Oxidative arylamination of 1,7-dihydroxynaphthalene

L. V. Ektova

Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 9 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation. Fax: +7 (383 2) 34 4752

1,7-Dihydroxynaphthalene reacts with aniline or *p*-toluidine in the presence of oxidants to give the corresponding *N*-aryl-7-hydroxy-1,4-naphthoquinone 4-imines, 2-arylamino- and 2,8-diarylamino-*N*-aryl-7-hydroxy-1,4-naphthoquinone 4-imines, and benzo[*a*]oxophenoxazinimine derivatives.

Key words: 1,7-dihydroxynaphthalene, oxidative arylamination, *N*-aryl-1,4-naphthoquinone 4-imines, benzo[*a*]oxophenoxazinimines.

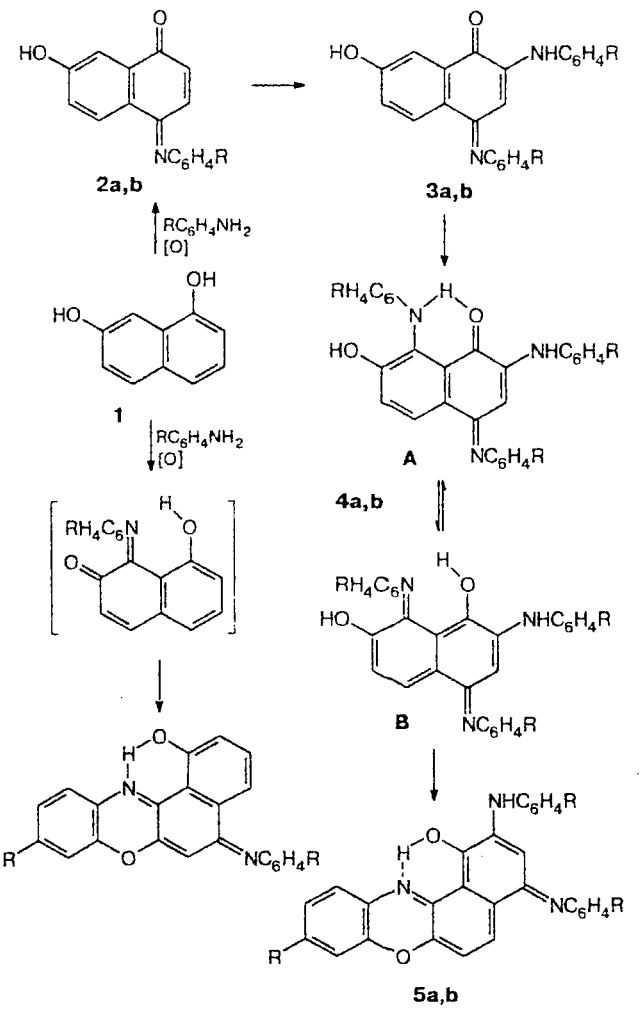
Oxidative arylamination of hydroxynaphthalenes is a convenient method for the preparation of *N*-arylnaphthoquinonimines,[1] which are widely used in color photography[2] and proposed for optical recording of information.[3] However, this reaction has been studied only for 1-hydroxy-[1] and 1,5-dihydroxynaphthalenes.[4,5] The latter is shown to react with arylamines in the presence of an oxidant to give the corresponding *N*-aryl-5-hydroxy-1,4-naphthoquinone 4-imines, which, in turn, are arylaminated at both rings of naphthoquinonimine.[4,5]

