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Activated Sterically Strained C=N Bond in N-Substituted *p*-Quinonemono- and -diimines: X.* Reactions of *N*-[*N*-Arylsulfonylbenz(acet)imidoyl]-3,5-dimethyl-1,4-benzoquinonimines with Alcohols

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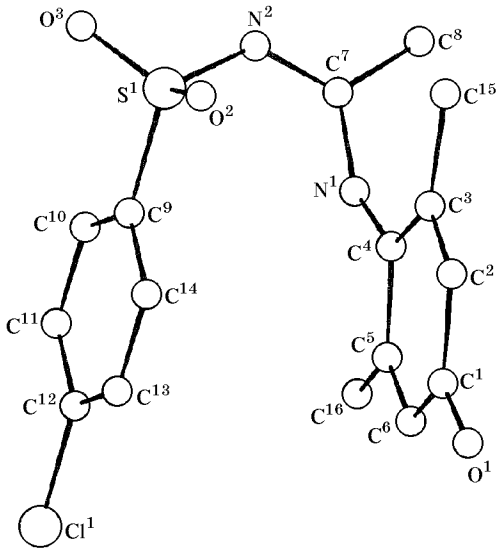
Abstract—*N*-[*N*-Arylsulfonylbenz(acet)imidoyl]-3,5-dimethyl-1,4-benzoquinonimines react with alcohols to give the corresponding adducts at the activated C=N bond. The adducts lose alcohol molecule on heating to afford initial quinonimines. Hydrolysis of the title compounds leads to formation of the corresponding quinones and *N*-arylsulfonylamidines.

Our previous studies of *N*-arylsulfonyl-1,4-benzoquinonimines having substituents in both *ortho*-positions with respect to the C=N bond revealed enhanced reactivity of that bond [2–5]. It was found that its reactivity originates from the steric effect leading to increase of the C=N–C bond angle [1, 6] rather than from electronic effects of the substituents. Obviously, the nature of substituents both at the nitrogen atom and in the ring should not affect the reactivity of the C=N bond.

In the present work we studied *N*-[*N*-arylsulfonylbenzimidoyl]- and *N*-[*N*-arylsulfonylacetimidoyl]-3,5-dimethyl-1,4-benzoquinonimines **Ia**–**Id**. These compounds can be regarded as analogs of *N*-aroyl-(acetyl)-1,4-benzoquinonimines in which the oxygen atom of the ArCO (Ac) group is replaced by arylsulfonylimino group ($ArSO_2N$). The reactivity of the C=N bond in benzoquinonimines **Ia**–**Id** was estimated on the basis of the X-ray diffraction data for **Ib**. The C=N–C bond angle in molecule **Ib** turned out to be 140.8°; this means that the C=N bond in **Ia**–**Id** is activated [6]. Figure shows the structure of molecule **Ib** determined by X-ray analysis. The quinoid fragment and the benzene ring in the $ArSO_2$ group are almost coplanar: the angle between the corresponding planes is 170.7°. The $ArSO_2N$ group is arranged in such a way that it shields the activated C=N bond from one side. The CH_3 group is located *trans* with respect to the $ArSO_2$ group relative to the $N^2=C^7$ bond. According to our recent data [7], benzoquinonimines **Ia** and **Ib** in solution give rise to dynamic *Z*,*E* isomerization about the C=N bond of the *N*-sulfonylimidoyl moiety, so that the $ArSO_2N=$ group in one isomer does not shield the quinonimine C=N bond. Therefore, nucleophilic attack on the C=N bond in **Ia** and **Ib** should not be sterically



Structure of the molecule of *N*-(4-chlorophenylsulfonyl)-*N*′-(2,6-dimethyl-4-oxo-2,5-cyclohexadienylidene)acetamidine (**Ib**) according to the X-ray diffraction data.

* For communication IX, see [1].

