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Solid-state photochemical reactions of 1-aryloxy(1-arylthio)-9,10-anthraquinone derivatives

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The photochemistry of derivatives of 1-aryloxy-2(4)-benzoylamino-9,10-anthraquinones and 1-aryloxy(1-arylthio)-2-azido-9,10-anthraquinones in a solid phase differs from that upon irradiation in a benzene solution.

The majority of organic photochemical reactions are carried out in liquid or gas phases. Solid-state photochemical reactions are less studied. Photochemical reactions in a solid state showed differences in the composition of reaction products in comparison with liquid-phase photolysis.[1] It was found[1(a)–(c),(e)] that the reaction direction in solution is determined by electronic effects, whereas the structure of the reaction products in solid-state photolysis is controlled kinetically and depends on organised distances and arrangements of reagent molecules in crystals. It is well known[2] that the velocity of a solid-state reaction can be substantially increased (up to ten orders of magnitude) by the mechanical activation of the reaction system. In many cases, solid-state organic reactions occur more efficiently and more selectively.[3] Furthemore, the solid-state reactions (or solvent-free reactions) have many advantages: reduced pollution, low costs, and simplicity in process and handling.[3]

Here, we report a comparative study of the row of photochemical reactions of 1-aryloxy(1-arylthio)-9,10-anthraquinone derivatives in the solid state. Previously, these reactions were carried out in solution.[4–7]

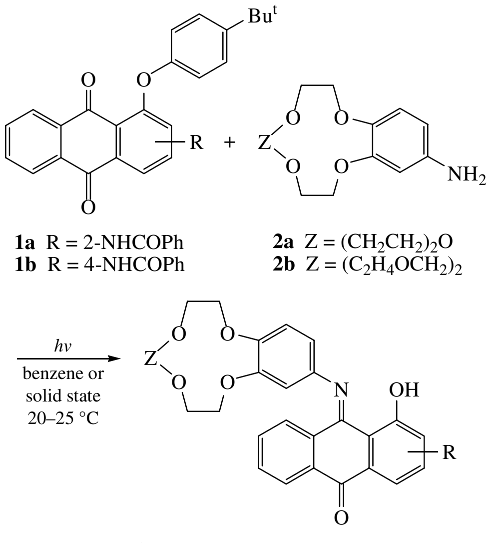
In the study on the photorearrangement of 1-aryloxy-9,10-anthraquinones in the presence of arylamines, we found that 1-aryloxy-2(4)-R-9,10-anthraquinones **1** undergo condensation with 4-aminobenzo-15-crown-5 **2a** and 4-aminobenzo-18-crown-6 **2b** under irradiation either in a benzene solution or in a solid state, leading to 4-[1-hydroxy-2(4)-R-9,10-anthraquinone-9-imino]-benzo-15-crown-5 ethers **3a**,**b** and -18-crown-6 ethers **3c**,**d**, respectively (Scheme 1, Table 1). At the initial step, the irradiation of compound **1** gives intermediate 1,10-anthraquinone, which reacts with aromatic amine **2** to form imine **3**.[4,5] The structures of **3a**–**d** were assigned on the basis of spectral data (IR, NMR, UV and visible spectroscopy and mass spectrometry) and elemental analysis.† The IR spectra of **3a**–**d** contain characteristic bands due to the vibration of N–H, C=O and C=N bonds.

Table 1 Reaction conditions and yield of **3**.

Reactants	Product	Time/h		Yield (%)	
		Benzene	Solid state	Benzene	Solid state
1a + **2a**	**3a**	5	1.5	73	92
1b + **2a**	**3b**	8	3.5	68	85
1a + **2b**	**3c**	4	2	75	90
1b + **2b**	**3d**	7	3.5	72	92

Products **3a**–**d** are brown and have maxima at 440–496 nm (depending on the character and position of the substituent). The solid-state synthesis gives higher yields of dyes **3a**–**d** than the synthesis in solution. Moreover, the rate of photorearrangement of **1** under solid-state conditions increases. The reason of the reactivity rise consists in the increase of potential energy because of crystal defects due to reagent activation in the solid state.

