Russian Journal of Organic Chemistry, Vol. 37, No. 3, 2001, pp. 382–387. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 3, 2001, pp. 408–413.

Halogenation of Some Alkyl-Substituted 4-Aroyloxyimino- and 4-Arylsulfonyloxyimino-2,5-cyclohexadienones

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Received January 14, 1999

Abstract—The chlorination and bromination of 2,3-dimethyl-, 3-methyl-6-isopropyl-, and 2,6-diisopropyl-4-aroyl(or arylsulfonyl)oxyimino-2,5-cyclohexadienones follow the proposed rules of halogenation of 4-aroyl-(or arylsulfonyl)oxyimino-2,5-cyclohexadienones: the reaction occurs preferentially at the *cis*-C=C bond of the quinoid ring; simultaneous halogenation at both double bonds is not observed; halogen adds mainly across unsubstituted C=C bond; no halogenation occurs at the double bond already substituted by a halogen; bromination of the C=C bond with an alkyl substituent is more difficult than chlorination; the second halogen molecule adds only after regioselective dehydrohalogenation.

In the preceding communications we reported on the chlorination and bromination of 4-aroyloxyimino- and 4-arylsulfonyloxyimino-2,5-cyclohexadienones [1–4]. Analysis of the results allowed us to postulate the following rules which govern halogenation of these compounds:

(1) The halogenation involves only one C=C bond of the quinoid ring. In no cases simultaneous addition of halogen at both C=C bonds was observed [1–4];

(2) The halogenation occurs preferentially at the *cis*-C=C bond relative to the RO substituent on the nitrogen atom (*cis*-stereoselectivity) [1];

(3) When an alkyl group is present at one double bond, halogen adds preferentially at the unsubstituted C=C bond [2];

(4) Bromination of C=C bond with an alkyl substituent is more difficult than chlorination, because of greater size of bromine atom compared to chlorine [3];

(5) Halogen does not add at a double bond already substituted by a halogen [1, 4];

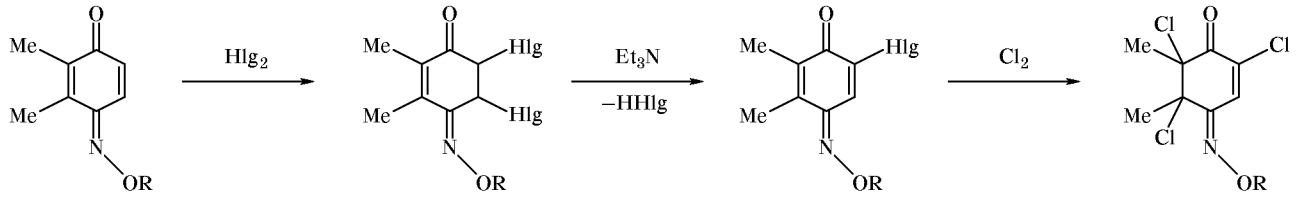
(6) Addition of the second halogen molecule is possible only after elimination of hydrogen halide; the dehydrohalogenation is strictly regioselective: hydrogen atom is abstracted from the α-position with respect to the carbonyl group, and halogen atom, from the α-position with respect to the imino group [1–4].

The goal of the present study was to obtain additional proofs for the above rules of halogenation of 4-aroyl(arylsulfonyl)oxyimino-2,5-cyclohexadienones. For this purpose, we examined the chlorination and bromination of 2,3-dimethyl-, 3-methyl-6-isopropyl-, and 2,6-diisopropyl-substituted 4-aroyloxyimino- and 4-arylsulfonyloxyimino-2,5-cyclohexadienones.

