Russian Journal of Organic Chemistry, Vol. 40, No. 9, 2004, pp. 1291–1294. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 9, 2004, pp. 1340–1343.
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N-Arylsulfinyl-1,4-Benzoquinonimines

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Received December 17, 2003

Abstract—Stable *N*-arylsulfinyl-1,4-benzoquinonimines were synthesized by acylation of the corresponding 1,4-benzoquinone monooximes with arenesulfenyl chlorides. The process involves transformation of sulfur(II) into sulfur(IV).

Titov and Burmistrov [1] reported on the reaction of 1,4-benzoquinone monooximes with arenesulfenyl chlorides, which was assumed to afford the corresponding sulfenyloxyimino derivatives, 4-arylsulfanyloxyimino-2,5-cyclohexadienones. However, no proofs for the structure of the products were given. Later on, it was shown that reactions of sulfenyl chlorides with compounds containing a hydroxy group give rise to sulfoxides through intermediate formation of unstable sulfenic acid esters [2].

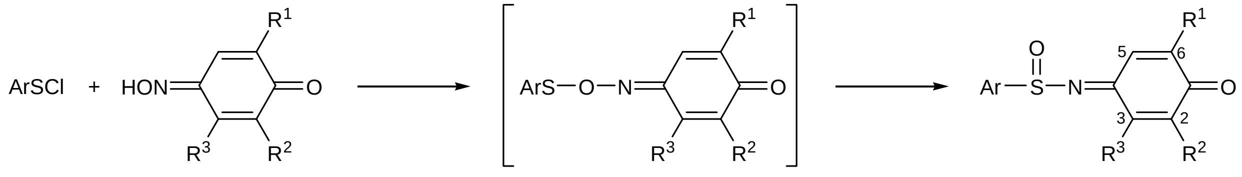
$$\mathrm{ROH} + \mathrm{R'SCl} \longrightarrow [\mathrm{R'SOR}] \longrightarrow \mathrm{R'S(O)R}$$

Therefore, the formation of 4-arylsulfanyloxyimino-2,5-cyclohexadienones described in [1] seems to be doubtful; it is more probable that the products are 4-arylsulfinylimino-2,5-cyclohexadienones. The synthesis of the only representative of such quinonimines, 4-*tert*-butylsulfinylimino-2,5-cyclohexadienone, was reported in [3]. It was obtained by oxidation of 4-*tert*-butylsulfanylimino-2,5-cyclohexadienone and was a very unstable compound: it decomposed within an hour [3].

We performed acylation of a series of 1,4-benzoquinone monooximes according to the procedure described in [1] with a view to refine the published data and probably obtain compounds of a new class. As a result (see below), we isolated 4-arylsulfinylimino-2,5-cyclohexadienones **Ia**–**Id** (Scheme 1, Table 1). Presumably, these compounds are formed through unstable intermediate **A** which was assumed in [1] to be the final product. 2-Isopropyl-5-methyl-4-(2-nitrophenylsulfinylimino)-2,5-cyclohexadienone (**Id**) was identical to the product described in [1]. In order to obtain an additional information for analysis of the ^{1}H and ^{13}C NMR spectra of benzoquinonimines **Ia**–**Id**, we synthesized 4-(4-nitrophenylsulfanylimino)-2,5-cyclohexadienones **IIa** and **IIb** and 4-(4-nitrophenylsulfonyloxyimino)-2,5-cyclohexadienones **IIIa** and **IIIb** (Tables 1–3).

The structure of benzoquinonimines **Ia**–**Id** was confirmed by the data of elemental analysis (Table 1) and ^{1}H and ^{13}C NMR spectra (Tables 2, 3). In the ^{1}H NMR spectra of compounds **Ia** and **Ib** having similar substituents in positions *2* and *6* of the quinoid ring, protons in positions *3* and *5* appear at room

Scheme 1.



A **Ia**–**Id**

Ar = 4-$NO_2C_6H_4$, $R^1 = R^2$ = Me, R^3 = H (**a**); $R^1 = R^2$ = *t*-Bu (**b**); Ar = 2-$NO_2C_6H_4$, R^1 = Me, R^2 = H, R^3 = *i*-Pr (**c**); R^1 = *i*-Pr, R^2 = H, R^3 = Me (**d**).