The photochemical cyclization of 1-aryloxy-2-azido-9,10-anthraquinone **4** leads to compounds **6**, **8**, **9** in the benzene solution and compounds **6**, **9** in the solid state. At the same time, the photo-

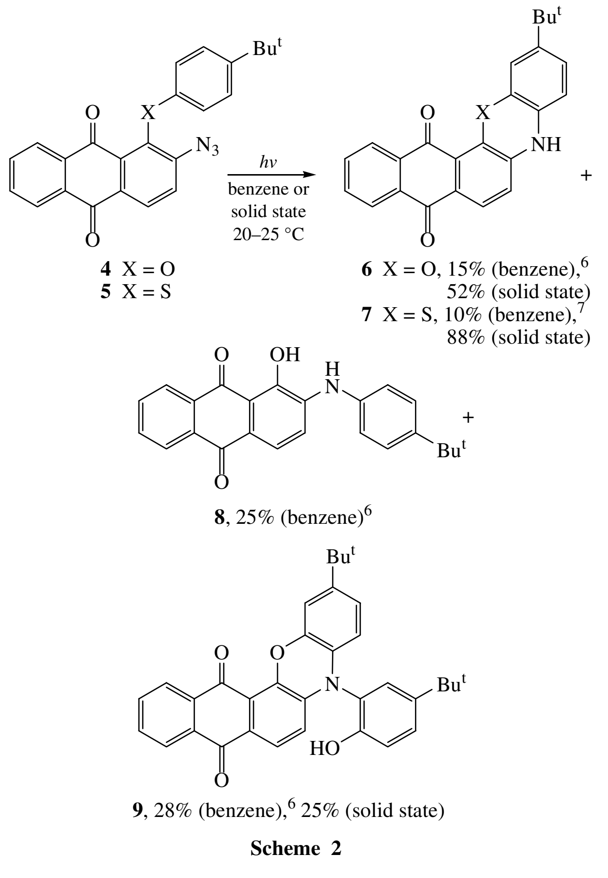


1a R = 2-NHCOPh
1b R = 4-NHCOPh

2a Z = $(CH_2CH_2)_2O$
2b Z = $(C_2H_4OCH_2)_2$

3a R = 2-NHCOPh, Z = $(CH_2CH_2)_2O$
3b R = 4-NHCOPh, Z = $(CH_2CH_2)_2O$
3c R = 2-NHCOPh, Z = $(C_2H_4OCH_2)_2$
3d R = 4-NHCOPh, Z = $(C_2H_4OCH_2)_2$

Scheme 1



4 X = O
5 X = S

6 X = O, 15% (benzene),[6] 52% (solid state)
7 X = S, 10% (benzene),[7] 88% (solid state)

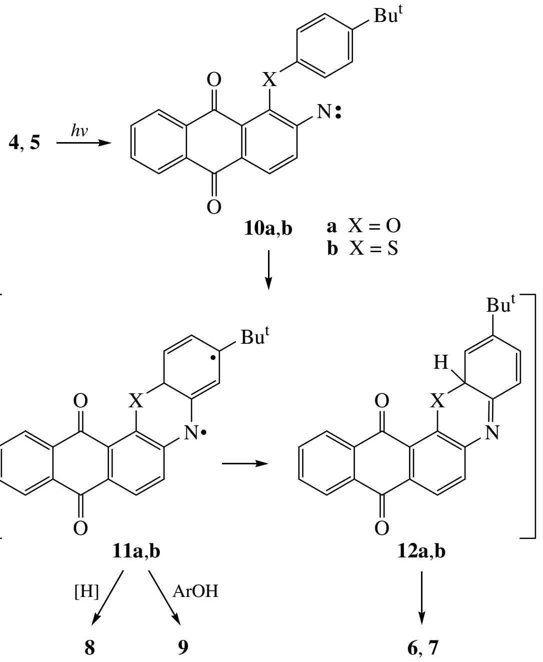
8, 25% (benzene)[6]

