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Halogenation of *N*-Substituted *p*-Quinonimines and *p*-Quinone Oxime Esters: I. Chlorination and Bromination of 4-Aroyloxyimino- and Arylsulfonyloxyimino-2,5-cyclohexadienones*

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Abstract—Chlorine and bromine addition to 4-aroyloxyimino- and 4-arylsulfonyloxymino-3-methyl-2,5-cyclohexadienones initially occurs at the $C^5=C^6$ double bond. The second chlorine molecule adds at both $C^2=C^3$ and $C^5=C^6$ double bonds. The chlorination of 2,5-dialkyl-substituted 4-aroyloxyimino- and 4-arylsulfonyloxymino-2,5-cyclohexadienones involves either of the C=C bonds in the quinoid ring.

In the previous communications we reported the results of our studies on chlorination and bromination of *N*-arylsulfonyl-1,4-quinonimines [1] and 4-aroyl(arylsulfonyl)oxyimino-2,5-cyclohexadienones [2]. Halogenation of 4-aroyl(arylsulfonyl)oxyimino-2,6-(3,5)-dimethyl-2,5-cyclohexadienones was studied in detail in [3]. Halogenation of 4-aroyloxyimino-2(3)-methyl(2,5-dimethyl)-2,5-cyclohexadienones [4, 5], 4-aroyl(arylsulfonyl)oxyimino-2,3-dimethyl-2,5-cyclohexadienones, 4-aroyl(arylsulfonyl)oxyimino-6-isopropyl-3-methyl-2,5-cyclohexadienones, and 4-aroyl(arylsulfonyl)oxyimino-2,6-di-*tert*-butyl-2,5-cyclohexadienones [6] and chlorination of 4-aroyloxyimino-2,6-diisopropyl-2,5-cyclohexadienones [5] were also examined. These studies allowed us to reveal some general relations holding in the halogenation processes of 1,4-benzoquinone oxime esters [6].

4-Arylsulfonyloxyimino derivatives **I** (X = $ArSO_2$) were not studied in [4, 5], and only the first stage of halogenation of 4-aroyloxyimino-3-methyl-2,5-cyclohexadienones **I** (X = ArCO) was examined. The goal of the present work was to obtain new differently halogenated products and reveal general relations inherent to halogenation of 1,4-benzoquinone oxime esters **I** (X = ArCO, $ArSO_2$).

4-Aroyl(arylsulfonyl)oxyimino-3-methyl-2,5-cyclohexadienones **I** exist as *E* isomers where the aroyloxy or arylsulfonyloxy group is located *trans* with respect to the $C^2=C^3$ bond. The chlorination of compounds **I** was performed using molecular chlorine in various solvents: ethanol, dimethylformamide (DMF), and DMF–acetic acid mixtures. The bromination was effected with bromine in acetic acid or chloroform. The results of halogenation of compounds **Ia**–**Ii** are illustrated by Scheme 1.

In all cases, the first halogenation stage occurs at the $C^5=C^6$ bond of the quinoid ring, i.e., at the double bond containing no substituents. The products are the corresponding 4-aroyl(arylsulfonyl)oxyimino-5,6-dihalo-3-methyl-2-cyclohexenones **II** and **III** having a semiquinoid structure (Scheme 1). By dehydrohalogenation of primary addition products **II** and **III** in chloroform in the presence of triethylamine or in glacial acetic acid containing sodium acetate we obtained 4-aroyl(arylsulfonyl)oxyimino-6-halo-3-methyl-2,5-cyclohexadienones **IV** and **V**.

In keeping with our previous data [6], addition of the second halogen molecule should occur at the $C^2=C^3$ bond. However, the chlorination of **IV** gave

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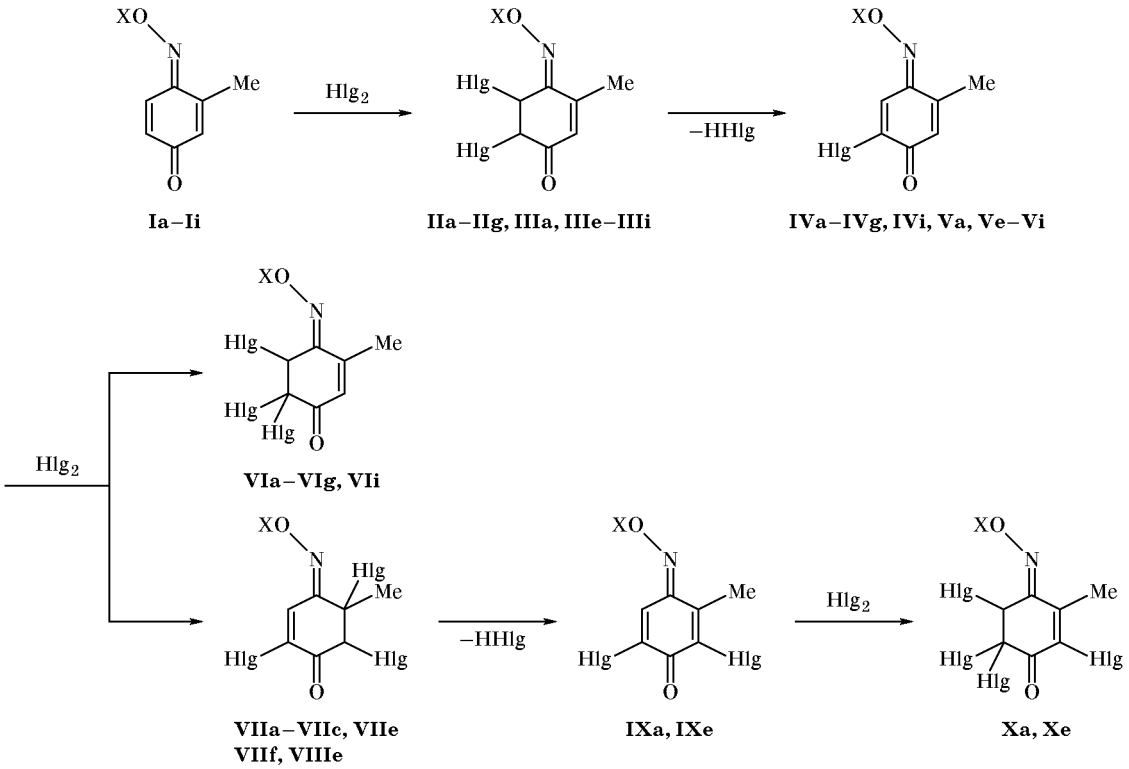
Scheme 1.



