Photochemical and thermal rearrangements of 2-arylamino-1-(4-*tert*-butylphenoxy)-9,10-anthraquinones

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Photochemical transformations of 2-arylamino-1-(4-*tert*-butylphenoxy)-9,10-anthraquinones involve migration of the *tert*-butylphenyl group either to the *peri*-located carbonyl oxygen to give 2-arylamino-9-(4-*tert*-butylphenoxy)-1,10-anthraquinones or to the nitrogen atom to give 2-aryl(4-*tert*-butylphenyl)amino-1-hydroxy-9,10-anthraquinones (typical products of the Smiles rearrangement).

Key words: photochemistry, Smiles rearrangement, 1-(4-*tert*-butylphenoxy)-2-(*p*-toluidino)-9,10-anthraquinone, 2-(*p*-anisidino)-1-(4-*tert*-butylphenoxy)-9,10-anthraquinone.

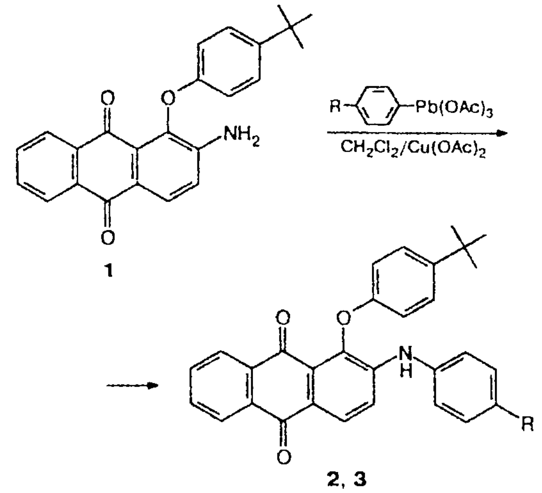
Photoisomerization of 1-aryloxy-9,10-anthraquinones giving deeply colored 9-aryloxy-1,10-anthraquinones is known[1] to be reversible in most cases. 2-Acylamino-derivatives of 1-aryloxyanthraquinone are typical photochromic compounds possessing good physicochemical characteristics.[2] Conversely, 2-monoalkylamino derivatives undergo irreversible photoisomerization; this enabled photochemical synthesis of 2-alkylamino-9-aryloxy-1,10-anthraquinones, the first stable derivatives of a new little studied class of 1,10-anthraquinones.[3]

The photochemical behavior of 2-arylamino-1-aryloxy-9,10-anthraquinones is difficult to predict; therefore, it seems especially interesting to prepare these compounds and study their properties. These compounds have been unknown previously because they are difficult to synthesize.

Results and Discussion

In this work, we study the synthesis of 2-arylamino-1-(4-*tert*-butylphenoxy)-9,10-anthraquinones by a procedure similar to that described previously,[4] namely, by the reaction of 2-amino-1-(4-*tert*-butylphenoxy)-9,10-anthraquinone (**1**) with 4-tolyl- and 4-anisyllead triacetates (Scheme 1).

Scheme 1



R = Me (**2**), OMe (**3**)

The photochemical properties of the obtained compounds (**2** and **3**) were studied by exposing their toluene solutions to UV radiation and simultaneously recording their electronic absorption spectra. The electronic absorption spectra of toluene solutions of **2** change at room temperature with retention of the isobestic points (Fig. 1). The deeply colored solution (λ_{max} 680 nm) resulting from photolysis exhibits an electronic absorption spectrum that completely coincides with the spectrum of 2-alkylamino-9-aryloxy-1,10-anthraquinones,[3] indicating that a derivative of 1,10-anthraquinone has formed as the photoinduced form. As for 2-alkylamino derivatives of 1-aryloxy-9,10-anthraquinone, in this case, too, the photo-induced reaction is irreversible. Neither exposure of the photolysate to the visible light in the region of the long-wavelength absorption maximum nor keeping it in the dark for 10 h changes its composition.