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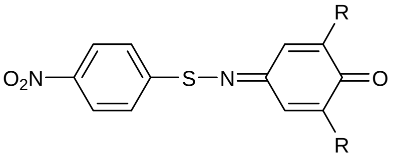
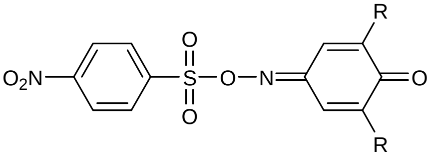


IIa, **IIb**



IIIa, **IIIb**

II, **III**, R = Me (**a**), *t*-Bu (**b**).

temperature as broadened singlets. Raising the temperature leads to even stronger broadening of these signals. An analogous pattern was observed for the signals from methyl (compound **Ia**) and *tert*-butyl groups (compound **Ib**). These data indicate a fairly fast *Z*,*E* isomerization which is not typical of esters derived from quinone monooximes: the corresponding barrier to isomerization exceeds 110 kJ/mol [4]. An appreciable magnetic nonequivalence of protons in positions *3* and *5* of the quinoid ring in compounds **I** should be noted (Table 2). In the ^1H NMR spectra of quinonimines **Ia** and **Ib** the difference between the chemical shifts of 3-H and 5-H [$\Delta\delta$(3-H, 5-H)] is 1.35–1.38 ppm, which is considerably larger than the corresponding difference for other quinonimines and 1,4-benzoquinone monooxime *O*-esters: $\delta\Delta$(3-H, 5-H) = 0.19–0.22 ppm for compounds **IIa** and **IIb** (Table 2), 1.12–1.17 ppm for 4-arylsulfonylimino-2,5-cyclohexadienones [5, 6], and 0.53–0.55 ppm for arenesulfonates **IIIa** and **IIIb** (Table 2).

The sulfoxide-like structure of **Ia**–**Id** also follows from analysis of their ^{13}C NMR spectra. The signal from the C=N carbon atom is located at δ_C 163–165 ppm (Table 3), while quinone oxime *O*-esters are characterized by the corresponding δ_C values in the range from ~153 to 155 ppm. The ^{13}C chemical shift of the C=N carbon atom in **Ia**–**Id** occupies an intermediate place between those found for arylsulfanyl (**IIa**, **IIb**; δ_C 156–157 ppm) and arylsulfonyl derivatives (δ_C 166–167 ppm) [5, 6].

Unambiguous support for the structure of quinonimines **I** was obtained from the ^1H NMR spectra of compounds **Ic** and **Id** which exist as a single conformer and contain isopropyl groups in the quinoid fragment. The shape of the signals from protons of the isopropyl groups may be indicative of the presence of an asymmetric center in the molecule. In the spectra of compounds having an –S–O–N= fragment, methyl protons of isopropyl groups should give rise to a doublet, while the corresponding signals in the spectra of sulfinylimino derivatives [–S(O)N=] should be doubled. The ^1H NMR spectra of **Ic** and **Id** contain a double set of signals from methyl protons of the isopropyl fragment; this means that molecules **Ic** and **Id** possess an asymmetric center, namely the sulfoxide sulfur atom. Compound **Ic** is characterized by a greater nonequivalence of the methyl protons ($\Delta\delta$ = 0.070 ppm), as compared to **Id** ($\Delta\delta$ = 0.015 ppm). This may be due to closer position of the isopropyl group to the sulfur atom in **Ic**.

As noted above, temperature variations of the ^1H NMR spectra of **Ia** and **Ib** suggest a fairly fast (on the NMR time scale) *Z*,*E* isomerization process. We have found no published data on the heights of barriers to *Z*,*E* isomerization of N-sulfinyl derivatives of benzoquinonimines. Therefore, it was interesting to estimate these values and compare them with those typical of other benzoquinonimines. The barrier to *Z*,*E*

Table 1. Yields, melting points, and elemental analyses of 4-arylsulfinylimino-2,5-cyclohexadienones **Ia**–**Id**, 4-(4-nitrophenylsulfanylimino)-2,5-cyclohexadienones **IIa** and **IIb**, and 4-(4-nitrophenylsulfonyloxyimino)-2,5-cyclohexadienones **IIIa** and **IIIb**

Compound no.	Yield, %	mp, °C (solvent)	Found C, %	Formula	Calculated C, %
Ia	20	119–122 (petroleum ether)	10.51, 10.76	$C_{14}H_{12}N_2O_4S$	10.54
Ib	33	149–150 (petroleum ether)	8.03, 8.22	$C_{20}H_{24}N_2O_4S$	8.25
Ic	34	151–152 (octane)	9.67, 9.74	$C_{16}H_{16}N_2O_4S$	9.65
Id	38	127–129 (octane)	9.48, 9.63	$C_{16}H_{16}N_2O_4S$	9.65
IIa	30	158–160 (acetic acid)	11.04, 11.11	$C_{14}H_{12}N_2O_3S$	11.12
IIb	9	167–168 (acetic acid)	8.48, 8.56	$C_{20}H_{24}N_2O_3S$	8.61
IIIa	80	175–177 (isopropyl alcohol)	9.29, 9.45	$C_{14}H_{12}N_2O_6S$	9.53
IIIb	78	166–167 (acetic acid)	7.52, 7.71	$C_{20}H_{24}N_2O_6S$	7.63