II, **IV**, **VI**, **VII**, **IX**, **X**, Hlg = Cl; **III**, **V**, **VIII**, Hlg = Br; X = PhCO (**a**), 4-ClC_6H_4CO (**b**), 4-MeC_6H_4CO (**c**), 4-BrC_6H_4CO (**d**), 4-$NO_2C_6H_4CO$ (**e**), $PhSO_2$ (**f**), 4-$ClC_6H_4SO_2$ (**g**), 4-$MeC_6H_4SO_2$ (**h**), 4-$NO_2C_6H_4SO_2$ (**i**).

semiquinoid structures, 4-aroyl(arylsulfonyl)oxyimino-5,6,6-trichloro-3-methyl-2-cyclohexenones **VI** and 4-aroyl(arylsulfonyl)oxyimino-2,5,6-trichloro-5-methyl-2-cyclohexenones **VII**, i.e., chlorine addition involved preferentially the quinoid double bond already containing chlorine atom. No products like **VI** were formed in the bromination. By reaction of **Ve** with bromine we obtained only 2,5,6-tribromo-5-methyl-4-(4-nitrobenzoyloxyimino)-2-cyclohexenone **VIIIe**. Presumably, the presence of a bulky bromine atom in position *6* of **Ve** hinders attack of the $C^5{=}C^6$ bond by the second bromine molecule.

Taking into account that dehydrohalogenation of semiquinoid structures derived from *p*-quinone oximes is a regioselective process [6], no HCl elimination from compounds **VI** was observed. By contrast, compounds **VII** readily lose HCl molecule even under the chlorination conditions to afford 4-aroyloxyimino-2,6-dichloro-3-methyl-2,5-cyclohexadienones **IXa** and **IXe**. The latter readily take up one more molecule of chlorine, yielding 4-aroyloxyimino-2,5,6,6-tetrachloro-3-methyl-2-cyclohexenones **Xa** and **Xe**. Like compounds **VI**, tetrachloro derivatives **Xa** and **Xe** do not undergo dehydrochlorination.

The structure of products **II**–**X** was proved by elemental analyses (Table 1) and ^1H (Table 2) and ^{13}C NMR (for **IIIg**) spectra. In the ^1H NMR spectra of **VIa**–**VIg** and **VIi** the 2-H signal appears as a quartet at δ 6.34–6.49 ppm. The chemical shift of this proton is consistent with its *ortho* position with respect to the carbonyl group; the signal is split due to coupling with the 3-CH_3 protons. The singlet from 5-H is located at δ 5.82–5.98 ppm, i.e., in the region typical of $C_{sp^3}H$ protons in the *ortho* position with respect to the C=N–O fragment. A singlet at δ 7.67–7.87 ppm in the spectra of **VIIa**–**VIIc**, **VIIf**, and **VIIIe** belongs to the 3-H proton. The 6-H signal is observed at δ 4.52–4.99 ppm as a singlet. Compound **IXa** shows in the ^1H NMR spectrum a singlet at δ 8.01 ppm from 5-H, and the corresponding signal in the spectra of **Xa** and **Xe** is located at δ 5.94–6.00 ppm. The ^{13}C NMR spectrum of 5,6-dibromo-4-(4-chlorophenylsulfonyloxyimino)-3-methyl-2-cyclohexenone (**IIIg**) contains characteristic upfield signals from two sp^3-hybridized carbon atoms (CHBr) at δ_C 43.62 and 34.43 ppm.

Oxime esters **Ig**, **IVc**–**IVg**, **IVi**, and **Vf**–**Vi** are characterized by IR absorption bands in the regions

Table 1. Melting points and elemental analyses of compounds **Id**, **If**, **Ig**–**Ii**, **IIa**, **IId**–**IIg**, **IIi**, **IIIf**–**IIIi**, **IVc**–**IVg**, **IVi**, **Va**, **Vf**–**Vi**, **VIa**, **VId**, **VIg**, **VIi**, **XIIa**, **XIIb**, **XIII**, **XVIIIa**, **XXI**, and **XXII**