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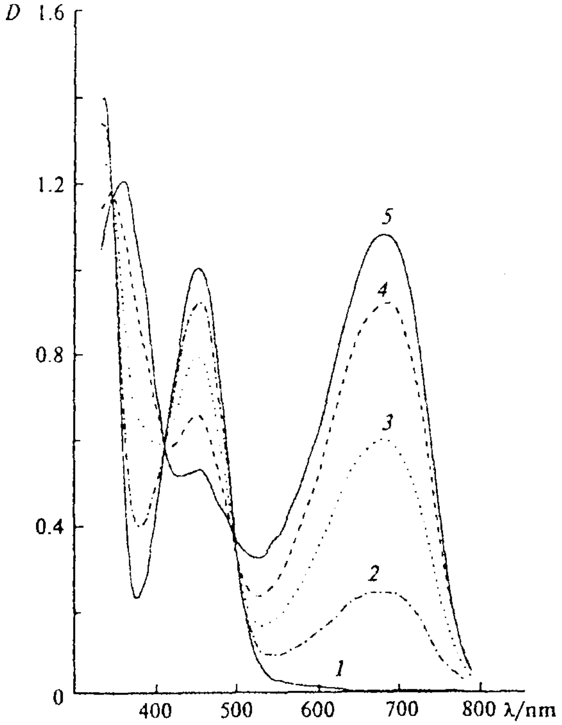


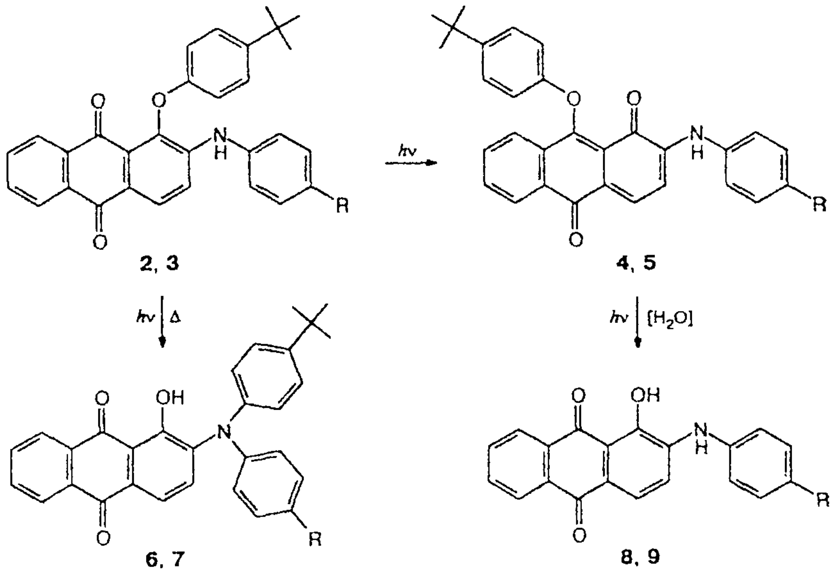
Fig. 1. Electronic absorption spectra of 1-(4-*tert*-butylphenoxy)-2-(*p*-toluidino)-9,10-anthraquinone (**2**) before (*1*) and after irradiation for 5 (*2*), 15 (*3*), 30 (*4*), and 60 (*5*) min.

The photorearrangement product, *viz.*, 9-(4-*tert*-butylphenoxy)-2-*p*-toluidino-1,10-anthraquinone (**4**) (Scheme 2), was isolated as a mixture with the product of its hydrolysis, 1-hydroxy-2-*p*-toluidino-9,10-anthraquinone (**8**). After preparative-scale photolysis, ~15% of a new product was isolated from the reaction mixture. Based on analytical and spectral data, this product was identified as 2-*N*-(4-*tert*-butylphenyl)-1-hydroxy-*p*-toluidino-9,10-anthraquinone (**6**).

