Synthesis of 5*H*-naphtho[2,3-*c*]phenothiazine-8,13-diones from 1-arylthio-2-azidoanthraquinones

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Thermolysis of 1-arylthio-2-azidoanthraquinones in DMSO at 150 °C afforded substituted 5*H*-naphtho[2,3-*c*]phenothiazine-8,13-diones. These compounds were also formed upon photolysis of azides at 77 K and were prepared in quantitative yields by the reactions of 1-arylthio-2-azidoanthraquinones with KOH in DMSO at 20 °C.

Key words: thermolysis, photolysis, cyclization under the action of a base, 1-arylthio-2-azidoanthraquinones, 5*H*-naphtho[2,3-*c*]phenothiazine-8,13-diones.

Cyclic sulfur-and-nitrogen-containing anthraquinone derivatives are used as dyes in recording media for recording, storing, and reproducing information.[1—3] For example, naphtho[2,3-*a*]phenothiazine-8,13-diones were synthesized and used as dyes that are introduced into liquid-crystalline materials.[3,4] The data on the synthesis and properties of isomeric naphtho[2,3-*c*]phenothiazine-8,13-diones are virtually lacking. In the present study, we examined the possibility of the preparation of these phenothiazines upon photolysis and thermolysis of 1-arylthio-2-azidoanthraquinones.

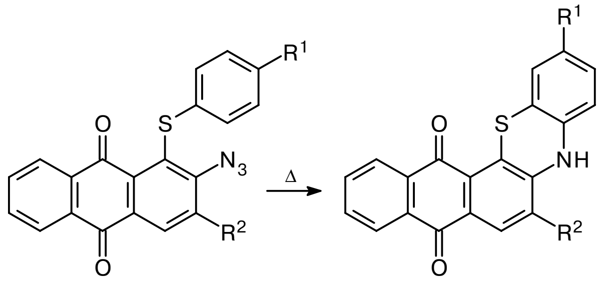
Photochemical and thermal reactions of aryl azides are well known.[5] The photochemical and thermal conversions of 1-azidoanthraquinones giving rise to anthra[1,9-*cd*]isoxazol-6-ones were studied. The latter compounds containing the aryloxy or arylthio group at position 3 undergo further conversions to form the corresponding phenoxazines and phenothiazines.[6,7] Previously, photolysis of 2-azidoanthraquinones has not been investigated. Only the data on thermolysis affording 2-aminoanthraquinone in low yield were reported.[8]

Results and Discussion

2-Amino-1-arylthioanthraquinones were synthesized from the corresponding 2-amino-1-chloroanthraquinones and substituted arenethiols according to a procedure reported previously.[9] Azides **1a—d** were prepared by diazotization of 2-amino-1-arylthioanthraquinones ($NaNO_2$ in AcOH) followed by the reaction of a solution of the diazonium salt with NaN_3.

Thermolysis of 1-arylthio-2-azidoanthraquinones. Thermolysis of azides **1a—d** was carried out by heating them in DMSO or triethylene glycol at 150 °C for 1 h. The major conversion products, *viz.*, phenothiazines **2a—d**, were isolated in 52—60% yields (Scheme 1). In addition, 2-amino-1-arylthioanthraquinone and a large amount of resinification products were obtained.

Scheme 1



1a—d **2a—d**

	a	**b**	**c**	**d**
R^1	H	Bu^t	OMe	Bu^t
R^2	H	H	H	Cl

The structures of phenothiazines **2a—d** were established by spectral methods. The position of the substituent R^1 in molecules **2b—d** was determined based on the proposed mechanism of cyclization[10,11] of aryl azides containing the arylthio or aryloxy group in the *ortho* position with respect to the azido group. It is assumed

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that singlet nitrene that formed upon photolysis and thermolysis attacks the *ipso*-C atom of the aryl substituent bound through the heteroatom to give a spiro compound. Subsequent rearrangement of the spiro compound brings about the migration of the substituent relative to the heteroatom.

The yields of phenothiazines **2a—d** can be substantially increased in the presence of a base. Thus cyclization of azides **1a—d** in DMSO in the presence of an equimolar amount of KOH at ~20 °C afforded phenothiazines **2a—d** in quantitative yields. These conversions of azides are very unusual and analogous examples are lacking in the literature. Only cyclization of aryl azides that contain the amide or keto group in the *ortho* position with respect to the azido group under the action of KOH or NaOH was described.[12] The reactions of azides **1a—d** in DMSO in the presence of KOH are of obvious preparative importance due to the simplicity of the procedure and the quantitative yields of individual products, which do not require additional chromatographic purification.