Comp. no.	mp, °C (solvent)	Found, %		Formula	Calculated, %	
		Hlg	N		Hlg	N
Id	172 (*i*-PrOH)	25.01, 25.17	4.39, 4.45	$C_{14}H_{10}BrNO_3$	24.96	4.38
If	87 (*i*-PrOH)	–	5.04, 5.16	$C_{13}H_{11}NO_4S$	–	5.05
Ig	146 (*i*-PrOH)	11.29, 11.36	4.40, 4.48	$C_{13}H_{10}ClNO_4S$	11.37	4.49
Ih	96 (*i*-PrOH)	–	4.74, 4.80	$C_{14}H_{13}NO_4S$	–	4.81
Ii	138 (*i*-PrOH)	–	8.69, 8.78	$C_{13}H_{10}N_2O_6S$	–	8.69
IIa	145–146 (AcOH)	22.77, 22.86	4.50, 4.58	$C_{14}H_{11}Cl_2NO_3$	22.72	4.49
IId	105 (AcOH)	38.60, 38.71	3.57, 3.69	$C_{14}H_{10}BrCl_2NO_3$	38.56	3.58
IIe	175 (AcOH)	19.90, 19.99	7.80, 7.81	$C_{14}H_{10}Cl_2N_2O_5$	19.85	7.84
IIf	84 (AcOH)	20.39, 20.52	4.00, 4.11	$C_{13}H_{11}Cl_2NO_4S$	20.36	4.02
IIg	111 (AcOH)	27.73, 27.76	3.60, 3.76	$C_{13}H_{10}Cl_3NO_4S$	27.80	3.66
IIi	131–133 (*i*-PrOH)	18.00, 18.08	7.01, 7.10	$C_{13}H_{10}Cl_2N_2O_6S$	18.03	7.12
IIIf	74 (*i*-PrOH)	36.50, 36.56	3.19, 3.28	$C_{13}H_{11}Br_2NO_4S$	36.56	3.20
IIIg	145 (*i*-PrOH)	39.98, 40.85	2.99, 3.04	$C_{13}H_{10}Br_2ClNO_4S$	41.41	2.97
IIIh	160 (*i*-PrOH)	35.37, 35.48	3.11, 3.17	$C_{14}H_{13}Br_2NO_4S$	35.42	3.10
IIIi	169 (*i*-PrOH)	33.09, 33.12	5.80, 5.89	$C_{13}H_{10}Br_2N_2O_6S$	33.15	5.81
IVc	168–170 (AcOH)	12.15, 12.18	4.87, 4.96	$C_{15}H_{12}ClNO_3$	12.24	4.83
IVd	190 (*i*-PrOH)	32.37, 32.60	3.85, 3.87	$C_{14}H_9BrClNO_3$	32.53	3.95
IVe	173 (AcOH)	11.09, 11.27	8.23, 8.26	$C_{14}H_9ClN_2O_5$	11.06	8.74
IVf	115–116 (AcOH)	11.41, 11.60	4.50, 4.57	$C_{13}H_{10}ClNO_4S$	11.37	4.49
IVg	152–154 (AcOH)	20.51, 20.72	4.06, 4.13	$C_{13}H_9Cl_2NO_4S$	20.48	4.05
IVi	168 (AcOH)	9.97, 10.04	7.74, 7.76	$C_{13}H_9ClN_2O_6S$	9.94	7.85
Va	185 (AcOH)	24.79, 24.98	4.38, 4.49	$C_{14}H_{10}BrNO_3$	24.96	4.38
Vf	134 (*i*-PrOH)	22.36, 22.47	3.92, 3.98	$C_{13}H_{10}BrNO_4S$	22.43	3.93
Vg	157 (AcOH)	29.38, 29.40	4.23, 4.24	$C_{13}H_9BrClNO_4S$	29.53	3.59
Vh	134 (*i*-PrOH)	21.54, 21.60	3.77, 3.89	$C_{14}H_{12}BrNO_4S$	21.58	3.78
Vi	161 (AcOH)	20.41, 20.52	7.07, 7.20	$C_{13}H_9BrN_2O_6S$	19.92	6.98
VIa	147–148 (AcOH)	30.55, 30.63	4.06, 4.15	$C_{14}H_{10}Cl_3NO_3$	30.69	4.04
VId	152 (AcOH)	43.07, 43.40	3.30, 3.39	$C_{14}H_9BrCl_3NO_3$	43.78	3.29
VIg	123–124 (AcOH)	34.08, 34.15	3.37, 3.46	$C_{13}H_9Cl_4NO_4S$	34.00	3.36
VIi	160–162 (AcOH)	24.80, 24.90	6.56, 6.67	$C_{13}H_9Cl_3N_2O_6S$	24.87	6.55
XIIa	156 (*i*-PrOH)	–	8.52, 8.58	$C_{17}H_{16}N_2O_5$	–	8.53
XIIb	130 (*i*-PrOH)	–	7.67, 7.76	$C_{16}H_{16}N_2O_6S$	–	7.69
XIII	240 (*i*-PrOH)	–	9.07, 9.22	$C_{15}H_{12}N_2O_5$	–	9.33
XVIIIa	158 (AcOH)	9.80, 9.98	7.70, 7.84	$C_{17}H_{15}ClN_2O_5$	9.77	7.72
XXI	143 (*i*-PrOH)	19.02, 19.13	7.52, 7.58	$C_{15}H_{12}Cl_2N_2O_5$	19.10	7.55
XXII	265 (AcOH)	10.40, 10.51	8.30, 8.39	$C_{15}H_{11}ClN_2O_5$	10.59	8.37

1665–1650, 1615–1580, and 1585–1580 cm^{-1}, which belong to the quinoid C=O, C=C, and C=N groups, respectively. In the IR spectra of semiquinoid compounds the carbonyl absorption band appears at higher frequencies. The bands at 1710–1680, 1625–1610, and 1600–1580 cm^{-1} in the spectra of **IIb**, **IId**–**IIg**, **IIi**, **Ve**–**Vh**, and **VId** correspond to the C=O, C=C, and C=N bonds of the cyclohexenone fragment.