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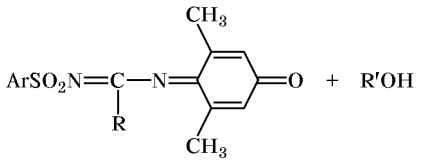
Table 1. Yields, melting points, and elemental analyses of *N*-(arylsulfonyl)-*N′*-(1-alkoxy-2,6-dimethyl-4-oxo-2,5-cyclohexadienyl)benz(acet)amidines **IIa**–**IIm**

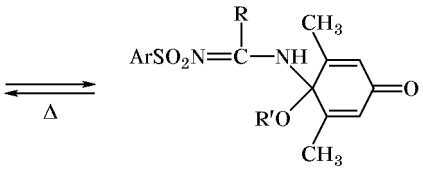
Compound no.	Yield, %	mp, °C	Found S, %	Formula	Calculated S, %
IIa	90	162	8.63, 8.72	$C_{18}H_{22}N_2O_4S$	8.85
IIb	83	170	8.49, 8.54	$C_{19}H_{24}N_2O_4S$	8.52
IIc	70	145	8.03, 8.11	$C_{20}H_{26}N_2O_4S$	8.21
IId	47	140	8.08, 8.22	$C_{20}H_{26}N_2O_4S$	8.21
IIe	93	154	8.30, 8.41	$C_{17}H_{19}ClN_2O_4S$	8.37
IIf	81	148	8.02, 8.13	$C_{18}H_{21}ClN_2O_4S$	8.08
IIg	63	146	7.75, 7.79	$C_{19}H_{23}ClN_2O_4S$	7.80
IIh	45	155	7.74, 7.86	$C_{19}H_{23}ClN_2O_4S$	7.80
IIi	32	165	7.15, 7.27	$C_{22}H_{21}ClN_2O_4S$	7.21
IIj	31	130	7.02, 7.06	$C_{23}H_{23}ClN_2O_4S$	6.99
IIk	29	160	6.59, 6.65	$C_{24}H_{25}ClN_2O_4S$	6.78
IIl	25	156	6.51, 6.64	$C_{22}H_{21}BrN_2O_4S$	6.55
IIm	23	146	6.28, 6.38	$C_{23}H_{23}BrN_2O_4S$	6.37

hindered. Then compounds **Ia** and **Ib** should react with alcohols as readily as do *N*-arylsulfonyl-1,4-benzoquinonimines with activated C=N bond [8]. In fact, the reactions of **Ia** and **Ib** with methanol, ethanol, 1-propanol, and 2-propanol occurred under mild conditions, following the 1,2-addition pattern, to afford the corresponding *N*-(arylsulfonyl)-*N′*-(1-alkoxy-2,6-dimethyl-4-oxo-2,5-cyclohexadienyl)acetamidines **IIa**–**IIh** (Scheme 1).

Scheme 1.



Ia–**Id**



IIa–**IIm**

I, R = CH_3, Ar = 4-$CH_3C_6H_4$ (**a**); R = CH_3, Ar = 4-ClC_6H_4 (**b**); R = C_6H_5, Ar = 4-ClC_6H_4 (**c**); R = C_6H_5, Ar = 4-BrC_6H_4 (**d**); **II**, Ar = 4-$CH_3C_6H_4$ (**a**–**d**), 4-ClC_6H_4 (**e**–**k**), 4-BrC_6H_4 (**l**, **m**); R = CH_3 (**a**–**h**), C_6H_5 (**i**–**m**); R′ = CH_3 (**a**, **e**, **i**, **l**), C_2H_5 (**b**, **f**, **j**, **m**), C_3H_7 (**c**, **g**, **j**), $CH(CH_3)_2$ (**d**, **h**).

Like *N*-arylsulfonyl-1,4-benzoquinonimines, compounds **Ia** and **Ib** failed to react with *tert*-butyl alcohol because of the large size of its molecule. *N*-(*N*-Arylsulfonylbenzimidoyl)-3,5-dimethyl-1,4-benzoquinonimines **Ic** and **Id** react only with unbranched alcohols, CH_3OH, C_2H_5OH, and *n*-C_3H_7OH, to give products **IIi**–**IIm** (Scheme 1). No reaction occurred with isopropyl and *tert*-butyl alcohols. It should be noted that the reactions of compounds **Ia** and **Ib** with alcohols were complete in 5–10 min under reflux, whereas the reactions with quinonimines **Ic** and **Id** required heating for 40–50 h, and traces of initial quinonimine were detected in the mixture by TLC. The reduced reactivity of **Ic** and **Id** as compared to **Ia** and **Ib** is explained by steric factor and hindered *Z*,*E* isomerization about the C=N bond in the imidoyl fragment.