In the present work, we studied the oxidative arylamination of 1,7-dihydroxynaphthalene (**1**) with aniline and *p*-toluidine in the presence of such oxidants as $K_3Fe(CN)_6$, $Cu(OAc)_2 \cdot H_2O$, and atmospheric oxygen, which are commonly used in the synthesis of quinoid compounds (Table 1). It was found that the reaction of compound **1** with arylamines at 25 °C in the presence of an excess of $K_3Fe(CN)_6$ (molar ratio 1 : 1 : 4) proceeds similarly to that described for 1,5-dihydroxynaphthalene[5] and yields the corresponding *N*-aryl-7-hydroxy-1,4-naphthoquinone 4-imines (**2a,b**). With higher amount of arylamine and longer reaction time, compounds **3a,b**—**6a,b** are formed (Scheme 1). The same compounds are formed when $Cu(OAc)_2 \cdot H_2O$ is used as the oxidant, while heating of 1,7-dihydroxynaphthalene with aniline at 100 °C with air passed through the reaction mixture is accompanied by extensive resinification and yields a mixture of compounds **3a**, **4a**, and **6a**.

The structures of compounds obtained were determined from spectral and analytical data (Tables 2 and 3).

The IR spectra of compounds **2a,b** and **3a,b** exhibit absorption bands of the C=O, C=N, and OH stretching vibrations. The characteristic band of the NH group is observed in the spectra of **3a,b**. The ^1H NMR spectra of compounds **2a,b** and **3a,b** contain two doublets for the H(5) and H(8) protons with J = 8 and 2 Hz, respectively, which unambiguously confirms the structures of

Scheme 1



Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 347—350, February, 1999.

1066-5285/99/4802-0346 $22.00

Table 1. Oxidative arylamination of 1,7-dihydroxynaphthalene (**1**), *N*-(*para*-tolyl)-7-hydroxy-1,4-naphthoquinone 4-imine (**2b**), and *N*-aryl-2-arylamino-7-hydroxy-1,4-naphthoquinone 4-imines (**3a,b**)

Starting compound	Arylamine	Oxidant	Molar ratio **1** : $ArNH_2$: [O]	*T*/°C	*t*/h	Solvent	Product yields (%)
1	$PhNH_2$	$K_3Fe(CN)_6$	1 : 1 : 4	25	3	EtOH—H_2O, 1 : 1	**2a** (24), **1** (68)
1	$MeC_6H_4NH_2$	$K_3Fe(CN)_6$	1 : 1 : 4	25	3	EtOH—H_2O, 1 : 1	**2b** (38), **1** (60)
1	$PhNH_2$	$K_3Fe(CN)_6$	1 : 8 : 4	25	4	EtOH—H_2O, 1 : 1	**3a** (44), **4a** (5), **5a**, **6a** (traces)
1	$MeC_6H_4NH_2$	$K_3Fe(CN)_6$	1 : 8 : 4	25	4	EtOH—H_2O, 1 :1	**3b** (40), **4b** (5), **5b**, **6b** (traces)
1	$PhNH_2$	$Cu(OAc)_2 \cdot H_2O$	1 : 8 : 4	25	4	EtOH	**3a** (70), **4a** (5), **5a** (3), **6a** (3)
1	$MeC_6H_4NH_2$	$Cu(OAc)_2 \cdot H_2$	1 : 8 : 4	25	4	EtOH	**3b** (66), **4b** (5), **5b** (3), **6b** (3)
1	$PhNH_2$	O_2	1 : 10	100	14	—	**3a** (4), **4a** (20), **6a** (3)
2b	$MeC_6H_4NH_2$	O_2	1 : 10	80	3	EtOH	**3b** (71), **4b** (5)
3a	$PhNH_2$	O_2	1 : 10	100	19	—	**3a** (12), **4a** (62)
3b	$MeC_6H_4NH_2$	$Cu(OAc)_2 \cdot H_2O$	1 : 10 : 1	100	7	—	**3b** (24), **4b** (23), **5b** (21)