We assumed in [5] *trans*-diaxial orientation of the chlorine atoms attached to the sp^3-hybridized carbon atoms in cyclohexene structures obtained by chlorination of *p*-quinone oxime esters. This assumption was confirmed by the results of X-ray analysis of compound **VIa** (Fig. 1). The cyclohexene fragment adopts a *distorted semichair* conformation. The C^5 and C^6 atoms deviate from the mean-square plane formed

Table 2. ^{1}H NMR spectra of compounds **IId**, **IIi**, **IIIf**, **IIIg**, **IIIh**, **IVd**, **IVf**, **IVi**, **Va**, **Vf**–**Vh**, **VIa**–**VIg**, **VIi**, **VIIa**–**VIIc**, **VIIf**, **IXa**, **Xa**, **Xe**, **XIV**, **XV**, **XVIa**, **XVIb**, **XVIIa**, **XVIIb**, **XVIIIa**, **XIXa**, **XXa**, and **XXI**–**XXIV**

Comp. no.	Chemical shift δ, ppm					$J_{Me,H}$, Hz
	2-H, 2-Me, 2-Pr-*i*	3-H, 3-Me	5-H, 5-Me	6-H, 6-Me, 6-Pr-*i*	protons in X	
IId	6.36 q (1H)	2.37 d (3H)	5.67 d (1H)	4.44 d.d (1H)	7.69–8.00 d.d (4H)	1.2
IIi	6.29 q (1H)	2.11 d (3H)	5.53 d (1H)	4.37 d.d (1H)	8.20–8.49 d.d (4H)	1.0
IIIf	6.19 q (1H)	2.15 d (3H)	5.61 d (1H)	4.52 d.d (1H)	7.50–8.03 m (5H)	1.3
IIIg	6.22 q (1H)	2.12 d (3H)	5.60 d (1H)	4.54 d.d (1H)	7.54–7.97 d.d (4H)	1.4
IIIh	6.19 q (1H)	2.11 d (3H)	5.60 d (1H)	4.53 d.d (1H)	7.35–7.91 d.d (4H), 2.47 s (3H, Me)	1.3
IVd	6.59 q (1H)	2.39 d (3H)	7.91 s (1H)	–	7.68–8.02 d.d (4H)	1.4
IVf	6.47 q (1H)	2.15 d (3H)	7.77 s (1H)	–	7.58–8.06 m (5H)	
IVi	6.50 q (1H)	2.15 d (3H)	7.76 s (1H)	–	8.20–8.49 d.d (4H)	1.2
Va	7.32 q (1H)	2.17 d (3H)	8.24 s (1H)	–	7.54–8.16 m (5H)	
Vf	6.49 q (1H)	2.13 d (3H)	8.04 s (1H)	–	7.50–8.08 m (5H)	1.3
Vg	6.50 q (1H)	2.14 d (3H)	8.03 s (1H)	–	7.55–8.01 d.d (4H)	
Vh	6.48 q (1H)	2.14 d (3H)	8.04 s (1H)	–	7.36–7.93 d.d (4H), 2.48 s (3H, Me)	1.4
VIa	6.46 q (1H)	2.39 d (3H)	5.98 s (1H)	–	7.55–8.15 m (5H)	
VIb	6.46 q (1H)	2.36 d (3H)	5.91 s (1H)	–	7.53–8.07 d.d (4H)	1.2
VIc	6.45 q (1H)	2.39 d (3H)	5.97 s (1H)	–	7.33–8.01 d.d (4H), 2.48 s (3H, Me)	
VId	6.46 q (1H)	2.38 d (3H)	5.93 s (1H)	–	7.69–8.00 d.d (4H)	1.3
VIe	6.49 q (1H)	2.39 d (3H)	5.96 s (1H)	–	8.29–8.45 d.d (4H)	1.2
VIf	6.35 q (1H)	2.11 d (3H)	5.82 s (1H)	–	7.56–8.06 m (5H)	0.9
VIg	6.37 q (1H)	2.12 d (3H)	5.82 s (1H)	–	7.56–8.00 d.d (4H)	1.2
VIi	6.39 q (1H)	2.12 d (3H)	5.83 s (1H)	–	8.21–8.48 d.d (4H)	1.5
VIIa	–	7.87 s (1H)	2.39 s (3H)	4.64 s (1H)	7.56–8.15 m (5H)	–
VIIb	–	7.80 s (1H)	2.15 s (3H)	4.61 s (1H)	7.53–8.07 d.d (4H)	–
VIIc	–	7.87 s (1H)	2.21 s (3H)	4.64 s (1H)	7.33–8.01 d.d (4H), 2.47 s (3H, Me)	–
VIIf	–	7.67 s (1H)	1.93 s (3H)	4.52 s (1H)	7.56–8.06 m (5H)	–
VIIIe	–	8.08 s (1H)	2.40 s (3H)	4.99 s (1H)	8.28–8.43 d.d (4H)	–
IXa	–	2.40 s (3H)	8.01 s (1H)	–	7.54–8.15 m (5H)	–
Xa	–	2.55 s (3H)	6.00 s (1H)	–	7.75–8.14 m (5H)	–
Xe	–	2.55 s (3H)	5.94 s (1H)	–	8.29–8.45 d.d (4H)	–
XIV	6.28 q (1H)	2.10 d (3H)	5.52 s (1H)	1.84 s (3H)	7.78–8.90 m (4H)	1.2
XV	2.08 d (3H)	7.29 q (1H)	1.93 s (3H)	4.38 s (1H)	7.78–8.90 m (4H)	1.8
XVIa	3.03–3.14 m (1H, CH), 1.23–1.27 d.d (6H, Me)	7.34 br.s (1H)	2.18 s (3H)	4.48 s (3H)	8.27–8.42 d.d (4H)	
XVIb	2.99–3.10 m (1H, CH), 1.17–1.25 d.d (6H, Me)	7.16 s (1H)	1.96 s (3H)	4.39 s (1H)	7.80–8.90 m (4H)	

Table 2. (Contd.)