The spectral changes observed during irradiation of a toluene solution of compound **3** (Fig. 2) differ substantially from those for compound **2**, since photolysis gives 2-*N*-(4-*tert*-butylphenyl)-*p*-anisidino-1-hydroxy-9,10-anthraquinone (**7**) as the major product. The content of quinone **5** in the photolysate was estimated based on the amount of 2-*p*-anisidino-1-hydroxy-9,10-anthraquinone (**9**) formed upon hydrolysis of quinone **5**. 2-Diarylamino-1-hydroxy-9,10-anthraquinones **6** and **7** are typical products of the base-catalyzed Smiles rearrangement[5] of compounds **2** and **3**. Previously,[6] analogous derivatives were obtained upon arylation of 2-amino-1-aryloxy-9,10-anthraquinones by bromo(iodo)benzenes in DMSO in the presence of a base. Note that no Smiles rearrangement products were found among the products of photolysis of a large number of 2-alkylamino- and 2-acylamino-1-aryloxy-9,10-anthraquinones. Thus, irradiation of 2-arylamino-1-(4-*tert*-butylphenoxy)-9,10-anthraquinones induces two competing reactions, photoisomerization to 1,10-anthraquinone derivatives and the Smiles photorearrangement. Examples of photoinitiated Smiles rearrangement are extremely rare; only one example of this rearrangement for a series of *N*-[ω-(4-nitrophenoxy)alkyl]aniline homologues occurring in MeOH and MeCN in the presence of Et_3N has been reported.[7,8]

Based on the available data, it might be expected that conducting the photolysis of arylamines **2** and **3** in polar solvents (MeCN, MeOH, DMSO) and addition of Et_3N would accelerate the photo-induced reaction and lead to predominant formation of the Smiles photorearrangement

Scheme 2



R = Me (**2**, **4**, **6**, **8**); OMe (**3**, **5**, **7**, **9**)

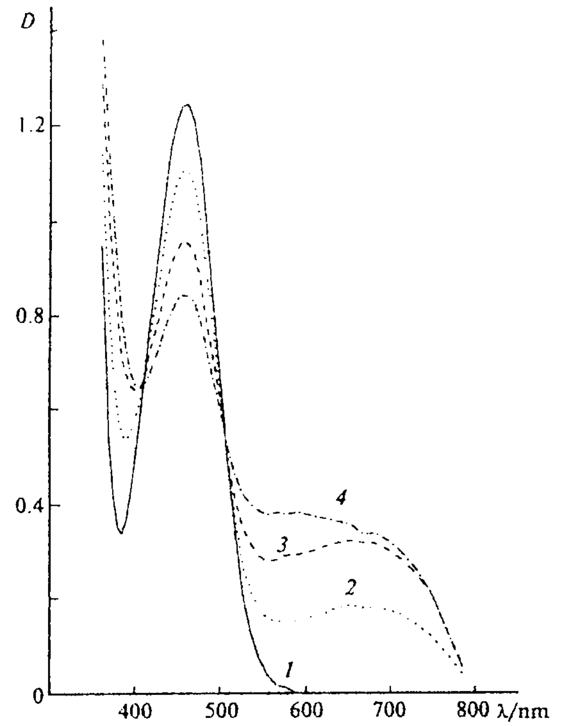


Fig. 2. Electronic absorption spectra of 2-(*p*-anisidino)-1-(4-*tert*-butylphenoxy)-9,10-anthraquinone (3) before (*1*) and after irradiation for 20 (*2*), 60 (*3*), and 120 (*4*) min.

products, compounds **6** and **7**; however, this did not occur in reality. Meanwhile, under the normal Smiles rearrangement conditions (DMSO, KOH), compounds **2** and **3** are rapidly (10 min) converted at room temperature to give compounds **6** and **7** in high yields.

The thermal Smiles rearrangement also occurs very readily. Thus, heating of compounds **2** and **3** in triethylene glycol (130 °C, 30 min) or without a solvent (210 °C, 10 min) results in their complete transformation into diarylamino derivatives **6** and **7**. The fact that the Smiles photorearrangement does not depend on the polarity of the medium and that thermolysis and photolysis of arylamino derivatives **2** and **3** give identical products suggests that both processes occur by a common radical mechanism. Radicals have also been assumed[9] to participate in the thermally and photo-initiated O→N migration of the aryl residue in 2-aryloxybenzohydroxamic acids. The radical mechanism might also be supported by the fact that the photo-induced Smiles rearrangement was observed for the first time in our study of photolysis of 2-arylamino derivatives, whereas in a study of photochemical properties of a large number of 2-alkyl-, 2-acylamino-1-(4-*tert*-butylphenoxy)-9,10-anthraquinones, no products of this type were detected. Apparently, the relatively efficient stabilization by the two aryl groups enables intermediate participation of the aminyl radical in this process. Investigation of the mechanism of the Smiles photorearrangement is the subject of future studies.