Photolysis of 1-arylthio-2-azidoanthraquinones. To study the photochemical properties of azides **1a—d**, we irradiated their solutions in benzene with total light of a mercury lamp or with sunlight until the initial compound disappeared. Chromatographic analysis of the photolysate showed substantial resinification and a large amount of slightly colored minor products among which we identified traces of 2-amino-1-arylthioanthraquinones. Interestingly, the formation of intensely colored phenothiazines **2a—d** was observed visually and chromatographically in the initial stage of irradiation in mixtures subjected to photolysis. The initial solutions were pale-yellow in color, whereas the solutions of phenothiazines were intensely blue.

To examine the stages of photoconversions of the azides in detail, we irradiated a dilute solution of compound **1b** in toluene with light with the wavelength 313 nm, the electronic absorption spectra being simultaneously recorded at intervals. Actually, the formation of a colored product with λ_{max} ~625 nm (Fig. 1), *viz.*, phenothiazine **2b** (TLC), was observed in the initial stages of irradiation of a solution of azidoanthraquinone **1b** in toluene at ~20 °C. However, the yield of **2b** was no higher than 10% (with respect to the initial concentration of the azide). Further irradiation of the solution (see Fig. 1, curve *4*) resulted in the disappearance of compound **2b** and the formation of slightly colored products.

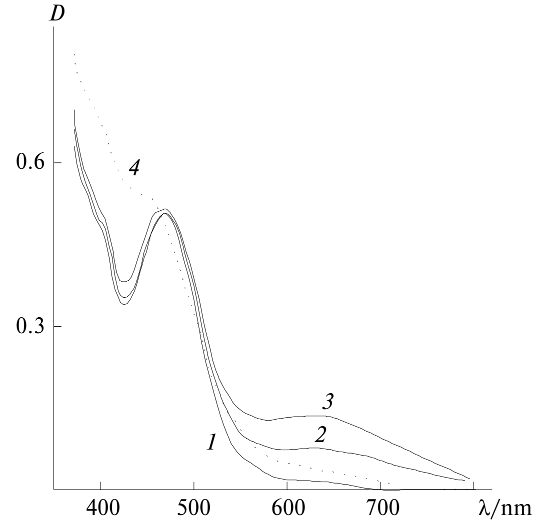

Fig. 1. Changes in the electronic absorption spectrum of 1-arylthio-2-azidoanthraquinone **1b** (*1*) (a solution in toluene) in the course of irradiation with light with the wavelength 313 nm at ~20 °C after 1.5 (*2*), 5 (*3*), and 45 min (*4*).

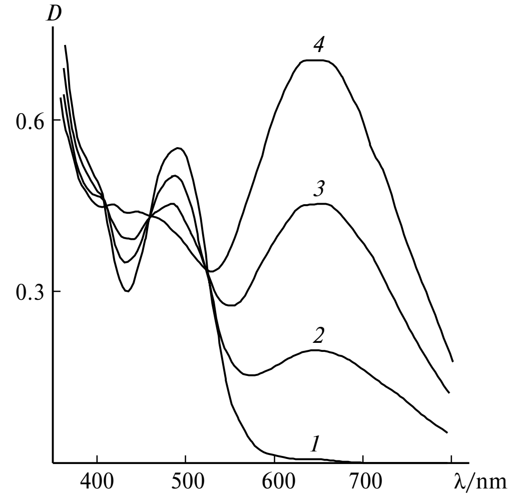

Fig. 2. Changes in the electronic absorption spectrum of 1-arylthio-2-azidoanthraquinone (*1*) (in methylcyclohexane glass) in the course of irradiation with light with the wavelength 313 nm at 77 K after 3 (*2*), 15 (*3*), and 30 min (*4*).

Phenothiazine **2b** was obtained in substantially higher yield upon photolysis of **1b** in a glassy matrix of methylcyclohexane at 77 K (Fig. 2). Chromatographic analysis demonstrated that compound **2b** was obtained as the major photolysis product in a yield of no less than 40%. Phenothiazine **2b** is resistant to prolonged irradiation both with visible (546 nm) and UV (313 nm) light in a methylcyclohexane matrix at 77 K. Apparently, compound **2b** was obtained in substantially higher yield in the case of low-temperature photolysis of **1b** due primarily to resistance to irradiation at 77 K. It should be noted that irradiation of product **2b**, which was accumulated upon low-temperature photolysis of **1b**, at ~20 °C led to its rapid destruction.

To summarize, 1-arylthio-2-azidoanthraquinones subjected to thermolysis, photolysis, or treatment with KOH gave substituted 5*H*-naphtho[2,3-*c*]phenothiazine-8,13-diones.