Comp. no.	Chemical shift δ, ppm				
	2-H, 2-Me, 2-Pr-*i*	3-H, 3-Me	5-H, 5-Me	6-H, 6-Me, 6-Pr-*i*	protons in X
XVIIa	6.34 q (1H)	2.33 d (3H)	5.67 s (1H)	2.71–2.76 m (1H, CH), 1.12–1.20 d.d (6H, Me)	8.27–8.42 d.d (4H)
XVIIb	6.24 q (1H)	2.08 d (3H)	5.49 s (1H)	2.59–2.69 m (1H, CH), 1.05–1.15 d.d (6H, Me)	7.80–8.90 m (4H)
XVIIIa	–	2.52 s (3H)	7.52 br.s (1H)	3.14–3.24 m (1H, CH), 1.21–1.23 d.d (6H, Me)	8.29–8.44 d.d (4H)
XIXa	–	2.48 s (3H)	5.69 s (1H)	2.74–2.84 m (1H, CH), 1.26–1.28 d.d (6H, Me)	8.25–8.43 d.d (4H)
XXa	3.14–3.20 m (1H, CH), 1.14–1.16 d.d (6H, Me)	7.38 s (1H)	2.39 br.s (3H)	–	8.25–8.43 d.d (4H)
XXI	2.12 s (3H)	2.37 s (3H)	5.68 d (1H)	4.52 d (3H)	8.29–8.41 d.d (4H)
XXII	2.14 s (3H)	2.38 s (3H)	7.89 br.s (1H)	–	8.30–8.42 d.d (4H)
XXIII	–	7.81 s (1H)	2.23 s (3H)	2.02 s (3H)	8.29–8.45 d.d (4H)
XXIV	2.18 s (3H)	2.37 s (3H)	5.94 s (1H)	–	8.29–8.45 d.d (4H)

by the other cyclohexene ring atoms by 0.23 and –0.43 Å, respectively. The Cl^1 and Cl^3 atoms occupy *trans*-diaxial positions, and the Cl^2 atom is equatorial: the torsion angles $C^3C^4C^5Cl^1$, $C^2C^1C^6Cl^3$, and $C^2C^1C^6Cl^2$ are –86.1(3), –73.3(3), and 167.5(2)°, respectively. The benzoyl C=O group is nearly antiperiplanar relative to the $N^1=C^4$ bond [torsion angle $C^8O^2N^1C^4$ 170.3(2)°] and is turned through an angle of –15.4(4)° with respect to the N^1-O^2 bond (torsion angle $N^1O^2C^8O^3$). Molecules **VIa** in crystal have *E* configuration, i.e., the OCOPh group is located *trans* with respect to the cyclohexene double bond.

On the whole, molecule **VIa** is considerably strained. This follows from the shortened intramolecular contacts $Cl^3\cdots C^3$ 3.44 Å (the sum of the corresponding van der Waals radii is 3.61 Å [7]), $H^5\cdots O^2$

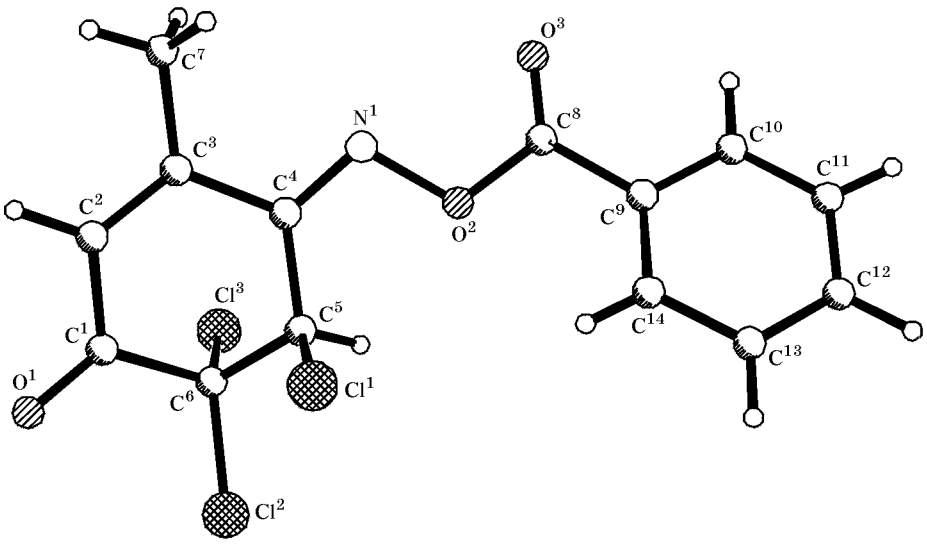


Fig. 1. Structure of the molecule of 4-benzoyloxyimino-5,6,6-trichloro-3-methyl-2-cyclohexenone (**VIa**) according to the X-ray diffraction data.

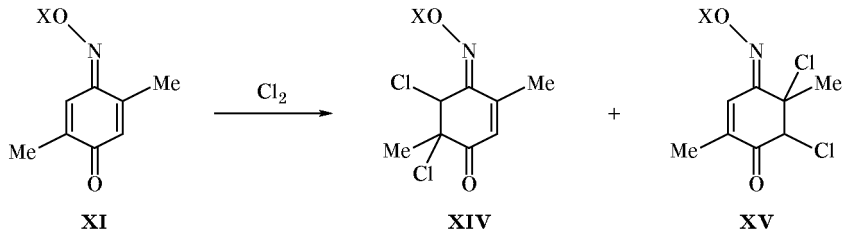
2.33 Å (2.45 Å), and $H^{14}\cdots O^{2}$ 2.39 Å (2.45 Å [7]). As a result, the bonds $C^{1}-C^{6}$ 1.565(4) Å (average value 1.506 Å [8]), $C^{2}-C^{3}$ 1.364(4) Å (1.326 Å [8]), $C^{3}-C^{4}$ 1.499 (4) Å (1.478 Å [8]), and $C^{8}-C^{9}$ 1.517(4) Å (1.487 Å [8]) are elongated.