these compounds. The electronic absorption spectra of compounds **2a,b** and **3a,b**, like those of the known *N*-aryl-1,4-naphthoquinone 4-imine derivatives,[6] exhibit a band in the visible region at 440—470 nm, which is characteristic of a *para*-quinoid structure. The ^1H NMR spectra of compounds **4a,b** show a singlet for the H(3) proton and a doublet for the H(5) proton, while the signal for the H(8) proton is missing, thus suggesting that a third arylamino group enters position C(8) of naphthalene. Elimination of two hydrogen atoms from compounds **4a,b** results in 2-arylamino-4-arylimino-4*H*-benzo[*a*]phenoxazin-1-ols (**5a,b**), whose ^1H NMR spectra are characterized by the presence of signals for the quinoid H(3) proton, a doublet for the H(5) proton, a singlet for the NH group at the C(2) atom, and a downfield singlet for the *peri*-hydroxy group (with respect to the C=N group). The electronic absorption spectra of compounds **5a,b** in both EtOH and CCl_4 exhibit one absorption band at 600 nm, while the spectra of *N*-aryl-7-hydroxy-2,8-diarylamino-1,4-naphthoquinone 4-imines (**4a,b**) markedly differ in solvents of different polarity. Thus, an intense band in the visible region at 500—513 nm is observed in the spectra recorded in CCl_4, while in EtOH, this band is less intense and experiences a bathochromic shift; in addition, a new band appears at 650—750 nm. Such changes in the electronic absorption spectra were noticed in the study of tautomeric equilibrium between the *para*- and *ana*-quinoid forms of 5-hydroxy-1,4-naphthoquinone 4-imines[6,7] and 1-hydroxy-9,10-anthraquinone 9-imines[8,9] in solvents of different polarity. In analogy with these literature data, we assume that the changes in the spectra of compounds **4a,b** on going from CCl_4 to EtOH are due to different contents of tautomers **A** and **B** in these solvents. The structure of 5-arylimino-5*H*-benzo[*a*]phenoxazin-1-ols (**6a,b**) is evidenced by the ^1H NMR (the presence of signals for the H(6) and H(4) protons and the OH group involved in intramolecular hydrogen bonding with the *peri*-located C=N group) and IR (no band in the region > 1600 cm^{-1}) spectra. The IR spectra of derivatives **5a,b** and **6a,b** exhibit no band in the range characteristic of the OH stretching vibrations. This is explained by the formation of a strong intramolecular hydrogen bond (IHB) with the *peri*-located C=N group, similarly to that described for *N*-aryl-5-hydroxy-1,4-naphthoquinone 4-imines,[4] resulting in the shift of the corresponding band to the region of CH vibrations at 3000 cm^{-1}.

Thus, the oxidative arylamination of 1,7-dihydroxynaphthalene functionalizes the naphthalene nucleus with one to three arylamino groups. Apparently, the primary process follows the cation-radical mechanism in accordance with the general scheme of formation of quinonimines.[1] The cation formed attacks mostly the *para*-carbon atom with respect to the α-hydroxy group to give compounds **2a,b**. Subsequent nucleophilic addition of arylamines to the latter (*cf.* Ref. 10) yields *N*-aryl-2-arylamino-7-hydroxy-1,4-naphthoquinone 4-imines (**3a,b**). The order in which the reaction products are formed was confirmed by special experiments (see Scheme 1 and Table 1). Compounds **4a,b** seem to result either from an electrophilic attack of the aryliminium cation at the C(8) atom of compounds **3a,b** or from nucleophilic addition of arylamine to compounds **3a,b** existing in the 2,4-diarylamino-1,7-naphthoquinoid tautomeric form. The attack of the initially formed aryliminium cation at *ortho*-position with respect to the β-hydroxy group occurs to much smaller extent and results in the formation of the intermediate *N*-aryl-8-hydroxy-1,2-naphthoquinone 1-imine, which undergoes cyclization to give compounds **6a,b**. The benzo[*a*]phenoxazine derivatives are probably formed through intramolecular oxidative cyclization, similarly to the preparation of Blue Meldola dye by oxidation of a mixture of 2-naphthol and *N,N*-dimethyl-*p*-phenylenediamine.[11]