9, 28% (benzene),[6] 25% (solid state)

Scheme 2

lysis of 1-arylthio-2-azido-9,10-anthraquinone **5** gives only compound **7** in both media. However, the yield of **7** under the solid-state conditions is higher (Scheme 2). Photolysis of compounds **4**, **5** is performed through intermediate arylnitrene.[6] Singlet arylnitrene **10** attacks the substituent carbon atom bound to the heteroatom to form biradical spirocomplex **11**. Final products **6**–**9** form *via* common biradical spirocomplex **11**, which also forms intermediate **12** (Scheme 3).[6,7]

The results obtained suggest that the photochemical reactions of **1a**,**b** and **4**, **5** can be carried out in the solid state without any solvent. Mechanically induced solid-state reactions are characterised by a substantial reaction rate rise, their selectivities and an increase of final product yields. The solid-state reactions (Schemes 1 and 2) open new avenues to the photochemistry of 1-aryloxy(1-arylthio)-9,10-anthraquinones.[4–7] At the same time, the mechanisms of formation of **3**, **6**–**9** are probably very close in both media.[4–7]



Scheme 3

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[†] The IR spectra were recorded on a Bruker Vector-22 spectrophotometer in KBr pellets. The electronic absorption spectra were measured on a Agilent 8453 spectrophotometer (1×10^{-4} M solutions in EtOH). The ^{1}H NMR spectra were recorded in CDCl$_3$ solutions on a Bruker WP-200SY instrument with Me$_4$Si as the internal standard. The mass spectra were obtained on a Finnigan MAT-8200 instrument. The TLC analysis was performed on Silufol UV-254 plates using a 9:1 toluene–ethanol mixture as the eluent. Column chromatography was performed using silica gel (140–350 mesh). Solvents of reagent grade were dried before use. Starting materials **1a**,**b**, **2a**,**b**, **4**, **5** were synthesised according to published procedures.[6–9]

Typical procedure of solid-state photolysis for the preparation of **3a**–**d**, **6**, **7**, **9**. Mechanochemical experiments were conducted in a AGO-2 planetary centrifugal mill with water cooling (acceleration, 60*g*; volume of one drum, 35 cm^3; diameter of steel balls, 5 mm; weight of balls, 75 g). Equimolar ratio of **1** and **2** (total mass of 1.5 g) were placed in the bowl for joint mechanical treatment for 5 min. For a case of azides **4**, **5**, 0.3 g of each compound was pressed in ceramic bowl. The reaction mixtures obtained were placed by thin layer onto a glass plate (100 mg on 1 dm^2), covered by another glass plate and irradiated with the complete spectrum of a CVD-120A Hg lamp or with sunlight until the disappearance of starting compounds **1a**,**b**, **4**, **5** (TLC monitoring, 30 min). The reaction mixture was dissolved in hexane, filtered, purified by column chromatography in CHCl$_3$ and crystallised from benzene–ethanol (1:1).

3a: mp 157–159 °C. ^{1}H NMR, δ: 3.78–4.17 (m, 16H, OCH$_2$CH$_2$), 6.65–7.61 (m, 10H, H^6, H^7, C$_6$H$_3$, Ph), 7.85 (d, 1H, H^3, ^4J 8.5 Hz), 7.95 (m, 1H, H^8), 8.32 (m, 1H, H^5), 8.79 (d, 1H, H^4, ^3J 8.5 Hz), 9.27 (s, 1H, NH), 17.14 (s, 1H, OH). IR (ν/cm^{-1}): 3431, 3378 (OH, NH), 3073 (CH$_{\text{arom.}}$), 2912, 2866 (CH$_2$), 1671, 1653 (C=O, C=N), 1590, 1513 (C=C). UV [λ/nm (lg ε)]: 240 (4.36), 440 (3.76). MS, *m*/*z*: 608 (M$^+$). Found (%): C, 69.07; H, 5.66; N, 4.49. Calc. for C$_{35}$H$_{32}$N$_2$O$_8$ (%): C, 69.08; H, 5.26; N, 4.61.