While studying the chlorination of 4-aroyl(arylsulfonyl)oxyimino-2,5-dialkyl-2,5-cyclohexadienones [4–6], we isolated products of halogen addition at only one of the two quinoid C=C bonds. The bromination gave addition products at both C=C bonds [4]. Taking these data into account, we performed a more detailed study of the chlorination of 2,5-dimethyl-4-(3-nitrophenylsulfonylimino)-2,5-cyclohexadienone (**XI**),* 4-aroyl(arylsulfonyl)oxyimino-6-isopropyl-3-methyl-2,5-cyclohexadienones **XIIa** and **XIIb**, and 2,3-dimethyl-4-(4-nitrobenzoyloxyimino)-2,5-cyclohexadienone (**XIII**). By chlorination of compounds **XI** (Scheme 2) and **XII** (Scheme 3) we obtained chlorine addition products at either of the quinoid C=C bonds. The chlorination of 2-chloro-6-isopropyl-3-methyl-4-(4-nitrobenzoyloxyimino)-2,5-cyclohexadienone (**XVIII**), which is formed by dehydrochlorination of **XVIa**, also results in halogen addition at both $C^{2}=C^{3}$ and $C^{5}=C^{6}$ bonds, yielding products **XIX** and **XX** (Scheme 3).

Treatment of 2,3-dimethyl derivative **XIII** with chlorine gave product **XXI** via halogen addition at the $C^{5}=C^{6}$ bond. Its dehydrochlorination afforded 6-chloro-2,3-dimethyl-4-(4-nitrobenzoyloxyimino)-2,5-cyclohexadienone (**XXII**). The chlorination of **XXII** resulted in formation of two compounds, 2,5,6-trichloro-5,6-dimethyl-4-(4-nitrobenzoyloxyimino)-2-cyclohexenone (**XXIII**) and 5,6,6-trichloro-2,3-dimethyl-4-(4-nitrobenzoyloxyimino)-2-cyclohexenone (**XXIV**). The latter is the product of chlorine addition at the C=C bond already containing chlorine atom (Scheme 4).

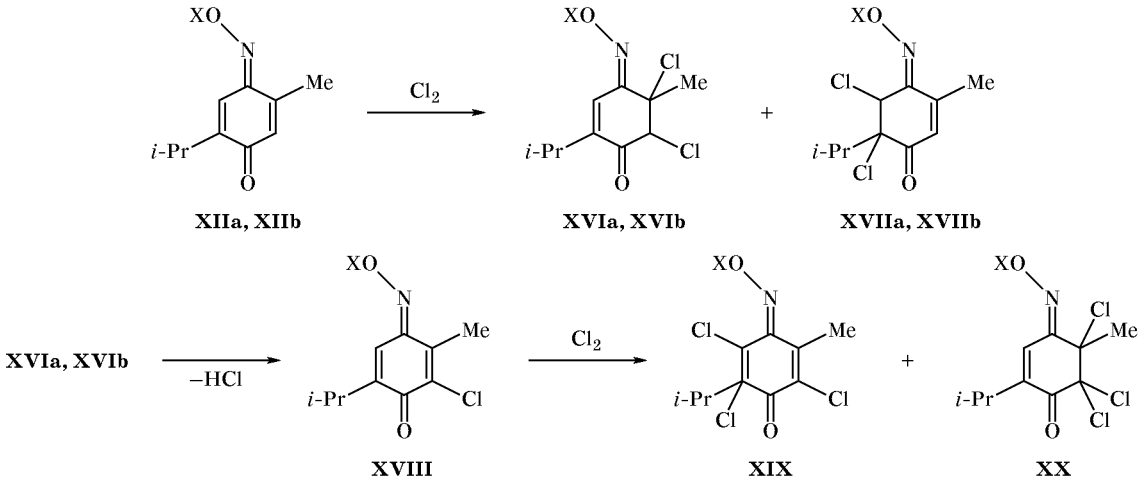
The structure of compounds **XII**–**XXIV** was confirmed by the data of elemental analysis (Table 1) and ^{1}H NMR spectroscopy (Table 2). In order to prove the structure of **XXI**, specifically the *trans*-diaxial orientation of chlorine atoms at the C_{sp^3} carbon atoms,

Scheme 2.



X = 3-$NO_2C_6H_4CO$.

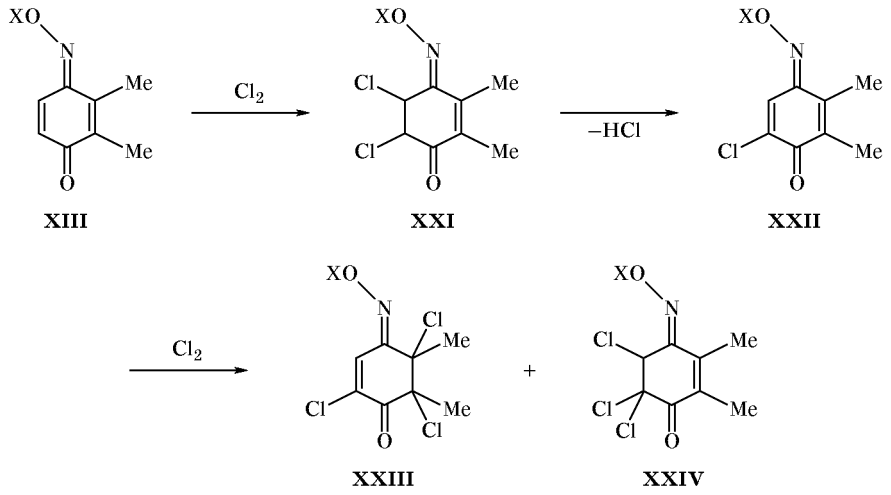
Scheme 3.