Experimental

The IR spectra were recorded on a Vector-22 spectrophotometer (Bruker) in KBr pellets. The electronic absorption

Table 1. Physicochemical characteristics of the compounds synthesized

Compound	Yield* (%)	M.p.**/°C	Found/Calculated (%) C	H	N	S	Molecular formula	IR, ν/cm^{-1}	Electronic spectrum, λ_{max}/nm (logε)
1a	83	148 (decomp.)	67.57 67.22	2.85 3.08	11.38 11.76	8.44 8.96	$C_{20}H_{11}N_3O_2S$	2990, 2116, 1669	246 (4.52), 278 (4.33), 460 (3.54)
1b	90	154 (decomp.)	69.38 69.71	4.21 4.63	10.05 10.17	7.89 7.75	$C_{24}H_{19}N_3O_2S$	2962, 2107, 1669	254 (4.54), 272 (4.52), 456 (3.55)
1c	89	144 (decomp.)	65.41 65.12	3.56 3.36	11.02 10.85	8.07 8.27	$C_{21}H_{13}N_3O_3S$	3069, 2111, 1667	256 (4.59), 334 (3.86), 468 (3.53)
1d	87	137 (decomp.)	64.70 64.35	3.92 4.05	9.12 9.38	7.31 7.16	$C_{24}H_{18}ClN_3O_2S$	2959, 2125, 1671	252 (4.44), 321 (4.09), 448 (3.43)
2a	55	297—299	73.12 72.95	3.48 3.34	4.23 4.26	9.91 9.73	$C_{20}H_{11}NO_2S$	3300, 2965, 1665, 1635	243 (4.59), 283 (4.92), 330 (3.60), 630 (4.27)
2b	58	315—317	74.38 74.79	4.86 4.97	3.64 3.63	8.28 8.30	$C_{24}H_{19}NO_2S$	3300, 2970, 1646, 1622	244 (4.48), 286 (4.77), 335 (3.68), 628 (4.03)
2c	60	285—287	70.52 70.19	3.34 3.65	3.63 3.90	8.60 8.91	$C_{21}H_{13}NO_3S$	3290, 2986, 1660, 1645	242 (4.45), 282 (4.80), 330 (3.64), 626 (3.87)
2d	52	256—258	68.95 68.65	4.42 4.32	3.17 3.34	7.92 7.62	$C_{24}H_{18}ClNO_2S$	3350, 2950, 1650	246 (4.50), 285 (4.61), 332 (3.64), 608 (3.96)

* For compounds **2a—d**, the yields are given for thermolysis of **1a—d** in DMSO at 150 °C.

** From an EtOH—C_6H_6 mixture.

spectra were measured on a Specord UV—VIS spectrophotometer for solutions in EtOH (the concentration was $1 \cdot 10^{-4}$ mol L^{-1}). The ^{1}H NMR spectra were recorded on a Bruker WP-200SY instrument with Me_4Si as the internal standard. The mass spectra (EI) were obtained on a Finnigan MAT-8200 instrument (the *m/z* values for the molecular ion $[M]^+$ are given). Column chromatography was carried out on silica gel L (5—40 μm). The TLC analysis was performed on Silufol UV-254 plates using a 9 : 1 toluene—ethanol mixture as the eluent. Photolysis was carried out with total light of a DRSh-500 lamp using UFS-1 (280—400 nm) and ZhZS-1 (546 nm) filters and a combination of UFS-2 and ZhS-3 filters (313 nm).

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

1-Arylthio-2-azidoanthraquinones (1a—d). A solution of $NaNO_2$ (0.012 mol) in water (2 mL) and concentrated HCl (1 mL) were added to a solution of 2-amino-1-arylthioanthraquinone (0.01 mol) in AcOH (100 mL). The reaction mixture was kept for 1 h and then cooled to 10 °C. Then NaN_3 (0.012 mol) was added and the reaction mixture was stirred in the dark for 30 min. The azide that precipitated was filtered off. An additional amount of the target product was precipitated from the filtrate by addition of water.

2-Azido-1-phenylthioanthraquinone (1a). ^{1}H NMR ($CDCl_3$), δ: 6.80—7.28 (m, 5 H, SPh); 7.50 (d, 1 H, H(3), *J* = 9 Hz); 7.68 (m, 2 H, H(6), H(7)); 8.12 (m, 1 H, H(5)); 8.27 (m, 1 H, H(8)); 8.35 (d, 1 H, H(4), *J* = 9 Hz).