Table 2. Spectral characteristics of compounds **2a,b—6a,b**

Compound	IR ($CHCl_3$), ν/cm^{-1}	UV (EtOH),[a] λ_{max}/nm ($\varepsilon \cdot 10^{-4}$)	^1H NMR (DMCO-d_6), δ (J/Hz)
2a	1650 (CO)[b] 1600 (C=N)	396 (0.47) 444 (0.48)	6.74 (d, 1 H, H(2), J = 10); 6.95 (d, 2 H, H arom.[c], J = 8); 7.13 (d, 1 H, H(3), J =10); 7.18—7.30 (m, 2 H, H arom.); 7.36 (d, 1 H, H(8), J = 2); 7.38—7.48 (m, 2 H, H arom., H(6)); 8.22 (d, 1 H, H(5), J = 8); 10.57 (br.s, 1 H, OH)
2b	3600 (OH) 1660 (C=O) 1605 (C=N)	401 (0.62) 464 (0.78)	2.33 (s, 3 H, Me); 6.70 (d, 1 H, H(2), J = 10); 6.83 (d, 2 H arom., J = 8); 7.00—7.30 (m, 4 H, H(3), H(6), 2 H arom.); 7.35 (d, 1 H, H(8), J = 2); 8.23 (d, 1 H, H(5), J = 8); 10.55 (br.s, 1 H, OH)
3a	3580 (OH) 3375 (NH) 1660 (C=O) 1620 (C=N)	458 (0.68)	6.43 (s, 1 H, H(3)); 6.97 (d, 2 H arom., J = 9); 7.00—7.47 (m, 9 H, 8 H arom., H(6)); 7.54 (d, 1 H, H(8), J = 2); 8.32 (d, 1 H, H(5), J = 8); 8.72 (s, 1 H, NH); 10.50 (br.s, 1 H, OH)
3b	3600 (OH) 3375 (NH) 1650 (C=O) 1600 (C=N)	475 (0.68)	2.22 (s, 3 H, Me); 2.28 (s, 3 H, Me); 6.38 (s, 1 H, H(3)); 6.80 (d, 2 H arom., J = 9); 7.08—7.22 (m, 7 H, 6 H arom., H(6)); 7.46 (d, 1 H, H(8), J = 2); 8.27 (d, 1 H, H(5), J = 8); 8.43 (s, 1 H, NH); 10.35 (br.s, 1 H, OH)
4a	3540 (OH) 3370 (NH) 1620 (C=O) 1590 (C=N)	519 (0.82) 658 (0.24) 710 (0.23) 500 (1.00)[d]	6.34 (s, 1 H, H(3)); 6.79—7.44 (m, 17 H, 15 H arom., H(6), NH); 8.06 (d, 1 H, H(5), J = 8); 8.62 (s, 1 H, NH); 9.87 (br.s, 1 H, OH)
4b	3530 (OH) 3370 (NH) 1630 (C=O) 1610 (C=N)	546 (0.92) 651 (0.56) 753 (0.74) 513 (0.99)[d]	2.24 (s, 3 H, Me); 2.28 (s, 3 H, Me); 2.36 (s, 3 H, Me); 6.55 (s, 1 H, H(3)); 6.75—7.20 (m, 14 H, 12 H arom., H(6), NH); 7.35 (s, 1 H, NH); 8.12 (d, 1 H, H(5), J = 9); 9.72 (br.s, 1 H, OH)[e]
5a	3360 (NH) 1590 (C=N)	584 (0.72) 600 (1.24)[d]	6.31 (s, 1 H, H(3)); 6.71—7.40 (m, 15 H, H(6), H(8), H(9)—H(11), 10 H arom.); 7.67 (d, 1 H, H(5), J = 8); 8.57 (s, 1 H, NH); 10.30 (s, 1 H, OH)
5b	3370 (NH) 1595 (C=N)	595 (0.78) 612 (1.24)[d]	2.18 (s, 3 H, Me); 2.27 (s, 3 H, Me); 2.33 (s, 3 H, Me); 6.35—6.70 (m, 4 H, H(3), H(8), 2 H arom.); 6.75—6.83 (m, 3 H, H(6), 2 H arom.); 6.87—7.20 (m, 6 H, H(10), H(11), 4 H arom.); 7.23 (s, 1 H, NH); 7.75 (d, 1 H, H(5), J = 8); 10.25 (s, 1 H, OH)[e]
6a	1590 (C=N) 1580 C=N)	435 (2.12)	6.21 (s, 1 H, H(6)); 6.89 (d, 2 H arom., J = 9); 7.10—7.37 (m, 4 H, H(8), 3 H arom.); 7.42 (m, 3 H, H(9)—H(11)); 7.61—7.79 (m, 2 H, H(2), H(5)); 8.02 (dd, 1 H, H(4), J_o = 9, J_m = 2); 13.50 (s, 1 H, OH)
6b	1590 (C=N) 1585 (C=N)	444 (2.00)	2.34 (s, 3 H, Me); 2.37 (s, 3 H, Me); 6.26 (s, 1 H, H(6)); 6.80 (d, 2 H arom., J = 9); 7.07—7.26 (m, 5 H, H(8), H(10), H(11), 2 H arom.); 7.60—7.64 (m, 2 H, H(2), H(3)); 7.98 (dd, 1 H, H(4), J_o = 9, J_m = 2); 13.53 (s, 1 H, OH)

