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Reaction of Polyhalo Semiquinoid Structures Originating from 4-Aroyl(arylsulfonyl)oximino-2,5-cyclohexadiene-1-ones with Arylsulfinic Acids

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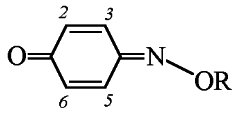
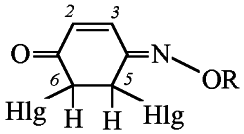
Abstract—Stable semiquinoid structures, 4-aroyl(arylsulfonyl)oximino-2,6-dimethyl-5,6-dichloro-2-cyclohexen-1-ones, do not react with dialkyl phosphites, alcohols, tosylhydrazine, p-toluidine, and hydrazoic acid. In reactions with arylsulfinic acids occurs a nucleophilic substitution of chlorine at the sp^3-hybridized C^5 carbon in the minor Z-isomer yielding 4-aroyl(arylsulfonyl)oximino-5-arylsulfonyl-2,6-dimethyl-6-chloro-2-cyclohexen-1-ones.

As known the halogenation of 4-aroyl(arylsulfonyl)-oximino-2,5-cyclohexadiene-1-ones results in the opening of the quinoid ring due to addition of one halogen molecule to the double bond in the quinoid ring [1–5]. As a result arises a mixture of *Z,E*-isomers of 4-aroyl(arylsulfonyl)oximino-2,6-dimethyl-5,6-dihalo-2-cyclohexen-1-ones with one of them prevailing due to the nonequivalence of the double bonds of the quinoid ring. The more active bond is that between the C^5 and C^6 atoms, namely the *cis*-C=C bond with respect to OR substituent at the nitrogen atom [6, 7].



In the halogenation products of the 4-aroyl(arylsulfonyl)oximino-2,5-cyclohexadiene-1-ones prevails the *E*-isomer since the OR substituent at nitrogen is in transoid position with respect to the C=C bond of the semiquinoid ring.



The halogenation products can be selectively dehydrohalogenated with elimination of proton from *6* position [1–5]. On addition of one Hlg_2 molecule to 4-aroyl(arylsulfonyl)oximino-2,6(2,5)-cyclohexadiene-1-ones Arise stable structures 4-aroyl(arylsulfonyl)oximino-2,6(2,5)-dimethyl-5,6-dihalo-2-cyclohexen-1-ones that cannot be dehydrohalogenated due to the lack of proton in position *6* [4, 5]. The obtained stable semiquinoid structures originating from *p*-quinone oximes provided a possibility to study their reactivity.

The most characteristic reactions for semiquinoid structures originating from *N*-arylsulfonyl-*p*-quinone imines are 1,2-addition, elimination of Cl_2 molecule to yield a quinoid structure that might be further reduced into the corresponding N-substituted *p*-aminophenol, and also the nucleophilic substitution of chlorine at sp^2-hybridized carbon atom [8].

As revealed the study the stable semiquinoid structures, 4-aroyl(arylsulfonyl)oximino-2,6-dimethyl-5,6-dichloro-2-cyclohexen-1-ones (**Ia–d**), did not react with dialkyl phosphites, alcohols, tosylhydrazine, *p*-toluidine, and hydrazoic acid. In reactions of compounds **Ia–d** with arylsulfinic acids occurs a nucleophilic substitution of chlorine at the sp^3-hybridized C^5 carbon in the minor Z-isomer (the OR substituent at nitrogen is in *cis*- position with respect to the C=C bond of the semiquinoid ring). As a result in all cases forms a mixture of the initial *E*-isomer of compound **Ia–d** and the reaction product of the *Z*-isomer and arylsulfinic acid, 4-aroyl(arylsulfonyl)oximino-5-arylsulfonyl-2,6-dimethyl-6-chloro-2-cyclohexen-1-one (**IIa–h**) (see scheme).