According to the X-ray diffraction data obtained for *N*-(phenylsulfonyl)-*N′*-(3,5-dimethyl-4-oxo-2,5-cyclohexadienylidene)benzamidine [7] which is structurally related to quinonimines **Ic** and **Id**, the phenylsulfonylimino group is located below the quinoid ring plane, and the benzene ring of the benzamidine moiety appears above that plane (cf. the data for **Ib**). Insofar as the phenyl group is considerably bulkier than methyl, the quinonimine C=N bond is shielded at both sides. The reaction of **Ic** and **Id** with alcohols is also hindered since these compounds in solution and in the crystalline state exist as the corresponding *E* isomers [7].

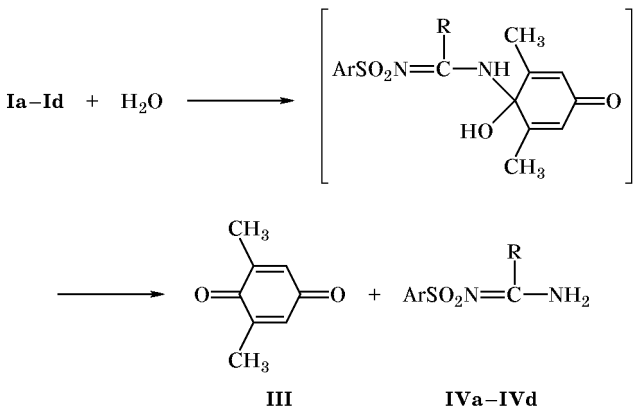
An additional support to the proposed explanation of the different reactivities of quinonimines **Ia** and **Ib**, on the one hand, and **Ic** and **Id**, on the other, was obtained by studying their hydrolysis. The hydrolysis follows the 1,2-addition–elimination pattern with

Table 2. ^{1}H NMR spectra of *N*-(arylsulfonyl)-*N′*-(1-alkoxy-2,6-dimethyl-4-oxo-2,5-cyclohexadienyl)benz(acet)amidines **IIc**–**IIg** and **IIi**, δ, ppm

Comp. no.	Solvent	Cyclohexene fragment		RC=N	$ArSO_2$	R′O	NH
		2-H, 6-H	3-CH_3, 5-CH_3				
IIc	$CDCl_3$	6.05 s (2H)	1.81 s (6H)	2.53 s (3H, CH_3)	7.16–7.55 d.d (4H), 2.40 s (3H, CH_3)	0.87 t (3H, CH_3), 1.50 q (2H, CH_2), 2.99 t (2H, CH_2O)	5.88 br.s
IId	$CDCl_3$	6.05 s (2H)	1.85 s (6H)	2.53 s (3H, CH_3)	7.16–7.55 d.d (4H), 2.39 s (3H, CH_3)	1.03 d (6H, CH_3), 3.56 m (1H, CH)	5.78 br.s
IIe	DMSO-d_6	6.10 s (2H)	1.73 s (6H)	2.35 s (3H, CH_3)	7.48–7.55 d.d (4H)	2.91 s (3H, CH_3)	9.53 br.s
	$CDCl_3$	6.09 s (2H)	1.81 s (6H)	2.53 s (3H, CH_3)	7.37–7.59 d.d (4H)	2.97 s (3H, CH_3)	6.11 br.s
IIf	$CDCl_3$	6.06 s (2H)	1.82 s (6H)	2.54 s (3H, CH_3)	7.35–7.60 d.d (4H)	1.13 t (3H, CH_3), 3.12 q (2H, CH_2)	5.89 br.s
IIg	$CDCl_3$	6.06 s (2H)	1.81 s (6H)	2.53 s (3H, CH_3)	7.35–7.60 d.d (4H)	0.86 t (3H, CH_3), 1.48 q (2H, CH_2), 2.98 t (2H, CH_2O)	6.34 br.s
IIi	DMSO-d_6	5.97 s (2H)	1.81 s (6H)	7.37–7.57 m (5H, C_6H_5)	7.45–7.53 d.d (4H)	2.89 s (3H, CH_3)	9.76 br.s