[a] In the visible region. [b] In KBr. [c] Arylamine fragment. [d] In CCl_4. [e] In $CDCl_3$.

Experimental

Electronic absorption spectra were recorded on Specord UV-VIS and Beckmann DU-8 spectrophotometers. IR spectra were recorded on a UR-20 instrument (KBr and $CHCl_3$). ^1H NMR spectra were obtained on a Bruker WP-200 SY instrument. Molecular masses and elemental compositions were determined from the exact mass numbers of molecular ions obtained on a Finnigan MAT-8200 instrument. The course of the reaction was monitored by TLC (Silufol plates, $CHCl_3$ and C_6H_6—acetone (45 : 1) as the eluent). Preparative chromatography was carried out on columns with PKN-200 SiO_2, 100—200 μm.

Oxidative arylamination of 1,7-dihydroxynaphthalene (1). A mixture of compound **1** (1 mmol), arylamine, and an oxidant was stirred in an organic solvent (80 mL) or an excess of arylamine. The reaction conditions are given in Table 1. The reaction mixture was poured into water and neutralized with 5% HCl (for experiments with an excess of arylamine). The precipitate was filtered off, washed with water, and dried. The filtrate was extracted with ether (3×20 mL), and the extracts were dried with $CaCl_2$ and concentrated to dryness. The residue was extracted with hot $CHCl_3$ (200 mL), and the extract was concentrated and chromatographed on SiO_2. Benzene eluted azobenzene (azotoluene) and compounds **6a,b** and **5a,b**; $CHCl_3$ eluted compounds **4a,b** and **2a,b**; and $CHCl_3$—acetone (1 : 1) eluted compounds **3a,b**. The residue after extraction with $CHCl_3$ was washed with ether (100 mL), and the ethereal extract was concentrated to dryness to give compound **1**. The residue remaining after extraction with ether is insoluble in organic solvents and does not melt below 360 °C. The yields and spectral characteristics of the products are given in Tables 1 and 2, respectively. The melting points, data from elemental analysis, and molecular masses are listed in Table 3.