Experimental

IR spectra were recorded on a UR-20 spectrophotometer for KBr pellets and electronic absorption spectra were measured on a Specord UV—VIS spectrophotometer in ethanol (concentration $1 \cdot 10^{-4}$ mol L^{-1}). ^1H NMR spectra were run on a Bruker WP-200SY instrument (chemical shifts are given in the δ scale in relation to internal $SiMe_4$). Mass spectra (EI) were obtained on a Finnigan MAT-8200 instrument; the *m/z* values for molecular ions $[M]^+$ are given. Chromatography was carried out on columns with silica gel L (100—250 μm). Preparative TLC was performed on plates with silica gel L (5—40 μm) and TLC was performed on Silufol UV-254 plates. Photolysis was carried out by the light of a DRSh-500 lamp with a UFC-1 filter (280—400 nm) or by the full-spectrum radiation from this lamp.

The melting points and physicochemical characteristics of the compounds synthesized are given in Table 1.

4-Tolyl- and 4-anisyllead triacetates were prepared by known procedures.[10,11]

1-(4-*tert*-Butylphenoxy)-2-(*p*-toluidino)-9,10-anthraquinone (2). 4-Tolyllead triacetate (0.71 g, 1.5 mmol), $Cu(OAc)_2$ (0.02 g, 0.1 mmol), and Bu_4NBr (0.03 g, 0.1 mmol) were added to a solution of 2-amino-1-(4-*tert*-butylphenoxy)-9,10-anthraquinone (**1**) (0.37 g, 1 mmol) in dry CH_2Cl_2, and the reaction mixture was stirred for 24 h at ~20 °C. After completion of the reaction, the mixture was filtered, the precipitate was washed with $CHCl_3$, and the combined filtrate was concentrated. Column chromatography of the residue (elution with benzene) gave 0.3 g (65%) of product **2**. ^1H NMR ($CDCl_3$), δ: 1.26 (s, 9 H, Bu^t); 2.33 (s, 3 H, Me); 6.65 (s, 1 H, NH); 6.90 (d, 2 H, H-2, H-6 (*O*-aryl), *J* = 8.5 Hz); 7.06 (d, 2 H, H-2, H-6 (*N*-aryl), *J* = 8.0 Hz); 7.16 (d, 2 H, H-3, H-5 (*N*-aryl), *J* = 8.0 Hz); 7.29 (d, 2 H, H-3, H-5 (*O*-aryl), *J* = 8.5 Hz); 7.44 (d, 1 H, H-3, *J* = 8.5 Hz); 7.67 (m, 2 H, H-6, H-7); 8.14 (d, 1 H, H-4, *J* = 8.5 Hz); 8.22 (m, 2 H, H-5, H-8).

2-(*p*-Anisidino)-1-(4-*tert*-butylphenoxy)-9,10-anthraquinone (3). Product **3** was isolated under the above-described conditions in a yield of 0.29 g (60%). ^1H NMR ($CDCl_3$), δ: 1.27 (s, 9 H, Bu^t); 3.80 (s, 3 H, OMe); 6.57 (s, 1 H, NH); 6.90 (d, 4 H, H-2, H-6 (*O*-aryl, *N*-aryl), *J* = 8.5 Hz); 7.11 (d, 2 H, H-3, H-5 (*N*-aryl), *J* = 8.5 Hz); 7.27 (d, 1 H, H-3, *J* = 8.5 Hz); 7.30 (d, 2 H, H-3, H-5 (*O*-aryl), *J* = 8.5 Hz); 7.66 (m, 2 H, H-6, H-7); 8.10 (m, 1 H, H-8); 8.12 (d, 1 H, H-4, *J* = 8.5 Hz); 8.22 (m, 2 H, H-5).