The halogenation of 4-aroyloxyimino- and arylsulfonyloxyimino-2,3-dimethyl-2,5-cyclohexadienones **Ia**–**Id** was expected to occur at the unsubstituted $C^5=C^6$ bond for the following reasons. First, the $C^5=C^6$ bond is more reactive since it is located *cis* with respect to the RO group on the nitrogen [2–6] and second, two methyl groups in positions *2* and *3* should hinder halogen addition at the $C^2=C^3$ bond. In fact, our experiments showed that the first halogen molecule adds at the unsubstituted $C^5=C^6$ double bond of compounds **Ia**–**Id** to give 4-aroyl(arylsulfonyl)oxyimino-5,6-dihalo-2,3-dimethyl-2-cyclohexenones **IIa**–**IId** and **IIIa**–**IIId** (Scheme 1). These products are *E* isomers with respect to the methyl groups. Treatment of compounds **IIa**–**IId** and **IIIa**–**IIId** with triethylamine in chloroform gave the corresponding 4-aroyl(arylsulfonyl)oxyimino-6-halo-2,3-dimethyl-2,5-cyclohexadienones **IVa**–**IVd** and **Va**–**Vd**. The dehydrohalogenation process is regioselective: halogen atom is abstracted exclusively from position *5* of the quinoid ring to form only *E* isomer with respect to the methyl groups (Scheme 1).

Addition of the second halogen molecule to compounds **IVa**–**IVd** and **Va**–**Vd** should occur at the $C^5=C^6$ bond located *cis* relative to the RO group. However, there is a halogen atom in the *ortho*-position with respect to the carbonyl group; in keeping with numerous experimental data [1–4], such double

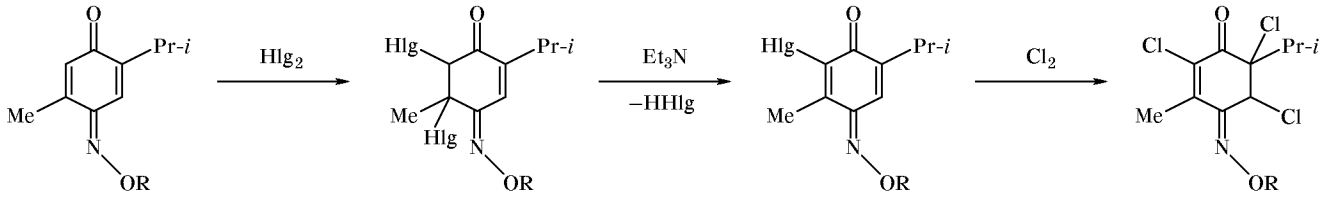
Scheme 1.



Ia–Id **IIa–IId, IIIa–IIId** **IVa–IVd, Va–Vd** **VIa–VId**

I–**VI**, R = PhCO (**a**), 4-ClC_6H_4CO (**b**), $PhSO_2$ (**c**), 3-$NO_2C_6H_4SO_2$ (**d**); **II**, **IV**, Hlg = Cl; **III**, **V**, Hlg = Br.

Scheme 2.



VIIa–VIIc **VIIIa–VIIIc, IXa–IXc** **Xa–Xc, XIa–XIc** **XIIa–XIIc**

R = PhCO (**a**), 4-$CH_3C_6H_4SO_2$ (**b**), 3-$NO_2C_6H_4SO_2$ (**c**); **VIII**, **X**, Hlg = Cl; **IX**, **XI**, Hlg = Br.

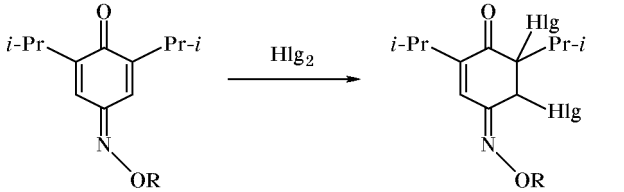
bond becomes inactive and it does not take up halogen. Therefore, the only possible is halogen addition at the $C^2=C^3$ bond already containing two methyl groups. Thus the chlorination of **IVa**–**IVd** afforded 4-aroyl(arylsulfonyl)oxyimino-2,5,6-trichloro-5,6-dimethyl-2-cyclohexenones **VIa**–**VId** as *E* isomers (Scheme 1). Bromination of compounds **Va**–**Vd** does not occur because of considerable steric hindrances to addition of bulky bromine atoms.