Table 3. The characteristics of compounds **2a,b—6a,b**

Compound	M.p./°C (solvent)	*m/z*, Found / Calculated	Found / Calculated (%) C	H	N	Molecular formula
2a	211—213 (benzene)	249.0790 / 249.0789				$C_{16}H_{11}NO_2$
2b	200—201 (benzene)	263.0952 / 263.0946				$C_{17}H_{13}NO_2$
3a	203—204 (benzene)	340.1211 / 340.1211	77.65 / 77.62	4.62 / 4.73	8.19 / 8.23	$C_{22}H_{16}N_2O_2$
3b	224—225 (benzene)	368.1536 / 368.1525	78.09 / 78.24	5.50 / 5.47	7.45 / 7.60	$C_{24}H_{20}N_2O_2$
4a	229—230 (benzene)	431.1650 / 431.1634	77.55 / 77.94	5.00 / 4.90	9.53 / 9.74	$C_{28}H_{21}N_3O_2$
4b	211—212 (benzene)	473.2111 / 473.2103				$C_{31}H_{27}N_3O_2$
5a	223—224 (benzene)	429.1477 / 429.1482	78.06 / 78.31	4.42 / 4.46	9.60 / 9.78	$C_{28}H_{19}N_3O_2$
5b	245—247 (benzene)	471.1924 / 471.1947	78.68 / 78.96	5.32 / 5.34	8.89 / 8.91	$C_{31}H_{25}N_3O_2$
6a	266—267 (hexane)	338.1054 / 338.1055				$C_{22}H_{14}N_2O_2$
6b	278—279 ($CHCl_3$—hexane)	366.1377 / 366.1368	78.61 / 78.67	5.30 / 4.95	7.66 / 7.65	$C_{24}H_{18}N_2O_2$

Reaction of *N*-(*para*-tolyl)-7-hydroxy-1,4-naphthoquinone 4-imine (2b) and *N*-aryl-2-arylamino-7-hydroxy-1,4-naphthoquinone 4-imines (3a,b) with arylamines (general procedure). A mixture of compound **2b** or compounds **3a,b** (1 mmol) with arylamine was heated with stirring in a solvent or an excess of arylamine. The reaction conditions are given in Table 1. The reaction mixture was cooled, poured into water, and neutralized with 5% HCl. The precipitate that formed was filtered off, dried, and chromatographed on SiO_2 as described above.

References

1. P. Grünanger, in *Methoden der organischen Chemie (Houben-Weyl)*, Thieme, Stuttgart, 1979, 7/3b, 235.
2. D. Baily and L. A. Williams, in *The Chemistry of Synthetic Dyes*, Ed. K. Venkataraman, Academic, New York, 1972, **1**, 487.
3. T. N. Gerasimova and V. V. Shelkovnikov, *Usp. Khim.*, 1992, **61**, 102 [*Russ. Chem. Rev.*, 1992, **61** (Engl. Transl.)].
4. L. V. Ektova and E. P. Fokin, *Zh. Org. Khim.*, 1984, **20**, 805 [*J. Org. Chem. USSR*, 1984, **20** (Engl. Transl.)].
5. L. V. Ektova and R. P. Shishkina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 2851 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 2588 (Engl. Transl.)].
6. L. V. Ektova, O. P. Petrenko, I. K. Korobeinicheva, and E. P. Fokin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2572 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 2359 (Engl. Transl.)].
7. L. V. Ektova, A. D. Bukhtoyarova, and O. P. Petrenko, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 358 [*Russ. Chem. Bull.*, 1997, **46**, 344 (Engl. Transl.)].
8. M. V. Gorelik, S. P. Titova, and V. A. Trdatyan, *Zh. Org. Khim.*, 1979, **15**, 166 [*J. Org. Chem. USSR*, 1979, **15** (Engl. Transl.)].
9. I. Ya. Mainagashev, L. S. Klimenko, V. P. Vetchinov, and V. I. Mamatyuk, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 940 [*Russ. Chem. Bull.*, 1993, **42**, 899 (Engl. Transl.)].
10. V. Calo and P. E. Todesco, *Chem. Commun.*, 1968, 571.
11. *Elsevier Encyclopaedia of Organic Chemistry*, 1990, **12B**, 1226.

Received December 19, 1997;
in revised form July 30, 1998