2-Azido-1-(*p-tert*-butylphenylthio)anthraquinone (1b). ^{1}H NMR ($CDCl_3$), δ: 1.27 (s, 9 H, $C(Me)_3$); 7.12 (d, 2 H, H(2´), H(6´), *J* = 8.5 Hz); 7.22 (d, 2 H, H(3´), H(5´), *J* = 8.5 Hz); 7.43 (d, 1 H, H(3), *J* = 8.5 Hz); 7.74 (m, 2 H, H(6), H(7)); 8.18 (m, 2 H, H(5), H(8)); 8.31 (d, 1 H, H(4), *J* = 8.5 Hz).

2-Azido-1-(*p*-methoxyphenylthio)anthraquinone (1c). ^{1}H NMR ($CDCl_3$), δ: 3.77 (s, 3 H, OMe); 6.78 (d, 2 H, H(2´), H(6´), *J* = 9 Hz); 7.20 (d, 2 H, H(3´), H(5´), *J* = 9 Hz); 7.39 (d, 1 H, H(3), *J* = 9 Hz); 7.77 (m, 2 H, H(6), H(7)); 8.21 (m, 2 H, H(5), H(8)); 8.28 (d, 1 H, H(4), *J* = 9 Hz).

2-Azido-1-(*p-tert*-butylphenylthio)-3-chloroanthraquinone (1d). ^{1}H NMR ($CDCl_3$), δ: 1.25 (s, 9 H, $C(Me)_3$); 7.19 (d, 2 H, H(2´), H(6´), *J* = 8.5 Hz); 7.29 (d, 2 H, H(3´), H(5´), *J* = 8.5 Hz); 7.78 (m, 2 H, H(6), H(7)); 8.21 (m, 2 H, H(5), H(8)); 8.24 (s, 1 H, H(4)).

Thermolysis of azides 1a—d. A solution of compound **1a—d** (1 mmol) in DMSO or triethylene glycol (20 mL) was heated at 150 °C for 1 h. After completion of the reaction, the mixture was poured into water. The precipitate that formed was purified by preparative TLC (benzene as the eluent).

Cyclization of azides 1a—d in the presence of KOH. Ground KOH (1 mmol) was added with stirring to a solution of compound **1a—d** (1 mmol) in DMSO (30 mL). The reaction mixture was kept at ~20 °C for 1 h and then poured into water. The precipitate that formed was filtered off and dried. Compounds **2a—d** were obtained in 100% yields.

5*H*-Naphtho[2,3-*c*]phenothiazine-8,13-dione (2a). ^{1}H NMR (DMSO-d_6), δ: 6.42—6.95 (m, 4 H, H(1), H(2), H(3), H(4)); 6.73 (d, 1 H, H(6), *J* = 8.5 Hz); 7.70 (d, 1 H, H(7), *J* = 8.5 Hz); 7.85 (m, 2 H, H(10), H(11)); 8.10 (m, 2 H, H(9), H(12)); 9.25 (s, 1 H, NH).

2-*tert*-Butyl-5*H*-naphtho[2,3-*c*]phenothiazine-8,13-dione (2b). ^{1}H NMR (DMSO-d_6), δ: 1.19 (s, 9 H, $C(Me)_3$); 6.46—6.94 (m, 3 H, H(1), H(3), H(4)); 6.65 (d, 1 H, H(6), *J* = 8.5 Hz); 7.69 (d, 1 H, H(7), *J* = 8.5 Hz); 7.83 (m, 2 H, H(10), H(11)); 8.07 (m, 2 H, H(9), H(12)); 9.31 (c, 1 H, NH).

2-Methoxy-5*H*-naphtho[2,3-*c*]phenothiazine-8,13-dione (2c). ^{1}H NMR (DMSO-d_6), δ: 3.65 (s, 3 H, OMe); 6.45—6.84 (m, 3 H, H(1), H(3), H(4)); 6.72 (d, 1 H, H(6), *J* = 8.5 Hz); 7.71 (d, 1 H, H(7), *J* = 8.5 Hz); 7.85 (m, 2 H, H(10), H(11)); 8.10 (m, 2 H, H(9), H(12)); 9.30 (s, 1 H, NH).

2-*tert*-Butyl-6-chloro-5*H*-naphtho[2,3-*c*]phenothiazine-8,13-dione (2d). ^{1}H NMR (DMSO-d_6), δ: 1.25 (s, 9 H, $C(Me)_3$); 6.21 (br.s, 1 H, NH); 6.93—7.30 (m, 3 H, H(1), H(3), H(4)); 7.71 (m, 2 H, H(10), H(11)); 8.11 (s, 1 H, H(7)); 8.22 (m, 2 H, H(9), H(12)).

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