The halogenation of 4-aroyl(arylsulfonyl)oxyimino-6-isopropyl-3-methyl-2,5-cyclohexadienones **VIIa**–**VIIc** should occur at the $C^5=C^6$ bond in the *cis* position with respect to the RON group. However, the presence of a bulky isopropyl group hinders halogen addition at that bond, and the reaction involves the $C^2=C^3$ bond to give 4-aroyl(arylsulfonyl)oxyimino-2,3-dihalo-6-isopropyl-3-methyl-2-cyclohexenones **VIIIa**–**VIIIc** and **IXa**–**IXc** (*E* isomers with respect to the methyl group; Scheme 2).

Regioselective dehydrohalogenation of compounds **VIIIa**–**VIIIc** and **IXa**–**IXc** leads to formation of (*E*)-4-aroyl(arylsulfonyl)oxyimino-2-halo-6-isopropyl-3-methyl-2,5-cyclohexadienones **Xa**–**Xc** and **XIa**–**XIc**. Taking into account that halogen does not add at a double bond already containing a halogen atom, further halogenation of **Xa**–**Xc** and **XIa**–**XIc** was expected to occur at the $C^5=C^6$ bond. This was the case in the reaction of **Xa**–**Xc** with chlorine. As a result, 4-aroyl(arylsulfonyl)oxyimino-2,5,6-trichloro-6-isopropyl-3-methyl-2-cyclohexenones **XIIa**–**XIIc** were obtained (*E* isomers with respect to the methyl group). Compounds **XIa**–**XIc** did not react with Br_2 for the same reason as stated above for **Va**–**Vd**.

4-Aroyl(arylsulfonyl)oxyimino-2,6-diisopropyl-2,5-cyclohexadienones **XIIIa**–**XIIIc** are capable of taking up only one halogen molecule to afford 4-aroyl(arylsulfonyl)oxyimino-5,6-dihalo-2,6-diisopropyl-2-cyclohexenones **XIVa**–**XIVc** and **XVa**–**XVc** existing in solution as a single *E* isomer (Scheme 3). This indicates high *cis*-stereoselectivity of the halogenation process. Regioselective dehydrohalogenation of compounds **XIVa**– **XIVc**, **XVa**, and **XVc** is impossible.

Scheme 3.



XIIIa–XIIIc **XIVa–XIVc, XVa–XVc**

XIII–**XV**, R = 4-ClC_6H_4CO (**a**), 4-$CH_3C_6H_4CO$ (**b**), 4-$CH_3C_6H_4SO_2$ (**c**); **XIV**, Hlg = Cl; **XV**, Hlg = Br.

Compounds **Ia**–**Id**, **IVa**–**IVd**, **VIIa**–**VIIc**, **Xa**–**Xc**, and **XIIIa**–**XIIIc** were chlorinated with gaseous

Table 1. Chlorination of alkyl-substituted 4-aroyl(arylsulfonyl)oxyimino-2,5-cyclohexadienones **Ia**–**Id**, **IVa**–**IVd**, **VIIa**–**VIIc**, **Xa**–**Xc**, and **XIIIa**–**XIIIc**

Substrate no.	Solvent (ratio)	Concentration, M	Temperature, °C	Product
Ia	DMF–AcOH (1:1)	0.39	70–75	**IIa**
Ib	DMF–AcOH (1:1)	0.35	50–60	**IIb**
Ic	DMF–AcOH (1:1)	0.35	40	**IIc**
Id	DMF–AcOH (1:1)	0.3	40–50	**IId**
IVa	DMF–AcOH (3:1)	0.25	60–70	**VIa**
IVb	DMF–AcOH (3:1)	0.25	60–70	**VIb**
IVc	DMF–AcOH (3:1)	0.3	50–60	**VIc**
IVd	DMF–AcOH (3:1)	0.25	60–75	**VId**
VIIa	DMF–AcOH (1:1)	0.35	40	**VIIIa**
VIIb	DMF–AcOH (3:1)	0.3	50–60	**VIIIb**
VIIc	DMF–AcOH (3:1)	0.3	60–70	**VIIIc**
Xa	DMF	0.25	80–90	**XIIa**, **Xa**
Xb	DMF	0.2	90	**XIIb**
Xc	DMF	0.2	90	**XIIc**
XIIIa	DMF	0.25	70–80	**XIVa**
XIIIb	DMF	0.2	60–70	**XIVb**
XIIIc	DMF	0.2	60–70	**XIVc**