Preparative-scale photolysis of compounds 2 and 3. A solution of compound **2** (0.11 g, 0.238 mmol) in 100 mL of dry benzene was irradiated with the light from a mercury lamp or with sunlight at ~20 °C until the initial compound disappeared (TLC monitoring). The solvent was evaporated. Preparative TLC of the residue (development with benzene) gave 0.018 g (0.039 mmol) of compound **6** and 0.044 g (0.113 mmol) of 1-hydroxy-2-*p*-toluidino-1,10-anthraquinone (**8**). Compound **8**. ^1H NMR (C_6D_6), δ: 2.02 (s, 3 H, Me); 6.50 (s, 1 H, NH); 6.64 (d, 2 H, H-2', H-6', *J* = 8.0 Hz); 6.80 (d, 2 H, H-3', H-5', *J* = 8.0 Hz); 7.01 (d, 1 H, H-3, *J* = 8.5 Hz); 6.92—7.08 (m, 2 H, H-6, H-7); 7.85 (d, 1 H, H-4, *J* = 8.5 Hz); 8.07 (m, 1 H, H-8); 8.27 (m, 1 H, H-5); 13.63 (s, 1 H, OH).

A solution of compound **3** (0.11 g, 0.235 mmol) in 100 mL of anhydrous benzene was subjected to photolysis. Workup of the reaction mixture similar to that described for compound **2** gave 0.054 g (0.113 mmol) of compound **7** and 0.012 g (0.035 mmol) of 2-*p*-anisidino-1-hydroxy-9,10-anthraquinone (**9**). Compound **9**. ^1H NMR (CCl_4), δ: 3.79 (s, 3 H, OMe);

Table 1. Physicochemical characteristics of the compounds synthesized

Compound	M.p./°C (ethanol—benzene)	$\frac{\text{Found}}{\text{Calculated}}$ (%) C	H	N	Molecular formula	$\frac{\text{Found}}{\text{Calculated}}$, m/z ([M]$^+$)	IR spectrum,[a] ν/cm^{-1}	UV spectrum, λ_{max}/nm (ε)
2	184 (decomp.)	80.41 80.67	5.91 5.90	2.99 3.03	$C_{31}H_{27}NO_3$	461.1996 461.1991	3360; 1670; 1650	249 (31400); 272 (23000); 309 (18200); 469 (7700)
3	187 (decomp.)	77.52 77.97	5.73 5.70	2.95 2.93	$C_{31}H_{27}NO_4$	477.1942 477.1940	3330; 1670; 1640	250 (34600); 273 (24000); 309 (17600); 472 (7300)
6	175—177	80.28 80.67	5.90 5.90	3.14 3.03	$C_{31}H_{27}NO_3$	461.1996 461.1991	1670; 1640	250 (27600); 279 (28200); 349 (15500); 563 (6750)
7	114—116	77.67 77.97	5.70 5.70	3.01 2.93	$C_{31}H_{27}NO_4$	477.1937 477.1940	3620; 1670; 1650	250 (29800); 278 (28200); 352 (13000); 569 (7400)
8	223—225	76.06 76.60	4.64 4.60	4.25 4.26	$C_{21}H_{15}NO_3$	329.1056 329.1052	3410; 1650; 1630	265 (31200); 334 (17600); 524 (9400)
9	218—220	72.92 73.04	4.40 4.38	4.00 4.06	$C_{21}H_{15}NO_4$	345.1002 345.1001	3400; 1660; 1630	265 (32300); 337 (15100); 530 (9800)

[a] Frequencies corresponding to vibrations of the OH, NH, and C=O groups are presented.

6.62 (s, 1 H, NH); 6.85 (d, 2 H, H-2′, H-6′, J = 8.5 Hz); 7.12 (d, 1 H, H-3, J = 8.5 Hz); 7.16 (d, 2 H, H-3′, H-5′, J = 8.5 Hz); 7.66 (d, 1 H, H-4, J = 8.5 Hz); 7.72 (m, 2 H, H-6, H-7); 8.26 (m, 2 H, H-5, H-8); 13.28 (s, 1 H, OH).