Table 2. ^{1}H NMR spectra of 4-arylsulfinylimino-2,5-cyclohexadienones **Ia**–**Id**, 4-(4-nitrophenylsulfanylimino)-2,5-cyclohexadienones **IIa** and **IIb**, and 4-(4-nitrophenylsulfonyloxyimino)-2,5-cyclohexadienones **IIIa** and **IIIb**

Comp. no.	Chemical shifts δ, ppm				
	2-H, 2-Me, 2-*t*-Bu	3-H, 3-Me, 3-*i*-Pr	5-H	6-Me, 6-*i*-Pr, 6-*t*-Bu	Ar
Ia	2.09 br.s (3H, Me)	6.81 br.s (1H)	8.16 br.s (1H)	2.04 br.s (3H, Me)	8.00–8.41 d.d (4H)
Ib	1.31 br.s (9H, *t*-Bu)	6.75 br.s (1H)	8.13 br.s (1H)	1.27 br.s (9H, *t*-Bu)	8.03–8.42 d.d (4H)
Ic	6.39 d (1H, *J* = 0.8 Hz)	0.94 d and 1.01 d (3H, Me, *J* = 6.9 Hz), 2.94 m (1H, CH)	8.09 q (1H, *J* = 1.2 Hz)	2.09 d (3H, Me, *J* = 1.2 Hz)	8.22–8.39 d.d (2H, 3'-H, 6'-H), 7.75–7.95 d.t (2H, 4'-H, 5'-H)
Id	6.42 q (1H, *J* = 1.3 Hz)	1.95 d (3H, Me, *J* = 1.2 Hz)	7.99 s (1H)	1.18 d and 1.19 d (3H, Me, *J* = 6.9 Hz), 3.08 m (1H, CH)	8.21–8.41 d.d (2H, 3'-H, 6'-H), 7.74–7.95 d.t (2H, 4'-H, 5'-H)
IIa	2.12 d (3H, Me, *J* = 1.2 Hz)	7.00 d (1H, *J* = 1.2 Hz)	7.22 d (1H, *J* = 1.2 Hz)	2.06 d (3H, Me, *J* = 1.2 Hz)	7.76–8.30 d.d (4H)
IIb	1.34 s (9H, *t*-Bu)	6.95 d (1H, *J* = 2.4 Hz)	7.14 d (1H, *J* = 2.4 Hz)	1.32 s (9H, *t*-Bu)	7.78–8.30 d.d (4H)
IIIa	2.02 d (3H, Me, *J* = 1.2 Hz)	6.85 q (1H, *J* = 1.2 Hz)	7.40 q (1H, *J* = 1.5 Hz)	2.08 d (3H, Me, *J* = 1.5 Hz)	8.22–8.44 d.d (4H)
IIIb	1.24 s (9H, *t*-Bu)	6.76 d (1H, *J* = 2.1 Hz)	7.29 d (1H, *J* = 2.4 Hz)	1.29 s (9H, *t*-Bu)	8.24–8.45 d.d (4H)

Table 3. ^{13}C NMR spectra of 4-arylsulfinylimino-2,5-cyclohexadienones **Ia**–**Id**, 4-(4-nitrophenylsulfanylimino)-2,5-cyclohexadienones **IIa** and **IIb**, and 4-(4-nitrophenylsulfonyloxyimino)-2,5-cyclohexadienones **IIIa** and **IIIb**