XIIa, **XVIa**, **XVIIa**, **XVIII**–**XX**, X = 4-$NO_2C_6H_4CO$; **XIIb**, **XVIb**, **XVIIb**, X = 3-$NO_2C_6H_4SO_2$.

* As in Russian original.—*Publisher*.

Scheme 4.



X = 4-$NO_2C_6H_4CO$.

we performed X-ray analysis of its structural analog, previously synthesized 4-benzoyloxyimino-5,6-dichloro-2,3-dimethyl-2-cyclohexenone (**XXV**). The $O^1C^1C^2C^3C^4N$ fragment in molecule **XXV** is planar, the average deviation of atoms from the mean-square plane is 0.033 Å. The C^5, C^6 and Cl^1, Cl^2 atoms are disordered by two positions *A* and *B* with equal populations (Fig. 2), presumably due to existence of two conformers. The deviations of C^5 and C^6 in conformer *A* from the mean-square plane formed by the O^1, C^1, C^2, C^3, C^4, and N atoms are, respectively, –0.51 and 0.27 Å. The corresponding deviations for conformer *B* are 0.05 and –0.48 Å. The chlorine atoms in both conformers occupy *trans*-diaxial positions, and the hydrogen atoms are nearly equatorial. The molecule of **XXV** has *E* configuration with the OCOPh group located *trans* with respect to the double C=C bond of the cyclohexene ring.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer in KBr. The ^{1}H NMR spectra were measured on a Varian VXR-300 instrument at 300 MHz relative to TMS as internal reference; $CDCl_3$ was used as solvent. The ^{13}C NMR spectrum of compound **IIIg** was obtained on the same instrument at 75.4 MHz in $CDCl_3$ using TMS as internal reference.

X-Ray diffraction data for a single crystal of compound **VIa** (monoclinic) were acquired on a Siemens

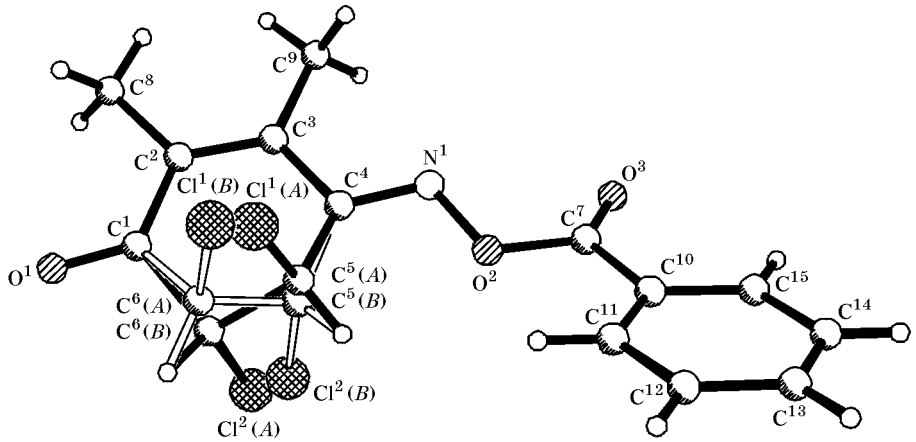


Fig. 2. Structure of the molecule of 4-benzoyloxyimino-5,6-dichloro-2,3-dimethyl-2-cyclohexenone (**XXV**) according to the X-ray diffraction data.

P3/PC four-circle automatic diffractometer (λMoK_α irradiation, graphite monochromator, $2\theta/\theta$-scanning, $2\theta_{max}$ 50°). The structure was solved by the direct method using SHELX-97 software package [9]. The positions of hydrogen atoms were determined from the difference synthesis of electron density and were refined in isotropic approximation. The structure was refined with respect to F^2 by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms.

X-Ray diffraction study of a single crystal of **XXV** (monoclinic) was performed on an Enraf–Nonius CAD-4 four-circle automatic diffractometer (λCuK_α irradiation, graphite monochromator, scan rates ratio $\omega/2\theta$ 1.2). The structure was solved by the direct method and was refined by the least-squares procedure in full-matrix anisotropic approximation using SHELXS-86 and SHELXL-93 software packages [10, 11]. All hydrogen atoms were visualized by the difference synthesis of electron density and were refined in isotropic approximation.

The reaction mixtures were analyzed by TLC on Silufol UV-254 plates using benzene–ethyl acetate (10:1) as eluent; development with UV light.

Alkyl-substituted 4-aroyl(arylsulfonyl)oxyimino-2,5-cyclohexadienones **Ia**–**Ii**, **XI**, **XIIa**, **XIIb**, and **XIII** were synthesized by acylation of the corresponding *p*-benzoquinone oximes with aroyl or arenesulfonyl chlorides in diethyl ether in the presence of triethylamine [12]. The newly synthesized compounds are characterized in Table 1.

