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Synthesis and Transformations of 2-Hydroxy-3-arylazo-1,4-naphthoquinones

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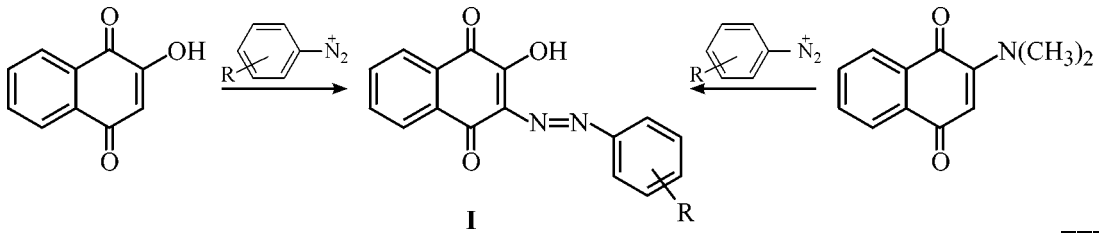
Abstract—A series of 2-hydroxy-3-arylazo-1,4-naphthoquinones were prepared by coupling of 2-hydroxy-1,4-naphthoquinone with aryldiazonium chlorides. The reactivity of the products toward electrophilic and nucleophilic agents was studied. In reaction with *o*-phenylenediamine they give condensation products, the corresponding benzo[*a*]phenazines.

Aromatic diazonium salts react with 2-hydroxy-1,4-naphthoquinones [1, 2] and 2-amino-1,4-naphthoquinones [3] to give the corresponding 2-hydroxy-3-arylazo-1,4-naphthoquinones **I**. However, the properties of compounds **I** were not studied.



I

According to [1], azo coupling of 2-hydroxy-1,4-naphthoquinone occurs in an acidic medium, whereas in a basic medium the initial quinone undergoes arylation to give the corresponding 2-hydroxy-3-aryl-1,4-naphthoquinones. Reactions of 2-amino-1,4-naphthoquinones with aromatic diazonium salts were also performed in acidic medium [3] assuming that the first stage of the reaction is hydrolysis of aminonaphthoquinone to hydroxynaphthoquinone [3].

Although azo derivatives of 2-hydroxy-1,4-naphthoquinones were reported, their spectral characteristics and reactivity toward electrophiles and nucleophiles are virtually unknown.

We have studied the reaction of 2-hydroxy-1,4-naphthoquinones with aromatic diazonium salts in a weakly basic medium and found that 2-hydroxy-3-arylazo-1,4-naphthoquinones are formed in high yields in water or aqueous alcohol (1 : 1) in the presence of sodium carbonate or hydrocarbonate. Apparently, azo coupling occurs similarly to reactions of diazonium salts with compounds containing an active methylene group. The yields and some physicochemical properties of the resulting azo compounds **I** are listed in Table 1.

The electronic absorption spectra of the synthesized compounds show absorption maxima in the range 413.5–451.5 nm, with the molar extinction coefficients ranging from 6×10^3 to 19.8×10^4 l mol^{-1} cm^{-1}. Compounds **I** with electron-donating substituents at the *o*- and *p*-positions of the arylazo moiety exhibit a red shift of λ_{max}, whereas with electron-withdrawing substituents at the *o*- and *p*-positions λ_{max} is blue-shifted. Substituents at the *m*-position affect λ_{max} insignificantly.

In the ^{1}H NMR spectra of 2-hydroxy-3-arylazo-1,4-naphthoquinones **I**, the naphthoquinone ring protons are manifested as a multiplet at 8.13–8.27 ppm; the position of the signal from aromatic protons of the arylazo moiety depends on the nature and position of substituents in the aromatic ring. The hydroxyl proton gives a signal at about 15 ppm. The ^{1}H NMR data for 2-hydroxy-3-arylazo-1,4-naphthoquinones are listed in Table 2.

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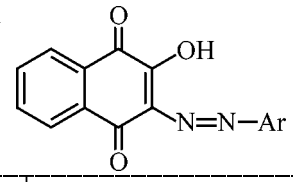
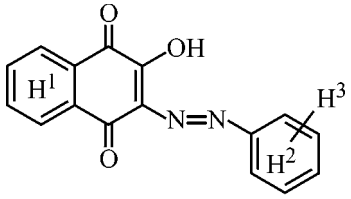
Table 1. Yields and constants of **Ia**–**Ik**



Comp. no.	Ar	Yield, %	mp, °C (solvent for crystallization)	λ_{max}, nm	$\varepsilon \times 10^{-3}$, l mol^{-1} cm^{-1}
Ia	C_6H_5	93	228–229 (alcohol)	427.0	19.8
Ib	4-$H_3COC_6H_4$	66	229–229.5 (THF)	451.0	6.60
Ic	4-$(CH_3)_2NC_6H_4$	31	134–135 (DMF–water)	451.5	6.36
Id	2-$NO_2C_6H_4$	69	249–250 (alcohol)	432.5	5.76
Ie	4-$H_3CC_6H_4$	76	201–201.5 (THF)	436.5	11.04
If	3-$NO_2C_6H_4$	81	167–168 (toluene)	413.5	7.77
Ig	4-$NO_2C_6H_4$	84	275–276 (toluene)	423.0	5.9
Ih	2-$H_3CC_6H_4$	72	209–210 (alcohol)	436.0	11.17
Ii	3-$H_3CC_6H_4$	70	193–194 (alcohol)	431.0	10
Ij	2-$H_3COC_6H_4$	68	224–225 (alcohol)	450.5	6.14
Ik	3-$H_3COC_6H_4$	55	155–156 (alcohol)	431.5	6.06

