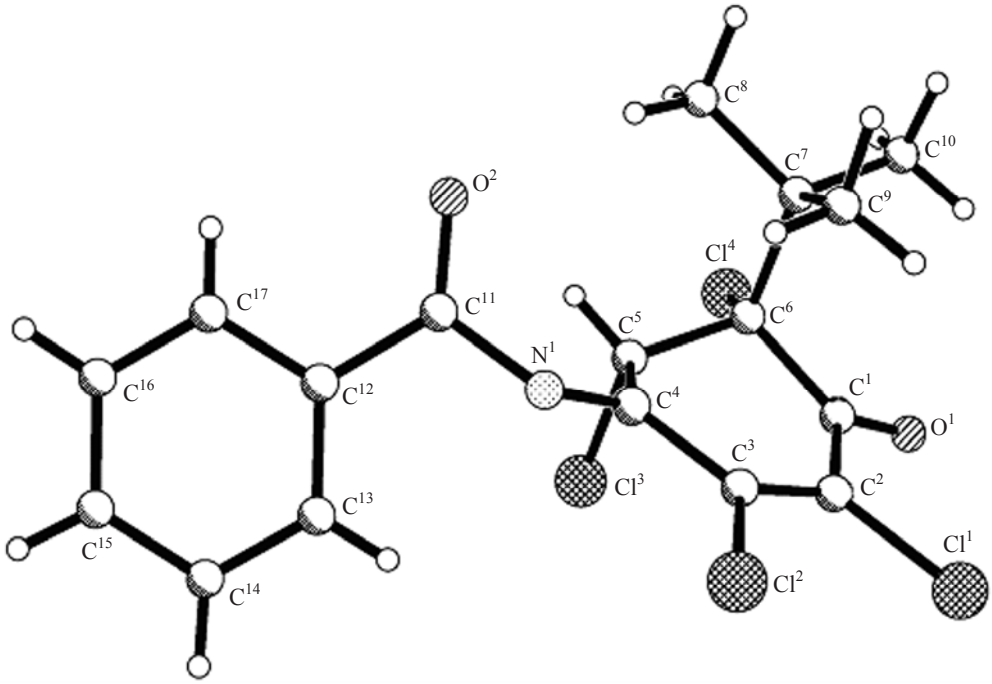


Fig. 2. Structure of the molecule of *N*-(5-*tert*-butyl-2,3,5,6-tetrachloro-4-oxocyclohex-2-en-1-ylidene)benzamide (**VIIIa**) according to the X-ray diffraction data.

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-aroyloxyimino- and 4-arylsulfonyloxymino-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-ones **IXa**–**IXc** and **Xa**–**Xc** [Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-$O_2NC_6H_4$ (**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 ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ 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, $C_{21}H_{24}Cl_3NO_2$, 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) Å^3; M 428.76; Z = 8; space group $C2/c$; d_{calc} = 1.336 g/cm^3; μ(MoK_α) = 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, $C_{17}H_{15}Cl_4NO_2$, 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) Å^3; M 407.10; Z = 4; space group $P2_1/n$; d_{calc} = 1.525 g×cm^{-3}; μ(MoK_α) = 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. ^{1}H 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 (**C**Me_3); 29.00, 28.22, 28.10 (**Me**$_3$C). Found, %: Cl 14.67, 15.01. $C_{20}H_{24}Cl_2N_2O_5$. 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. ^{1}H 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 (C=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_3**C**), 29.52 and 28.99 (**Me**$_3$C). Found, %: Cl 24.52, 24.77. $C_{21}H_{24}Cl_3NO_2$. 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. ^{1}H 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 (C=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_3**C**), 29.56 and 29.02 (Me_3C), 21.86 (**Me**C_6H_4). Found, %: Cl 23.68, 23.90. $C_{22}H_{26}Cl_3NO_2$. 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. ^{1}H 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. $C_{21}H_{23}Cl_3N_2O_4$. 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. ^{1}H 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_3**C**), 29.48 and 29.07 (Me_3C). Found, %: Cl 22.81, 22.99. $C_{20}H_{24}Cl_3NO_3S$. Calculated, %: Cl 22.88.

***N*-(5-*tert*-Butyl-2,3,5,6-tetrachloro-4-oxocyclohex-2-en-1-ylidene)benzamide (VIIIa).** Yield 60%, mp 104–106°C. ^{1}H 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 (C=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_3**C**), 27.45 (**Me**$_3$C). Found, %: Cl 34.56, 34.78. $C_{17}H_{15}Cl_4NO_2$. Calculated, %: Cl 34.83.

***N*-(5-*tert*-Butyl-2,3,5,6-tetrachloro-4-oxocyclohex-2-en-1-ylidene)-4-methylbenzamide (VIIIb).** Yield 42%, mp 158–160°C. ^{1}H 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. $C_{18}H_{17}Cl_4NO_2$. Calculated, %: Cl 33.67.

***N*-(5-*tert*-Butyl-2,3,5,6-tetrachloro-4-oxocyclohex-2-en-1-ylidene)-4-nitrobenzamide (VIIIc).** Yield 59%, mp 162–164°C. ^{1}H 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. $C_{17}H_{14}Cl_4N_2O_4$. 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.

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