Chlorination of 4-aroyl(arylsulfonyl)oxyimino-3-methyl-2,5-cyclohexadienones Ia–Ig and Ii. *a*. Gaseous chlorine was passed at 40–50°C at a rate of 15–20 ml/min through a solution of 0.3 g of oxime ester **Ib**–**Ig** or **Ii** in 3 ml of EtOH or a DMF–AcOH mixture (1:1 or 5:1) until saturation. When the reaction was performed in EtOH, the product precipitated in several hours and was filtered off. The mixtures obtained in DMF–AcOH were diluted with water, and the precipitate was filtered off. The products were purified by recrystallization (Table 1). The following compounds were obtained: in EtOH: **IIb** (10%; hereinafter, the yield was determined from the ^1H NMR data), **IVb** (29%), **VIb** (62%); **IIc** (85%); **IVf** (95%); in DMF–AcOH (1:1): **IId** (92%); **IIe** (93%); in DMF–AcOH (5:1): **IIf** (80%); **IIg** (98%), **IIi** (83%).

b. A solution of 0.5 g of oxime ester **Ia**, **Ib**, or **Ie** in 3 ml of EtOH or DMF was saturated with chlorine at a flow rate of 15–20 ml/min (50–60°C). The products were isolated as described above in *a*. The following compounds were obtained: in EtOH: **IIa** (93%); **IVb** (51%), **VIb** (49%); in DMF: **VIa** (38%), **IXa** (12%), **Xa** (50%); **VIe** (50%), **Xe** (50%).

Chlorination of 4-aroyl(arylsulfonyl)oxyimino-2-chloro-5-methyl-2,5-cyclohexadienones IVa–IVg and IVi. Gaseous chlorine was passed at a rate of 15–20 ml/min through a solution of 0.4 g of compound **IVa**–**IVg** or **IVi** in 3 ml of EtOH, DMF, or DMF–AcOH (1:1 or 5:1), heated to 70°C, until saturation. The mixture was diluted with water, and the precipitate was filtered off and recrystallized. The following products were obtained: in EtOH: **VIa** (98%); **VIf** (93.2%), **VIIf** (6.8%); **VIg** (98%); **VIi** (97%); in DMF: **VIb** (54%), **VIIb** (46%); **VIc** (26%), **VIIc** (74%); in DMF–AcOH (1:1): **VIa** (15%), **Xa** (85%); **VId** (97%); in DMF–AcOH (5:1): **VIa** (79%), **VIIa** (21%); **VIe** (50%), **Xe** (50%).

Chlorination of oxime esters XI, XIIa, XIIb, XIII, XVIIIa, and XXII. Gaseous chlorine was passed at a rate of 15–20 ml/min through a solution of 0.3 g of compound **XI**, **XIIa**, **XIIb**, **XIII**, **XVIIIa**, or **XXII** in 3 ml of DMF or DMF–AcOH (1:1, 3:1, or 5:1), heated to 70–80°C, until saturation. The mixture was diluted with water, and the precipitate was filtered off and recrystallized from acetic acid. The following compounds were obtained: in DMF from **XI**: **XIV** (67%), **XV** (33%); in DMF–AcOH (1:1) from **XIIa**: **XVIa** (67%), **XVIIa** (33%); from **XIII**: **XXI** (98%); in DMF–AcOH (3:1) from **XIIb**: **XVIb** (64%), **XVIIb** (36%); from **XXII**: **XXIII** (64%), **XXIV** (36%); in DMF–AcOH (5:1) from **XVIIIa**: **XIXa** (94%), **XXa** (6%).

Bromination of oxime esters If–Ii and Ve. *a*. A solution of 0.2 ml of bromine in 2 ml of $CHCl_3$ or AcOH was added dropwise under vigorous stirring to a solution of 0.4 g of compound **If**–**Ii** in 2 ml of the same solvent, maintaining the temperature in the range from 20 to 40°C. After 24 h, the precipitate was filtered off and recrystallized. The following products were obtained: in $CHCl_3$: **IIf** (91%); in AcOH: **IIIg** (89%); **IIIh** (92%); **IIIi** (94%).

b. A solution of 0.3 ml of bromine in 1 ml of $CHCl_3$ was added dropwise under vigorous stirring to a solution of 0.2 g of compound **Ve** in 2 ml of $CHCl_3$, maintaining the temperature at 20°C. After 24 h, the precipitate was filtered off and recrystallized from acetic acid. A mixture of compounds **Ve** and **VIIIe** was thus obtained.

^{13}C NMR spectrum of 5,6-dibromo-4-(4-chlorophenylsulfonyloxyimino)-3-methyl-2-cyclohexenone (**IIIg**), δ_C, ppm: 187.03 (C=O), 157.34 (C=N), 145.15 (C^4 in $ArSO_2$), 142.09 (C^3), 133.35 (C^1 in

$ArSO_2$), 130.81 (C^3 in $ArSO_2$), 129.97 (C^2 in $ArSO_2$), 129.59 (C^2), 43.62 (C^5), 34.43 (C^6), 18.49 (Me).

Dehydrohalogenation of 4-aroyl(arylsulfonyl)-oxyimino-5,6-dihalo-3-methyl-2-cyclohexenones IId, IIi, IIIa, and IIIe–IIIi. Triethylamine, 0.1–0.15 ml, was added to a solution of 1 mmol of compound **IId**, **IIIa**, or **IIIe–IIIi** in a minimal amount of chloroform, and the solution was heated until it turned yellow. The mixture was cooled, and the precipitate was filtered off, washed with a small amount of acetic acid, and recrystallized from acetic acid.

Dehydrohalogenation of compound **IIi** was carried out in glacial acetic acid in the presence of an equimolar amount of sodium acetate. The mixture was heated to the boiling point and cooled, and the precipitate was filtered off, washed with acetic acid, and recrystallized from acetic acid.

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