Table 2. Bromination of alkyl-substituted 4-aroyl(arylsulfonyl)oxyimino-2,5-cyclohexadienones **Ia**–**Id**, **VIIa**–**VIIc**, **XIIIa**, and **XIIIc**

Substrate no.	Solvent	Substrate–Br_2 molar ratio	Temperature, °C	Product
Ia	$CHCl_3$	1:3	25	**IIIa**[a]
Ib	$CHCl_3$	1:3	25	**IIIb**[a]
Ic	$CHCl_3$	1:3	25	**IIIc**[a]
Id	$CHCl_3$	1:3	25	**IIId**[a]
VIIa	AcOH	1:5	40–50	**IXa**[b]
VIIb	AcOH	1:5	50	**IXb**[b]
VIIc	AcOH	1:5	40–50	**IXc**[b]
XIIIa	DMF	1:7	40–50	**XVa**[b]
XIIIc	DMF	1:3	50–60	**XVc**[c]

[a] Crystallizes after removal of the solvent by half.

[b] Crystallizes after addition of 10–15 ml of water to the reaction solution.

[c] The oily substance formed after addition of 10–15 ml of water was extracted with diethyl ether. The solvent was removed, and the tarry residue was recrystallized.

chlorine in dimethylformamide or in a mixture of dimethylformamide with acetic acid. The conditions are given in Table 1. The bromination of compounds **Ia**–**Id**, **VIIa**–**VIIc**, **XIIIa**, and **XIIIc** was effected with molecular bromine in $CHCl_3$, AcOH, or DMF. The conditions are summarized in Table 2.

Compounds **VIIa**, **IXa**, and **XIa** were identical to those reported previously [3, 7]. The structure of the newly synthesized compounds was proved by elemental analyses (Table 3) and IR and ^{1}H NMR spectra. The IR spectra of quinoid compounds **IV**, **V**, **X**, and **XI** contain characteristic carbonyl absorption bands in the region 1644–1665 cm^{-1}; the carbonyl band in the spectra of semiquinoid derivatives **II**, **III**, **VI**, **VIII**, **IX**, **XII**, **XIV**, and **XV** is observed at 1675–1721 cm^{-1}. All the products show in the spectra absorption bands from C=C and C=N bonds at 1453–1543 and 1582–1615 cm^{-1} and SO_2 group at 1335–1403 and 1195–1210 cm^{-1} (or benzoyl carbonyl group at 1748–1773 cm^{-1}). The ^{1}H NMR spectra of the compounds prepared were consistent with the proposed structures (Table 4).

EXPERIMENTAL

The IR spectra were measured on a UR-20 spectrophotometer in KBr. The ^{1}H NMR spectra were obtained on a Varian VXR-300 instrument at 300 MHz; The chemical shifts were measured relative to tetramethylsilane. The reaction mixtures were analyzed by TLC on Silufol UV-254 plates using 10:1 benzene–hexane as eluent; spots were visualized by UV irradiation.

Compounds **Ia**–**Id**, **VIIa**–**VIIc**, and **XIIIa**–**XIIIc** were synthesized by acylation of the corresponding *p*-benzoquinone monooximes with aroyl chlorides or arenesulfonyl chlorides in diethyl ether in the presence of triethylamine, following the procedure reported in [7]. Table 3 contains yields, melting points, and analytical data of the newly synthesized compounds.

Chlorination of 4-aroyloxyimino- and 4-arylsulfonyloxyimino-2,5-cyclohexadienones Ia–Id, IVa–IVd, VIIa–VIIc, Xa–Xc, and XIIIa–XIIIc. Dry gaseous chlorine was passed at a flow rate of 15–20 ml/min (at a temperature specified in Table 1) through a solution of appropriate substrate in 10 ml of DMF or DMF–acetic acid (see Table 1) until complete saturation. The mixture was diluted with 10–15 ml of water, and the product was filtered off and recrystallized from appropriate solvent. The yields, melting points, and elemental analyses of compounds **IIa**–**IId**, **VIa**–**VId**, **VIIIa**–**VIIIc**, **XIIb**, **XIIc**, and **XIVa**–**XIVc** are given in Table 3.