The reaction product **IIe** obtained from compound **Ic** and benzenesulfinic acid was identified by ^1H NMR spectrum (see Table). According to ^1H NMR spectrum the original compound 4-phenylsulfonyloximino-2,6-dimethyl-5,6-dichloro-2-cyclohexen-1-one (**Ic**) is a mixture of *Z*- and *E*-isomers with the latter prevailing (70%). The reaction product

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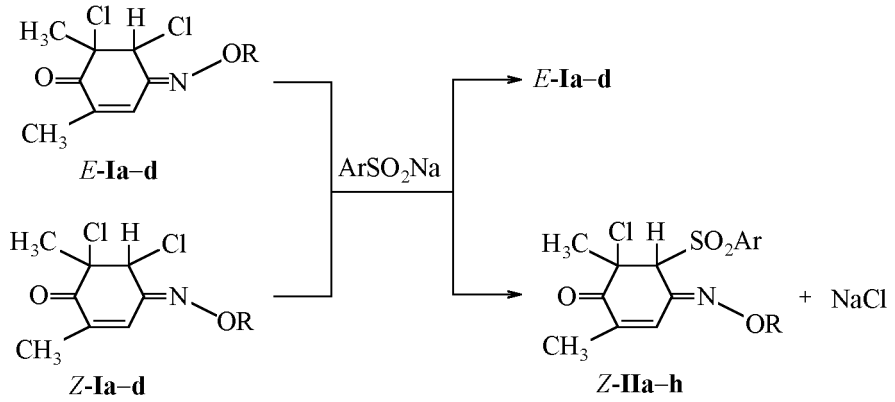
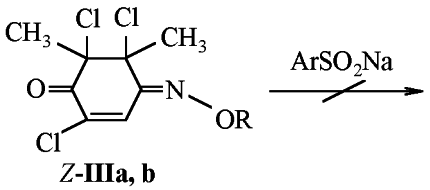
Scheme.



I, R = C_6H_5CO (**a**), 4-ClC_6H_4CO (**b**), $C_6H_5SO_2$ (**c**), 3-$NO_2C_6H_4SO_2$ (**d**); **II**, R = C_6H_5CO (**a, b**), 4-ClC_6H_4CO (**c, d**), $C_6H_5SO_2$ (**e, f**), 3-$NO_2C_6H_4SO_2$ (**g, h**); Ar = C_6H_5 (**a, c, e, g**), 4-$CH_3C_6H_4$ (**b, d, f, h).**

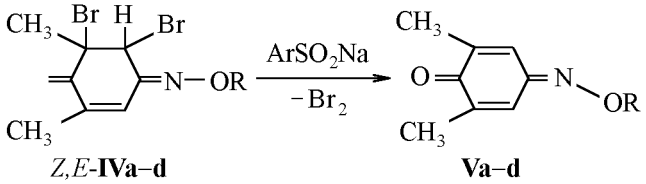
consists of the initial *E*-isomer of compound **Ic** (73%) and 4-phenylsulfonyloximino-5-phenylsulfonyl-2,6-dimethyl-6-chloro-2-cyclohexen-1-one (**IIe**) (27%) as *Z*-isomer formed by nucleophilic replacement of chlorine (see Table). In the other cases the formation of compounds **II** was revealed by TLC. In the ^{1}H NMR spectra of recrystallized reaction products appeared only the *E*-isomer of the original imino-ketone **I**. The reaction product **II** due to its low content and higher solubility at recrystallization remained in the filtrate as showed also TLC. Compounds **II** were not isolated as individual substances. No reaction between the *E*-isomers of compounds **Ia–d** and arylsulfinic acids is due to steric hindrance: The sterically shielded chlorine atom does not undergo nucleophilic substitution with a bulky $ArSO_2$ group.

In 4-aroyl(arylsulfonyl)oximino-5,6-dimethyl-2,5,6-trichloro-2-cyclohexen-1-ones (**IIIa, b**) that exist exclusively as *Z*-isomers the nucleophilic substitution of chlorine at the sp^3-hybridized carbon C^5 does not occur apparently due to the steric hindrance effected by CH_3 group.



R = C_6H_5CO (**a**), 4-ClC_6H_4CO (**b**).

The stable semiquinoid structures 4-aroyl(arylsulfonyl)oximino-5,6-dibromo-2,6-dimethyl-2-cyclohexen-1-ones (**IVa–d**) react with arylsulfinic acids with liberation of Br_2 molecule as we have previously observed at dehydrobromination [3, 5]. As a result arise the initial 4-aroyl(arylsulfonyl)oximino-2,6-dimethyl-2,5-cyclohexadiene-1-ones (**Va–d**) [5].



R = C_6H_5CO (**a**), 4-ClC_6H_4CO (**b**), $C_6H_5SO_2$ (**c**), 3-$NO_2C_6H_4SO_2$ (**d**).