intermediate formation of 4-hydroxy-4-amino-2,5-cyclohexadienone structure and yields 2,6-dimethyl-1,4-benzoquinone (**III**) and the corresponding *N*-arylsulfonylbenz(or acet)amidine **IVa**–**IVd** (Scheme 2).

Scheme 2.

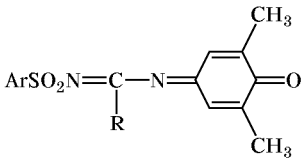


III **IVa–IVd**

IV, Ar = 4-$CH_3C_6H_4$, R = CH_3 (**a**); Ar = 4-ClC_6H_4, R = CH_3 (**b**); Ar = 4-ClC_6H_4, R = C_6H_5 (**c**); Ar = 4-BrC_6H_4, R = C_6H_5 (**d**).

Taking into account that water molecule is much smaller than any alcohol molecule, steric factor in compounds **Ic** and **Id** should affect the rate of hydrolysis to a lower extent; i.e., the rates of hydrolysis of acetamidine (**Ia**, **Ib**) and benzamidine derivatives (**Ic**, **Id**) should be comparable. We have found that the hydrolysis of compounds **Ia** and **Ib** is complete in 10 min and that the reaction with quinonimines **Ic** and **Id** requires 40–50 min.

On heating to the melting point compounds **IIa**–**IIm** undergo dealkoxylation with formation of initial quinonimines **Ia**–**Id**. *N*-(Arylsulfonyl)-*N′*-(3,5-dimethyl-4-oxo-2,5-cyclohexadienylidene)benz(acet)amidines **Va**–**Vd** did not react with alcohols (CH_3OH, C_2H_5OH, C_3H_7OH) under similar conditions (100 h). Such a behavior is typical of N-substituted 1,4-benzoquinonimines in which the C=N bond is not activated.



Va–Vd

V, Ar = 4-$CH_3C_6H_4$, R = CH_3 (**a**); Ar = 4-ClC_6H_4, R = CH_3 (**b**); Ar = 4-ClC_6H_4, R = C_6H_5 (**c**); Ar = 4-BrC_6H_4, R = C_6H_5 (**d**).

The structure of compounds **IIa**–**IIm** was proved by the data of elemental analysis (Table 1) and IR, ^{1}H NMR (Table 2), and ^{13}C NMR spectroscopy. The

Table 3. Coordinates of atoms and their equivalent isotropic temperature factors U_{iso} (Å^2) in the structure of *N*-(4-chlorophenylsulfonyl)-*N*′-(2,6-dimethyl-4-oxo-2,5-cyclohexadienylidene)acetamidine (**Ib**)