Table 3. Yields, melting points, and elemental analyses of alkyl-substituted 4-aroyl(arylsulfonyl)oxyimino-2,5-cyclohexadienones **Ia**–**Id**, **VIIb**, **VIIc**, and **XIIIa**–**XIIIc** and their halogenated derivatives **II**–**VI**, **VIIIa**–**VIIIc**, **IXb**, **IXc**, **Xa**–**Xc**, **XIb**, **XIc**, **XIIa**–**XIIc**, **XIVa**–**XIVc**, **XVa**, and **XVc**

Compound no.	Yield, %	mp, °C (solvent)	Found, %		Formula	Calculated, %	
			Hlg	N		Hlg	N
Ia	63	170 (*i*-PrOH)	–	5.26, 5.33	$C_{15}H_{13}NO_3$	–	5.49
Ib	78	158 (*i*-PrOH)	12.06, 12.19	4.79, 4.84	$C_{15}H_{12}ClNO_3$	12.25	4.83
Ic	67	109 (*i*-PrOH)	–	4.75, 4.81	$C_{14}H_{13}NO_4S$	–	4.81
Id	91	134 (*i*-PrOH)	–	8.27, 8.30	$C_{14}H_{12}N_2O_6S$	–	8.33
IIa	60	136 (*i*-PrOH)	21.63, 21.71	4.20, 4.27	$C_{15}H_{13}Cl_2NO_3$	21.74	4.29
IIb	51	118 (*i*-PrOH)	29.50, 29.54	3.75, 3.84	$C_{15}H_{12}Cl_3NO_3$	29.54	3.88
IIc	45	95 (*i*-PrOH)	19.48, 19.57	3.80, 3.85	$C_{14}H_{13}Cl_2NO_4S$	19.58	3.87
IId	67	127 (*i*-PrOH)	17.40, 17.43	6.80, 6.83	$C_{14}H_{12}Cl_2N_2O_6S$	17.42	6.88
IIIa	74	157 (*i*-PrOH)	38.41, 38.47	3.29, 3.34	$C_{15}H_{13}Br_2NO_3$	38.50	3.37
IIIb	86	137 (*i*-PrOH)	43.37, 43.41	3.05, 3.09	$C_{15}H_{12}ClBr_2NO_3$	43.44	3.11
IIIc	73	110 (*i*-PrOH)	35.39, 35.43	3.01, 3.07	$C_{14}H_{13}Br_2NO_4S$	35.43	3.10
IIId	53	125 (*i*-PrOH)	32.17, 32.22	–	$C_{14}H_{12}Br_2N_2O_6S$	32.22	–
IVa	89	166 (AcOH)	12.07, 12.21	4.75, 4.80	$C_{15}H_{12}ClNO_3$	12.24	4.83
IVb	79	193 (AcOH)	21.80, 21.84	4.30, 4.32	$C_{15}H_{11}Cl_2NO_3$	21.88	4.32
IVc	90	200 (AcOH)	10.80, 10.87	–	$C_{14}H_{12}ClNO_4S$	10.89	–
IVd	67	112 (AcOH)	9.47, 9.53	–	$C_{14}H_{11}ClN_2O_6S$	9.56	–
Va	63	166 (AcOH)	23.82, 23.89	–	$C_{15}H_{12}BrNO_3$	23.92	–
Vb	76	192 (AcOH)	31.32, 31.26	3.73, 3.75	$C_{15}H_{11}ClBrNO_3$	31.30	3.80
Vc	53	132 (AcOH)	21.50, 21.56	3.74, 3.79	$C_{14}H_{12}BrNO_4S$	21.59	3.78
Vd	49	208 (AcOH)	32.17, 32.21	5.60, 5.67	$C_{14}H_{11}BrN_2O_6S$	32.28	5.66
VIa	90	146 (AcOH)	29.46, 29.50	3.85, 3.87	$C_{15}H_{12}Cl_3NO_3$	29.54	3.88
VIb	53	157 (AcOH)	35.79, 35.88	3.41, 3.49	$C_{15}H_{11}Cl_4NO_3$	35.90	3.54