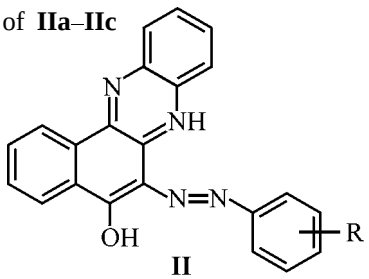
Table 2. ^{1}H NMR data for 2-hydroxy-3-arylazo-1,4-naphthoquinones **Ia**, **Ib**, **Id**, and **Ie**, δ, ppm



Comp. no.	H^1	H^2	H^3	OH
Ia	8.214 d (1H), 8.104 d (1H), 7.914 m (2H)	7.766 d (2H), 7.534 t (2H), 7.343 t (1H)	–	15.00 d (1H)
Ib	8.208 d (1H), 8.089 d (1H), 7.90 m (2H)	7.75 d (2H), 7.11 d (2H)	3.823 s (3H)	15.443 s (1H)
Id	[a]	[b]	–	15.803, 15.643
Ie	8.213 d (1H), 8.10 d (1H), 7.91 m (2H)	7.67 d (2H), 7.34 d (2H)	2.35 s (3H)	15.18 s (1H)

[a] Overlaps with the signals of the arylazo moiety in the range 8.26–7.93 ppm. [b] Overlaps with the signals of the naphthoquinoid moiety in the range 8.26–7.93 and at 7.47 ppm (1H).

Table 3. Yields, constants, and elemental analyses of **IIa**–**IIc**

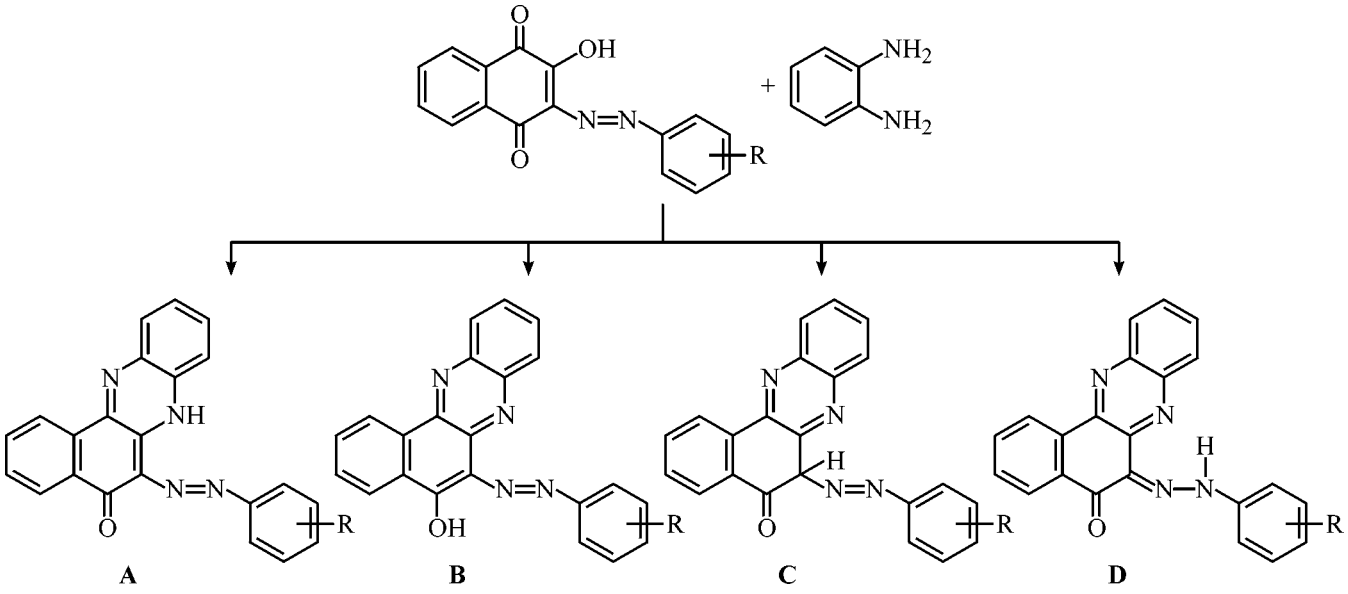


II

Comp. no.	R	mp, °C	Yield, %	λ_{max}, nm	$\varepsilon \times 10^{-3}$, l mol^{-1} cm^{-1}	Found N, %	Formula	Calculated N, %
IIa	H	258–259	63	465	17.6	15.81	$C_{22}H_{14}N_4O$	16.00
IIb	4-CH_3	238–239	74	454	7.75	15.32	$C_{23}H_{16}N_4O$	15.38
IIc	2-NO_2	277–278	80	475	4.52	17.54	$C_{22}H_{13}N_5O_3$	17.72

In the IR spectra of compounds **I**, the hydroxy group gives two weak broad bands at 3500–3380 and approximately 1115 cm^{-1}. The vibrations of two carbonyl groups are manifested as a single broad band at about 1715 cm^{-1}.