Comp. no.	C^1	C^2	C^3	C^4	C^5	C^6	$C^{1'}$	$C^{2'}$	$C^{3'}$	$C^{4'}$	$C^{5'}$	$C^{6'}$	R^1, R^2, R^3
Ia	186.66	143.70	135.83	162.08	126.01	142.35	151.21	126.69	124.30	149.55	124.30	126.69	16.78, 15.81
Ib	186.18	155.73	132.64	163.27	123.09	154.60	151.45	126.78	124.32	149.52	124.32	126.78	29.43, 36.29, 35.61
Ic	187.06	128.47	157.15	163.02	126.65	142.52	141.36	145.66	125.22, 126.26, 132.09, 134.84				27.14, 21.68, 15.92
Id	186.22	132.04	147.31	164.77	123.51	152.14	141.58	145.85	125.09, 126.54, 132.04, 134.77				27.16, 21.46, 21.49, 17.21
IIa	187.65	141.65	123.91	156.03	135.48	137.81	146.63	124.16	124.26	146.29	124.26	124.16	16.64, 15.75
IIb	187.04	153.65	120.78	156.76	132.24	149.93	[a]	124.08	124.21	146.44	124.21	124.08	29.47, 35.19, 36.01
IIIa	186.48	144.35	120.38	154.48	130.15	141.80	140.53	124.35	130.55	151.27	130.55	124.35	16.10, 16.74
IIIb	185.97	156.47	126.96	154.97	117.07	153.98	140.54	124.31	130.48	151.15	130.48	124.31	29.22, 29.37, 35.71, 36.31

[a] No signal was observed.

isomerization of compound **Ib** was determined by the total curve shape analysis of the ^{1}H NMR spectra; the resulting value, $\Delta G^{\neq}_{298\,\mathrm{K}}$ = 67.1 kJ/mol, is considerably lower than the known values for both quinone oxime derivatives and other sulfur-containing benzoquinonimines. For example, the $\Delta G^{\neq}_{298\,\mathrm{K}}$ value for 2,6-di-*tert*-butyl-4-(4-nitrophenylsulfonylimino)-2,5-cyclohexadienone is 72.2 kJ/mol [4], and for 2,6-di-*tert*-butyl-4-(4-nitrophenylsulfanylimino)-2,5-cyclohexadienone (**IIb**), 79.8 kJ/mol (calculated in the present work). We also calculated the enthalpy and entropy of *Z*,*E* isomerization of quinonimine **Ib**, $\Delta H^{\neq}$ = 52.8 kJ/mol and $S^{\neq} = 48.0$ J mol^{-1} K^{-1}; the corresponding values for compound **IIb** are 82.8 kJ/mol and 10.1 J mol^{-1} K^{-1}, respectively.

Thus we were the first to synthesize a series of stable 4-arylsulfinylimino-2,5-cyclohexadienones having a quadrivalent sulfur atom and to reveal a transformation of benzoquinone monooximes into benzoquinonimines via conversion of sulfur(II) into sulfur (IV). The described procedure can be regarded as a synthetic route to 4-arylsulfinylimino-2,5-cyclohexadienones.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer using $CDCl_3$ as solvent; the chemical shifts were measured relative to tetramethylsilane as internal reference. Calculations of the barriers to *Z*,*E* isomerization by the total curve shape analysis of the ^{1}H NMR spectra were performed using the program described in [7].

4-Arylsulfinylimino-2,5-cyclohexadienones Ia–Id. To a solution of 0.05 mol of the corresponding 1,4-benzoquinone oxime in 40 ml of dry diethyl ether we added 0.05 mol of arenesulfenyl chloride. The mixture was filtered from the undissolved material, and the filtrate was cooled to –10 to –5°C in an ice bath. Triethylamine, 0.05 mol, was added dropwise under vigorous stirring at such a rate that the temperature of the mixture did not exceed 0°C; a solid precipitated during the addition. The mixture was stirred on cooling for an additional 10 min.

In the synthesis of quinonimines **Ic** and **Id**, the precipitate was filtered off, washed with water to remove triethylamine hydrochloride, dried in air, and recrystallized from octane. In the synthesis of quinonimines **Ia** and **Ib**, the precipitate was filtered off, and the filtrate was evaporated under reduced pressure. The residue was treated with 15 ml of 2-propanol to obtain a crystalline product. The product was filtered off and repeatedly crystallized from petroleum ether (bp 40–70°C) or hexane.

4-Arylsulfanylimino-2,5-cyclohexadienones IIa and IIb were synthesized by reaction of 4-nitrobenzenesulfenyl chloride with the corresponding *p*-aminophenols in diethyl ether in the presence of triethylamine according to the procedure reported in [8].

4-Arylsulfonyloxyimino-2,5-cyclohexadienones IIIa and IIIb were synthesized by reaction of 4-nitrobenzenesulfonyl chloride with the corresponding 1,4-benzoquinone oximes in diethyl ether in the presence of triethylamine according to the procedure reported in [9].

This study was performed under financial support by the ES INTAS program (grant no. 00157-1999) and by the Ministry of Education and Science of Ukraine.

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