VIc	43	104 (AcOH)	26.71, 26.78	3.50, 3.51	$C_{14}H_{12}Cl_3NO_4S$	26.82	3.53
VId	61	124 (AcOH)	23.97, 23.99	6.25, 6.31	$C_{14}H_{12}Cl_3N_2O_6S$	24.03	6.33
VIIb	39	87 (*i*-PrOH)	–	4.12, 4.18	$C_{17}H_{19}NO_4S$	–	4.20
VIIc	93	130 (*i*-PrOH)	–	7.70, 7.35	$C_{16}H_{16}N_2O_6S$	–	7.78
VIIIa	31	121 (*i*-PrOH)	19.29, 19.33	3.79, 3.80	$C_{18}H_{17}Cl_2NO_3$	19.37	3.83
VIIIb	54	114 (AcOH)	17.47, 17.51	3.41, 3.44	$C_{17}H_{19}Cl_2NO_4S$	17.55	3.47
VIIIc	48	129 (AcOH)	16.25, 16.27	6.37, 6.42	$C_{16}H_{16}Cl_2N_2O_6S$	16.30	6.44
IXb	45	141 (AcOH)	32.25, 32.39	2.77, 2.81	$C_{17}H_{19}Br_2NO_4S$	32.41	2.84
IXc	51	142 (*i*-PrOH)	30.41, 30.47	–	$C_{16}H_{16}Br_2N_2O_6S$	30.50	–
Xa	83	127 (AcOH)	11.12, 11.15	–	$C_{17}H_{16}ClNO_3$	11.17	–
Xb	85	118 (AcOH)	9.57, 9.61	3.73, 3.77	$C_{17}H_{18}ClNO_4S$	9.64	3.81
Xc	91	156 (AcOH)	8.83, 8.85	7.00, 7.02	$C_{16}H_{15}ClN_2O_6S$	8.90	7.03
XIb	52	137 (AcOH)	19.31, 19.37	3.32, 3.37	$C_{17}H_{18}BrNO_4S$	19.39	3.40
XIc	73	148 (AcOH)	18.01, 18.02	6.23, 6.29	$C_{16}H_{15}BrN_2O_6S$	18.04	6.32
XIIb	58	143 (AcOH)	24.17, 24.20	3.13, 3.20	$C_{17}H_{18}Cl_3NO_4S$	24.25	3.19
XIIc	44	88 (AcOH)	22.49, 22.59	5.91, 5.94	$C_{16}H_{15}Cl_3N_2O_6S$	22.65	5.96
XIIIa	75	117 (*i*-PrOH)	10.19, 10.23	3.97, 4.01	$C_{19}H_{20}ClNO_3$	10.26	4.05
XIIIb	63	74 (*i*-PrOH)	–	4.27, 4.30	$C_{20}H_{23}NO_3$	–	4.31
XIIIc	56	91 (*i*-PrOH)	–	3.80, 3.85	$C_{19}H_{23}NO_4S$	–	3.88
XIVa	53	128 (AcOH)	25.48, 25.51	3.31, 3.37	$C_{19}H_{20}Cl_3NO_3$	25.54	3.36
XIVb	81	112 (AcOH)	17.75, 17.88	3.39, 3.49	$C_{20}H_{23}Cl_2NO_3$	17.90	3.53
XIVc	40	128 (*i*-PrOH)	16.35, 16.40	–	$C_{19}H_{23}Cl_2NO_4S$	16.41	–
XVa	47	138 (AcOH)	38.59, 38.62	2.70, 2.76	$C_{19}H_{20}ClBr_2NO_3$	38.63	2.77
XVc	42	145 (AcOH)	30.59, 30.67	2.58, 2.67	$C_{19}H_{23}Br_2NO_4S$	30.67	2.69

Table 4. ^{1}H NMR spectra ($CDCl_3$) of alkyl-substituted 4-aroyl(arylsulfonyl)oxyimino-2,5-cyclohexadienones **Ia**–**Ic**, **VIIb**, and **XIIIa**–**XIIIc** and their halogenated derivatives **IIa**, **IIc**, **IIIb**, **IIId**, **IVc**, **Vb**, **Vd**, **VIb**, **VIc**, **VIIIb**–**XIIb**, **XIVa**–**XIVc**, **XVa**, and **XVc**