Atom	*x*	*y*	*z*	U_{iso}	Atom	*x*	*y*	*z*	U_{iso}
Cl^1	–0.61755 (8)	–0.03259 (4)	0.12114 (5)	0.0581	C^{13}	–0.4378 (3)	0.05526 (12)	0.27298 (18)	0.0425
S^1	–0.31953 (7)	0.28528 (3)	0.30941 (4)	0.0382	C^{14}	–0.3703 (3)	0.12567 (12)	0.31416 (17)	0.0387
O^1	0.2101 (3)	–0.02265 (12)	0.48398 (17)	0.0762	C^{15}	0.1857 (3)	0.25656 (14)	0.40859 (19)	0.0480
O^2	–0.2344 (2)	0.26870 (11)	0.41460 (13)	0.0545	C^{16}	–0.0576 (3)	0.05245 (15)	0.1319 (2)	0.0529
O^3	–0.4594 (2)	0.34037 (9)	0.30391 (18)	0.0616	H^{21}	0.2465	0.1208	0.5215	0.0543
N^1	–0.0240 (2)	0.2035 (1)	0.21140 (14)	0.0368	H^{61}	0.0528	–0.0481	0.2991	0.0642
N^2	–0.1804 (2)	0.3214 (1)	0.22837 (14)	0.0377	H^{81}	0.0445	0.3721	0.1189	0.0836
C^1	0.1595 (3)	0.03006 (15)	0.4211 (2)	0.0516	H^{82}	0.1797	0.3257	0.1796	0.0907
C^2	0.1878 (3)	0.11295 (15)	0.44956 (18)	0.0487	H^{83}	0.1027	0.2930	0.0733	0.0907
C^3	0.1439 (3)	0.17245 (13)	0.38205 (16)	0.0381	H^{101}	–0.5241	0.2442	0.1190	0.0425
C^4	0.0473 (2)	0.15240 (12)	0.27621 (15)	0.0329	H^{111}	–0.6398	0.1231	0.0532	0.0559
C^5	0.0240 (3)	0.06919 (13)	0.24349 (17)	0.0400	H^{131}	–0.4165	0.0080	0.3098	0.0524
C^6	0.0737 (3)	0.01200 (13)	0.3141 (2)	0.0480	H^{141}	–0.3013	0.1222	0.3763	0.0436
C^7	–0.0462 (3)	0.28173 (12)	0.20138 (16)	0.0351	H^{151}	0.0840	0.2901	0.4109	0.0653
C^8	0.0829 (3)	0.32357 (15)	0.1360 (2)	0.0501	H^{152}	0.2479	0.2626	0.4793	0.0793
C^9	–0.4021 (2)	0.19486 (11)	0.25589 (16)	0.0333	H^{153}	0.2662	0.2780	0.3612	0.0751
C^{10}	–0.5044 (3)	0.19490 (13)	0.15820 (17)	0.0394	H^{161}	–0.0741	–0.0007	0.1240	0.0888
C^{11}	–0.5712 (3)	0.12445 (13)	0.11743 (17)	0.0416	H^{162}	–0.1741	0.08036	0.1193	0.0645
C^{12}	–0.5365 (3)	0.05560 (12)	0.17499 (17)	0.0393	H^{163}	0.0168	0.0743	0.0817	0.0740

IR spectra of **IIa**–**IIm** contain absorption bands at 3300–3200, 1680–1670, 1635–1630, 1610–1580, 1390–1305, and 1170–1105 cm^{-1}, which are typical of the NH, C=O, C=N, C=C, and SO_2 groups. In the ^{1}N NMR spectra we observed signals from magneticaly equivalent protons of the quinoid ring, singlets from equivalent methyl groups, broadened singlets from NH protons, and also appropriate signals from the RC=N, $ArSO_2$, and R′O fragments. Compounds **IIe** and **IIf** showed in the ^{13}C NMR spectra signals from the carbonyl carbon atom at δ_C 184.25–184.32 ppm) and sp^3-hybridized carbon atom in the region δ_C 84.10–84.54 ppm. The other carbon signals correspond to the proposed structures.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer in KBr. The ^{1}H and ^{13}C NMR spectra were measured on a Varian VXR-300 instrument (300 MHz for ^{1}H) relative to tetramethylsilane.