3b: mp 161–163 °C. ^{1}H NMR, δ: 3.75–4.15 (m, 16H, OCH$_2$CH$_2$), 6.49–7.60 (m, 9H, H^8, C$_6$H$_3$, Ph), 6.86 (d, 1H, H^3, ^2J 8.5 Hz), 8.12 (m, 2H, H^6, H^7), 8.32 (dd, 1H, H^5, ^6J 9 Hz, ^8J 2 Hz), 9.12 (d, 1H, H^2, ^3J 8.5 Hz), 13.24 (s, 1H, NH), 15.55 (s, 1H, OH). IR (ν/cm^{-1}): 3356, 3308 (OH, NH), 3062 (CH$_{\text{arom.}}$), 2950, 2921 (CH$_2$), 1671, 1630 (C=O, C=N), 1601, 1582 (C=C). UV [λ/nm (lg ε)]: 282 (4.39), 496 (3.97). MS, *m*/*z*: 608 (M$^+$). Found (%): C, 68.77; H, 5.31; N, 4.65. Calc. for C$_{35}$H$_{32}$N$_2$O$_8$ (%): C, 69.08; H, 5.26; N, 4.61.

3c: mp 139–141 °C. ^{1}H NMR, δ: 3.28–4.11 (m, 20H, OCH$_2$CH$_2$), 6.62–7.71 (m, 10H, H^6, H^7, C$_6$H$_3$, Ph), 8.00 (d, 1H, H^3, ^4J 8.5 Hz), 8.19 (m, 1H, H^8), 8.32 (m, 1H, H^5), 8.49 (d, 1H, H^4, ^3J 8.5 Hz), 9.70 (s, 1H, NH), 16.97 (s, 1H, OH). IR (ν/cm^{-1}): 3433, 3388 (OH, NH), 3071 (CH$_{\text{arom.}}$), 2933, 2874 (CH$_2$), 1670, 1655 (C=O, C=N), 1589, 1513 (C=C). UV [λ/nm (lg ε)]: 248 (4.40), 440 (3.78). MS, *m*/*z*: 652 (M$^+$). Found (%): C, 68.00; H, 5.46; N, 4.39. Calc. for C$_{37}$H$_{36}$N$_2$O$_9$ (%): C, 68.10; H, 5.52; N, 4.29.

3d: mp 149–151 °C. ^{1}H NMR, δ: 3.70–4.15 (m, 20H, OCH$_2$CH$_2$), 6.55–7.62 (m, 9H, H^8, C$_6$H$_3$, Ph), 6.86 (d, 1H, H^3, ^2J 8.5 Hz), 8.10 (m, 2H, H^6, H^7), 8.28 (dd, 1H, H^5, ^6J 9 Hz, ^8J 2 Hz), 9.08 (d, 1H, H^2, ^3J 8.5 Hz), 13.23 (s, 1H, NH), 15.50 (s, 1H, OH). IR (ν/cm^{-1}): 3365, 3312 (OH, NH), 3052 (CH$_{\text{arom.}}$), 2955, 2923 (CH$_2$), 1670, 1635 (C=O, C=N), 1595, 1582 (C=C). UV [λ/nm (lg ε)]: 280 (4.38), 494 (3.93). MS, *m*/*z*: 652 (M$^+$). Found (%): C, 67.82; H, 5.48; N, 4.35. Calc. for C$_{37}$H$_{36}$N$_2$O$_9$ (%): C, 68.10; H, 5.52; N, 4.29.

The structures of compounds **6**, **7** and **9** were determinated by comparison with the samples obtained according to published procedures.[6,7]