Comp. no.	Chemical shifts δ, ppm					Coupling constants $J_{H,H}$, Hz
	2-H, 2-CH_3, 2-CH	3-H, 3-CH_3	5-H, 5-CH_3	6-H, 6-CH	R	
Ia[a]	1.97 s, CH_3	2.26 s, CH_3	7.95–7.99 d, CH	6.59–6.61 d, CH	7.58–8.16 m, C_6H_5	10.5 (5–6)
Ib[a]	1.98 s, CH_3	2.26 s, CH_3	7.98–8.02 d, CH	6.59–6.63 d, CH	7.66–8.19 d.d, C_6H_4	10.2 (5–6)
Ic	1.98 s, CH_3	2.10 s, CH_3	7.54–7.58 d, CH	6.46–6.49 d, CH	7.58–8.06 m, C_6H_5	10.2 (5–6)
IIa[a]	2.04 s, CH_3	2.29 s, CH_3	6.29 d, CH	4.87 d, CH	7.64–8.19 m, C_6H_5	2.1 (5–6)
IIc	2.00 s, CH_3	2.08 s, CH_3	5.52 d, CH	4.40 d, CH	7.57–8.04 m, C_6H_5	2.7 (5–6)
IIIb	2.12 s, CH_3	2.36 s, CH_3	5.77 d, CH	4.70 d, CH	7.51–8.08 d.d, C_6H_4	2.1 (5–6)
IIId	2.03 s, CH_3	2.09 s, CH_3	5.60 d, CH	4.60 d, CH	7.84 t, 5-H, 8.37 d, 6-H, 8.55 d, 4-H, 8.89 s, 2-H	2.4 (5–6)
IVc	2.04 s, CH_3	2.11 s, CH_3	7.76 s, CH	–	7.58–8.06 m, C_6H_5	
Vb	2.13 s, CH_3	2.36 s, CH_3	8.17 s, CH	–	7.51–8.09 d.d, C_6H_4	
Vd	2.05 s, CH_3	2.10 s, CH_3	8.02 s, CH	–	7.85 t, 5-H, 8.37 d, 6-H, 8.56 d, 4-H, 8.91 s, 2-H	
VIb	2.01 s, CH_3	2.22 s, CH_3	7.80 s, CH	–	7.51–8.07 d.d, C_6H_4	
VIc	1.91 s, CH_3	1.93 s, CH_3	7.65 s, CH	–	7.57–8.03 m, C_6H_5	
VIIb	6.31 d.q, CH	2.09 s, CH_3	7.29 s, CH	1.10 s, CH_3, 1.12 s, CH_3, 3.05 m, CH	7.37–7.94 d.d, C_6H_4, 2.47 s, CH_3	
VIIIb	4.34 s, CH	1.90 s, CH_3	7.17 s, CH	1.10 d, CH_3, 1.17 d, CH_3, 3.00 m, CH	7.36–7.91 d.d, C_6H_4, 2.47 s, CH_3	
IXb	4.67 s, CH	2.10 s, CH_3	7.13 s, CH	1.10 d, CH_3 1.17 d, CH_3 3.02 m, CH	7.36–7.91 d.d, C_6H_4, 2.47 s, CH_3	
Xb	–	2.25 s, CH_3	7.34 s, CH	1.27 s, CH_3, 1.15 s, CH_3 3.10 m, CH	7.36–7.95 d.d, C_6H_4, 2.47 s, CH_3	
XIb	–	2.30 s, CH_3	7.33 s, CH	1.13 s, CH_3, 1.15 s, CH_3, 3.11 m, CH	7.38–7.95 d.d, C_6H_4, 2.48 s, CH_3	
XIIb	–	2.19 s, CH_3	5.51 s, CH	1.09 d, CH_3, 1.21 d, CH_3, 2.69 m, CH	7.37–7.91 d.d, C_6H_4, 2.47 s, CH_3	
XIIIa	1.14 s, CH_3, 1.17 s, CH_3, 3.15 m, CH	7.18 d, CH	7.46 d, CH	1.87 s, CH_3, 1.21 s, CH_3, 3.15 m, CH	7.52–8.09 d.d, C_6H_4	2.4 (3–5)
XIIIb	1.14 s, CH_3, 1.16 s, CH_3, 3.15 m, CH	7.19 q, CH	7.51 q, CH	1.19 s, CH_3, 1.21 s, CH_3, 3.15 m, CH	7.34–8.04 d.d, C_6H_4, 2.47 s, CH_3	1.5 (3–5)
XIIIc	1.07 s, CH_3, 1.10 s, CH_3, 3.08 m, CH	6.79 q, CH	7.29 q, CH	1.12 s, CH_3, 1.14 s, CH_3, 3.08 m, CH	7.38–7.95 d.d, C_6H_4, 2.47 s, CH_3	2.7 (3–5)
XIVa	1.09 d, 1.13 d, $2CH_3$, 3.06 m, CH	6.91 q, CH	5.58 d, CH	1.19 d, 1.20 d, $2CH_3$, 2.81 m, CH	7.51–8.04 d.d, C_6H_4	1.5 (3–5)