The X-ray diffraction data for a single crystal of compound **Ib** (crystal habit $0.22 \times 0.56 \times 0.59$ mm) were obtained at room temperature on an Enraf–Nonius CAD-4 automatic four-circle diffractometer (CuK_α irradiation, scan rate ratio $\omega/2\theta = 1.2$, $\theta_{max} = 65°$, spherical segment $0 \le h \le 8$, $0 \le k \le 19$, $-14 \le l \le 14$). Total of 3016 reflections were measured, 2683 of which were symmetry-independent ($R_{int} = 0.041$). Monoclinic crystals with the following unit cell parameters: $a = 7.760(2)$, $b = 16.937(3)$, $c = 12.245(4)$ Å; $\beta = 93.97(2)°$; $V = 1605.5$ Å^3; $M = 350.82$; $Z = 4$; $d_{calc} = 1.45$ g/cm^3; $\mu = 34.69$ cm^{-1}; space group $R2_1/n$ ($N = 14$). The structure was solved by the direct method and was refined by the least-squares procedure in the full-matrix anisotropic approximation using CRYSTALS software package [9]. In the refinement 2424 reflections with $I > 3(I)$ were used (208 parameters were refined; the number of reflections per parameter was equal to 11.7). All hydrogen atoms were visualized from the difference synthesis of electron density and were involved in the calculation with fixed positional and thermal factors. The absorption by the crystal was taken into account by the azimuth scanning technique [10]. The Chebyshev weight scheme [11] including four parameters: 2.89, –2.79, 1.23, and –2.10 was used in the refinement. The final divergence factors were $R = 0.046$ and $R_w = 0.049$; GOF = 1.169. The residual electron density from the Fourier difference series was 0.35 and –0.47 $\bar{e}$/Å^3. Table 3 lists the coordinates of atoms in molecule **Ib**.

Compounds **Ia**–**Id** were synthesized by the procedure reported in [7].

Reaction of *N*-(arylsulfonyl)-*N′*-(2,6-dimethyl-4-oxo-2,5-cyclohexadienylidene)acet(benz)amidines Ia–d with alcohols (*general procedure*). A solution of 2 mmol of quinonimine **Ia** or **Ib** in 8 ml of the corresponding anhydrous alcohol was refluxed for 5–10 min or for 40–50 h in the case of compound **Ic** or **Id**. The yellow color due to initial quinonimine **Ia**–**Id** gradually disappeared. The progress of the reactions was monitored by TLC, following the disappearance of initial compound **Ia**–**Id**. The mixture was cooled, the solvent was removed, and the product was recrystallized from benzene.

Compound **IIe**. ^{13}C NMR spectrum, δ_C, ppm: 184.32 (C^1), 140.95 (C^3, C^5), 131.03 (C^2, C^6), 84.54 (C^4), 16.90 (3-CH_3, 5-CH_3), 14.97 (CH_3 in R′O) (cyclohexadiene fragment); 152.50 (C^4), 135.15 (C^1), 128.65 (C^3, C^5), 127.40 (C^2, C^6) (arylsulfonyl fragment); 161.41 (C=N), 20.82 (CH_3) (N=CR).

Compound **IIf**. ^{13}C NMR spectrum, δ_C, ppm: 184.25 (C^1), 140.95 (C^3, C^5), 130.66 (C^2, C^6), 84.10 (C^4), 58.18 (CH_2 in R′O), 16.97 (3-CH_3, 5-CH_3), 14.98 (CH_3 in R′O) (cyclohexadiene fragment); 152.67 (C^4), 138.32 (C^1), 128.76 (C^3, C^5), 127.37 (C^2, C^6) (arylsulfonyl fragment); 161.26 (C=N), 20.83 (CH_3) (N=CR).

Dealkoxylation of *N*-(arylsulfonyl)-*N′*-(1-alkoxy-2,6-dimethyl-4-oxo-2,5-cyclohexadienyl)acet(benz)amidines IIa–IIm. A 0.1-g portion of compound **IIa**–**IIm** was slowly heated on a watch glass to the melting point. When the substance began to melt, a weak foaming occurred, and a yellow liquid material was obtained which crystallized on cooling to give quinonimine **Ia**–**Id**.

Hydrolysis of *N*-(arylsulfonyl)-*N′*-(2,6-dimethyl-4-oxo-2,5-cyclohexadienylidene)acet(benz)amidines Ia–d. A solution of 0.5 g of quinonimine **Ia**–**Id** in 10 ml of a 1:1 DMSO–H_2O mixture was refluxed for 10 min (compounds **Ia** and **Ib**) or 40–50 min (**Ic** and **Id**). The progress of the reaction was monitored by TLC, following the disappearance of initial quinonimine **Ia**–**Id**.

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