To study the reactivity of the electrophilic and nucleophilic centers in 2-hydroxy-3-arylazo-1,4-naphthoquinones, we performed their reactions with nucleophilic and electrophilic agents, in particular, with *o*-phenylenediamine, aniline, benzoyl chloride, and benzenesulfonyl chloride. Reactions of compounds **I** with *o*-phenylenediamine yield the condensation products, substituted benzo[*a*]phenazines **II**. The constants, yields, and elemental analyses of **IIa**–**IIc** are listed in Table 3.



R = H (**a**), 4-CH_3 (**b**), 2-NO_2 (**c**).

It is known that molecules with quinoid fragments show tautomerism: the *p*-quinoid structure can transform into the *o*-quinoid or dihydro structure [4]. At the same time, hydroxy azo compounds show azo–hydrazo tautomerism [5]. Therefore, for compounds **II** we can suggest formation of four structures **A**–**D**.

To determine the structure of condensation products **II**, we measured their ^1H NMR and IR spectra. The ^1H NMR spectra of **II** show a singlet (1H) at 16.25 ppm. Its position is typical of an enolic proton [6], which is present in structure **B** only.

The IR spectra in the range 3490–3380 cm^{-1} contain a hydroxyl absorption band. A band at 1670 cm^{-1} can be assigned to the C=N stretching vibrations [6]. Thus, reactions of 2-hydroxy-3-arylazo-1,4-naphthoquinones with *o*-phenylenediamine yield 5-hydroxy-6-arylazobenzo[*a*]phenazines **B**.

As expected, in the electronic absorption spectra of **IIa**–**IIc** λ_{max} is shifted bathochromically relative to compounds **I**, but the molar extinction coefficient changes insignificantly (Table 3).

The reaction of **I** with aniline was performed in refluxing ethanol for 6 h. No nucleophilic substitution products were detected. The reactions with benzoyl chloride and benzenesulfonyl chloride were performed in pyridine at 50°C; no acylation products were detected.

EXPERIMENTAL

The IR spectra were taken from KBr pellets on a Specord IR-75 spectrophotometer. The ^1H NMR spectra were recorded with a Varian VXR-300 spectrometer (300 MHz, DMSO-d_6, external reference HMDS), and the electronic absorption spectra, on a Shimadzu UV-1601 spectrophotometer (ethanol solutions).

The product purity was checked by TLC on Silufol UV-254 plates, eluent acetone–hexane, 1 : 1.

2-Hydroxy-3-phenylazo-1,4-naphthoquinone Ia. To 0.93 g of aniline we added 4 ml of concentrated HCl and 2 ml of water. After the amine dissolved, the mixture was cooled to 0°C, and a solution of 0.7 g of $NaNO_2$ in 3 ml of water was added; in the process,

the reaction temperature was kept below 5°C. To the resulting solution of the aryldiazonium salt, sodium hydrocarbonate was added in small portions at 0–5°C with continuous stirring. Immediately after the solution became weakly acidic, a solution of 1.74 g of 2-hydroxy-1,4-naphthoquinone and 0.84 g of $NaHCO_3$ in 15 ml of water was added. The mixture was stirred for 1–1.5 h, after which the mixture was acidified with dilute HCl. The precipitate was filtered off and washed with water. Red crystals were obtained; yield 2.58 g (93%), mp 228–229°C (from ethanol). IR spectrum, ν, cm^{-1}: 3470–3380 (O–H), 3095 (C–H arom.), 1710 (C=O), 1625 (C=C in quinone), 1520 (arom.), 1400 (N=N), 1115 (O–H).

Compounds **Ib**–**Ik** were prepared similarly.

2-Hydroxy-6-phenylazobenzo[*a*]phenazine IIa. A solution of 0.81 g of *o*-phenylenediamine in 25 ml of ethanol was added to a suspension of 1.39 g of 2-hydroxy-3-phenylazo-1,4-naphthoquinone in 100 ml of ethanol. The mixture was refluxed for 2 h and cooled; the precipitate was filtered off, washed with alcohol, and recrystallized from DMF. A red product was obtained; yield 1.1 g (63%), mp 258–259°C. IR spectrum, ν, cm^{-1}: 3490–3380 (O–H), 3085 (C–H arom.), 1670 (C=N), 1610 (N=N of quinone), 1545, 1500 (arom. ring), 1440 (N=N), 1115 (O–H). ^1H NMR spectrum, δ, ppm: 16.25 s (1H), 8.78 d (1H), 8.39 m (1H), 8.28 d (1H), 8.15 m (1H), 7.89 m, 7.77 m (total 9H), 7.54 m (2H), 7.28 m (1H).

Compounds **IIb** and **IIc** were prepared similarly.

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