9-(4-*tert*-Butylphenoxy)-2-*p*-toluidino-1,10-anthraquinone (4). A solution of compound **3** (0.3 g, 0.65 mmol) in 300 mL of anhydrous benzene was irradiated with the full spectrum of a mercury lamp or with sunlight until a noticeable amount of 1-hydroxy-2-toluidino-9,10-anthraquinone (**8**) appeared (TLC). After evaporation of the solvent, the residue was reprecipitated twice from a $CHCl_3$ solution by hexane to give 0.1 g of a mixture of compounds **4** and **8**. Compound **4**. ^{1}H NMR (C_6D_6), δ: 1.92 (s, 3 H, Me); 6.14 (d, 1 H, H-3, J = 8.0 Hz); 6.33 (d, 2 H, H-2, H-6 (N-aryl), J = 8.0 Hz); 7.78 (d, 1 H, H-8, J = 7.5 Hz); 7.95 (d, 1 H, H-4, J = 8.0 Hz); 8.54 (d, 1 H, H-5, J = 7.5 Hz); 6.80—7.20 (m, H arom.). IR (C_6H_6), ν/cm^{-1}: 3240 (N—H); 1625 (C=O).

The Smiles rearrangement of compounds 2 and 3. 2-*N*-(4-*tert*-Butylphenyl)-1-hydroxy-*p*-toluidino-9,10-anthraquinone (6). Potassium hydroxide (0.05 g, 0.9 mmol) was added to a solution of compound **2** (0.1 g, 0.217 mmol) in 10 mL of DMSO. The mixture was stirred for 10 min at ~20 °C. After completion of the reaction, the mixture was poured in water and neutralized with AcOH, and the precipitate was filtered off and dried. After preparative TLC, the yield of the product was 0.095 g (95%). ^{1}H NMR ($CDCl_3$), δ: 1.30 (s, 9 H, Bu^t); 2.31 (s, 3 H, Me); 6.94 (d, 4 H, H-2, H-6 (N-aryl), J = 8.5 Hz); 7.07 (d, 2 H, H-3, H-5 (MeAr), J = 8.5 Hz); 7.25 (d, 2 H, H-3, H-5 (Bu^{t}Ar), J = 8.5 Hz); 7.34 (d, 1 H, H-3, J = 8.0 Hz); 7.75 (d, 1 H, H-4, J = 8.0 Hz); 7.78 (m, 2 H, H-6, H-7); 8.28 (m, 2 H, H-5, H-8); 13.15 (s, 1 H, OH).

2-*N*-(4-*tert*-Butylphenyl)-*p*-anisidino-1-hydroxy-9,10-anthraquinone (7) was prepared similarly to compound **6**. Yield 96%. ^{1}H NMR (CCl_4), δ: 1.31 (s, 9 H, Bu^t); 3.76 (s, 3 H, OMe); 6.72 (d, 2 H, H-2, H-6, Bu^{t}Ar, J = 8.5 Hz); 6.82 (d, 2 H, H-2, H-6, MeOAr, J = 8.0 Hz); 6.95 (d, 2 H, H-3, H-5, MeOAr, J = 8.0 Hz); 7.15 (d, 2 H, H-3, H-5, Bu^{t}Ar, J = 8.5 Hz); 7.30 (d, 1 H, H-3, J = 8.0 Hz); 7.63 (d, 1 H, H-4, J = 8.0 Hz); 7.73 (m, 2 H, H-6, H-7); 8.24 (m, 2 H, H-5, H-8); 12.94 (s, 1 H, OH).

Thermolysis of compounds 2 and 3. ***A.*** A solution of compound **2** or **3** (0.1 g) in triethylene glycol was heated for 30 min at 130 °C. After completion of the reaction, the mixture was poured in water, and the precipitate was filtered off and dried to give compound **6** or **7** in a quantitative yield.

B. Compound **2** or **3** (0.1 g) was heated for 10 min at 210 °C. After cooling, the mixture was subjected to preparative TLC (development with benzene) to give 0.09 g of compound **6** or **7**.

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