EXPERIMENTAL

^{1}H NMR spectra were registered on a spectrometer Varian VXR-300 (300 MHz) in $CDCl_3$, reference TMS. The initial compounds **Ia–d, IVa–d** were prepared as in [5]. The composition of reaction products and filtrates after recrystallization were determined by TLC on Silufol UV-254 plates (eluent benzene–ethyl acetate, 10:1), development under UV light.

Reaction between 4-benzoyl(phenylsulfonyl)-oximino-2,6-dimethyl-5,6-dichloro-2-cyclohexen-1-ones (**Ia, c**) and dialkyl phosphites (**a**), alcohols (**b**), tosylhydrazine (**c**), hydrazoic acid (**d**), *p*-toluidine (**d**). (a) To 0.4 ml of dialkyl phosphite (dimethyl phosphite, diethyl phosphite, diisopropyl phosphite) was added 0.2 g of the original compound **Ia, c**. The reaction mixture was heated to 130°C. The compound added dissolved, the solution got dark color.

(b) In 5 ml of anhydrous alcohol (methanol, ethanol, 2-propanol) was refluxed for 1 h 5 mmol of

^{1}H NMR spectra ($CDCl_3$) of 4-phenylsulfonyloximino-2,6-dimethyl-5,6-dichloro-2-cyclohexen-1-one (**Ic**) and 4-phenylsulfonyloximino-2,6-dimethyl-6-chloro-5-phenylsulfonyl-2-cyclohexen-1-one (**IIe**)

Compd. no.	Isomer content, %	δ, ppm					*J*, Hz
		CH_3C^2	CH_3C^6	H^3	H^5 ($PhSO_2C^5$)	R	
Initial compounds							
Z-Ic	30	2.07 d	1.85 s	7.26 q	4.90 d	7.58–8.02 m	$J(H^3–H^5)$ 1.5
E-Ic	70	2.02 d	1.85 s	6.76 q	5.47 d	7.58–8.02 m	$J(H^3–H^5)$ 1.5
Reaction products							
Z-IIe	27	2.26 s	2.15 s	6.70 s	5.08 s (7.52–8.02 m)	7.52–8.02 m	–
E-Ic	73	2.02 d	1.85 c	6.76 q	5.47 d	7.58–8.02 m	$J(H^3–H^5)$ 1.5

compound **Ia, c.** (c) To a solution of 5 mmol of compound **Ia, c** in 5 ml of ethanol was added 10 mmol of tosylhydrazine, and the mixture was boiled for 15–20 min. d. To a solution of 2.5 mmol of compound **Ia, c** in 10 ml of acetic acid was added 5 mmol of sodium azide, and the mixture was boiled for 5–10 min. e. To a solution of 5 mmol of compound **Ia, c** in 7 ml of ethanol was added 15 mmol of *p*-toluidine, and the mixture was boiled for 30 min.

On cooling the reaction mixtures separated a precipitate that was filtered off and recrystallized from acetic acid. We isolated the initial compounds.

Reaction between 4-aroyl(arylsulfonyl)oximino-2,6-dimethyl-5,6-dichloro-2-cyclohexen-1-ones (Ia–d) and arylsulfinic acids. To a solution of an appropriate initial compound in 10 ml of boiling acetic acid was added 6 mmol of sodium arylsulfinate, and the mixture was boiled for 3–5 min. The reaction progress was monitored by TLC. On cooling to the reaction mixture was added 2–3 ml of water. The separated precipitate was filtered off and recrystallized from acetic acid. In reaction of compound **Ic** with sodium benzenesulfinate was isolated a mixture of compounds *E*-**Ic** and **IIe**, in the rest of experiments were isolated the *E*-isomers of compounds **Ia, b, d**.

Reaction between 4-aroyl(arylsulfonyl)oximino-5,6-dimethyl-2,5,6-trichloro-2-cyclohexen-1-ones (IIIa,b) and arylsulfinic acids was carried out as above. The reaction progress was monitored by TLC. We isolated the initial compounds.

Reaction between 4-aroyl(arylsulfonyl)oximino-5,6-dibromo-2,6-dimethyl-2-cyclohexen-1-ones (IIa–d) and arylsulfinic acids was carried out as above. Yields of compounds, %: **Va** 60, **Vb** 53, **Vc** 74, **Vd** 41.

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