Table 4. (Contd.)

Comp. no.	Chemical shifts δ, ppm					Coupling constants $J_{H,H}$, Hz
	2-H, 2-CH_3, 2-CH	3-H, 3-CH_3	5-H, 5-CH_3	6-H, 6-CH	R	
XIVb	1.09 d, 1.13 d, 2CH_3, 3.05 m, CH	6.92 q, CH	5.62 d, CH	1.19 d, 1.21 d, 2CH_3, 2.81 m, CH	7.32–8.00 d.d, C_6H_4, 2.46 s, CH_3	1.2 (3–5)
XIVc	1.02 d, 1.08 d, 2CH_3, 2.98 m, CH	6.54 q, CH	5.43 d, CH	1.12 d, 1.15 d, 2CH_3, 2.70 m, CH	7.36–7.91 d.d, C_6H_4, 2.48 s, CH_3	1.5 (3–5)
XVa	1.20 d, 1.24 d, 2CH_3, 3.05 m, CH	6.86 q, CH	5.73 d, CH	1.10 s, 1.12 s, 2CH_3, 2.49 m, CH	7.51–8.06 d.d, C_6H_4	2.1 (3–5)
XVc	1.12 d, 1.19 d, 2CH_3, 2.99 m, CH	6.49 q, CH	5.57 d, CH	1.04 t, 2CH_3, 2.38 m, CH	7.36–7.92 d.d, C_6H_4, 2.46 s, CH_3	1.5 (3–5)

[a] In DMSO-d_6.

Bromination of 4-aroyloxyimino- and 4-arylsulfonyloxyimino-2,5-cyclohexadienones Ia–Id, VIIa–VIIc, XIIIa, and XIIIc. A 3 M solution of bromine was added dropwise under vigorous stirring to 10 ml of a 0.5 M solution of compound **Ia**–**Id**, **VIIa**–**VIIc**, **XIIIa**, or **XIIIc** in the same solvent (Table 2). The product was filtered off and recrystallized from appropriate solvent. The yields, melting points, and elemental analyses of compounds **IIIa**–**IIId**, **IXb**, **IXc**, **XVa**, and **XVb** are given in Table 3.

Dehydrohalogenation of 4-aroyloxyimino- and 4-arylsulfonyloxyimino-2-cyclohexenones IIa–IId, IIIa–IIId, VIIIa–VIIIc, and IXa–IXc. Halogen derivative **IIa**–**IId**, **IIIa**–**IIId**, **VIIIa**–**VIIIc**, or **IXa**–**IXc**, 1 mmol, was dissolved in a minimal amount of chloroform, and 0.1–0.15 ml of triethylamine was added dropwise. After 3–5 min, the product was filtered off, washed with small portions of water and acetic acid, and recrystallized. The yields, melting points, and elemental analyses of compounds **IVa**–**IVd**, **Xa**–**Xc**, **XIb**, and **XIc** are given in Table 3.

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