Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron 64 (2008) 1459–1466
Tetrahedron
www.elsevier.com/locate/tet

Products of photoreduction of 9,10-phenanthrenequinone in the presence of *N*,*N*-dimethylanilines and polymethylbenzenes

M.P. Shurygina*, Yu.A. Kurskii, S.A. Chesnokov, G.A. Abakumov

G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 49, Tropinina Street, 603950 Nizhny Novgorod, Russian Federation

Received 10 July 2007; received in revised form 31 October 2007; accepted 15 November 2007
Available online 19 November 2007

Abstract

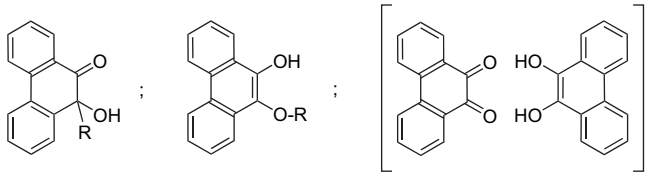
Photoreduction of 9,10-phenanthrenequinone (PQ) in the presence of *p*-substituted *N*,*N*-dimethylanilines and polymethylbenzenes affords corresponding phenolethers as primary products. In the subsequent process shielded from light, phenolethers, which were formed by photoreaction of PQ with *N*,*N*-dimethylanilines, were quantitatively converted to give corresponding ketols. Phenolethers of 9,10-phenanthrenequinone and polymethylbenzenes are rearranged only under irradiation and in the presence of second molecule of PQ to form ketols. Stability of phenolethers is determined by redox properties and structure of hydrogen donors.

Keywords: Photoreduction; 9,10-Phenanthrenequinone; Phenolether; Ketol

1. Introduction

9,10-Phenanthrenequinone (PQ) occupies a special position among *o*-quinones (themselves one of the most interesting class of compounds in photochemistry). 9,10-Phenanthrenequinone is used as sensitizer,[1,2] photosensitive component,[3] photoinitiator,[4] photolacing agent[5] of various photosensitive systems which are applied in electronics, polygraphy and dental practice. Amongst the other compounds, 9,10-phenanthrenequinone is the subject of numerous studies in spectrometry of exciting states,[6–8] photosensitization[9] and photoreduction of carbonyl compounds.[10–13] However, the results of investigation into the products of photoreduction of PQ in the presence of different H-donors are ambiguous. The study of photoreduction of 9,10-phenanthrenequinone shows that predominant formation of one or another product is determined by the nature of the hydrogen donor. Photoreduction of PQ in the presence of hydrocarbons (alkanes,[5,14–16] alkenes[5,17] and alkynes[17,18]) leads to ketols (Scheme 1, structure *a*). At the same time photoreaction of PQ with *o*-, *p*-xylenes and 1,2,4-trimethylbenzene affords corresponding phenolethers (Scheme 1, structure *b*).[17,19] Moreover formation of phenolethers was observed upon photoreduction of PQ in the presence of H-donors, containing heteroatom, such as alcohols,[18] ethers[17,20,21] and aldehydes.[17,18] Phenolethers[20] and ketols[22] are decomposed under UV-irradiation accompanied by heating to give a product which was identified as quinhydrone.[17,20,22] Processes occur according to a radical mechanism (Scheme 1, structure *c*).

Since the reaction of photoreduction of 9,10-phenanthrenequinone can be used for the simulation of biochemical processes such as photosynthesis,[23] investigation and identification of the intermediate and final products of photoreduction of PQ are very important.



a *b* *c*

Scheme 1.

* Corresponding author. Fax: +7 831 4627497.
E-mail address: sch@iomc.ras.ru (M.P. Shurygina).

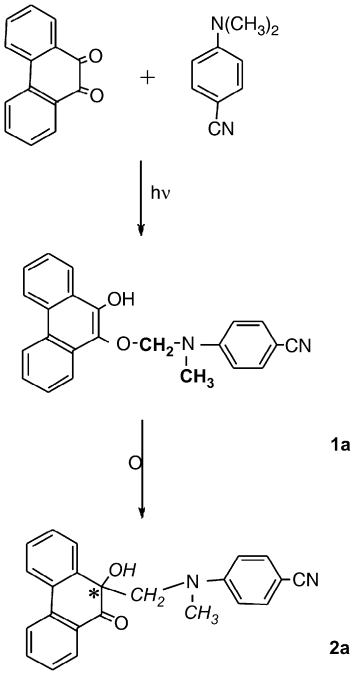
0040-4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.11.050

Table 1
The oxidative potentials of substituted *N*,*N*-dimethylanilines and polymethylbenzenes[24]

Hydrogen donor	Labels	$E_{1/2}$ (V)
p-Cyano-*N*,*N*-dimethylaniline	CN-DMA	1.12
p-*N*,*N*-Dimethylamino-benzaldehyde	H(O)C-DMA	0.84
N,*N*-Dimethylaniline	DMA	0.71
p-Methyl-*N*,*N*-dimethylaniline	CH_3-DMA	0.65
p-Xylene	*p*-XYL	1.87
m-Xylene	*m*-XYL	1.86
o-Xylene	*o*-XYL	1.86
1,3,5-Trimethylbenzene (mesitylene)	MES	1.85
1,2,4,5-Tetramethylbenzene (durene)	DUR	1.59
Hexamethylbenzene	HMB	1.46

Here the products of photoreduction of 9,10-phenanthrenequinone in the presence *p*-substituted *N*,*N*-dimethylanilines (*p*-X-DMA) and polymethylbenzenes were investigated by ^{1}H NMR spectroscopy. Table 1 presents the electrochemical potentials of hydrogen donors.

It was established that photoreduction of phenanthrenequinone proceeds to give the corresponding phenolethers (**1**) and ketols (**2**). The ratio between phenolethers and ketols is determined by the nature of H-donors and reaction conditions.



Scheme 2.

2. Results and discussion

2.1. The products of photoreduction of 9,10-phenanthrenequinone in the presence p-substituted N,N-dimethylanilines

Irradiation ($380<\lambda<430$ nm, 5 min) of the reaction mixture of PQ and *p*-cyano-*N*,*N*-dimethylaniline in C_6D_6 (Fig. 1a, Scheme 2) results in the appearance of new signals attributed to protons of the methyl group (δ=2.07 ppm), methylene group (δ=4.81 ppm) and hydroxyl group (δ=5.28 ppm) of the phenolether (**1a**) (Fig. 1b, Scheme 2). In the dark, under vacuum, at ambient temperature the intensity of the signals for the protons of **1a** gradually decreases followed by the simultaneous appearance of signals attributed to ketol (**2a**), namely to protons of the methyl group (δ=2.24 ppm), methylene group (two doublets δ=3.16 and 3.33 ppm, J=15 Hz) and hydroxyl group (δ=4.25 ppm) (Fig. 1c, Scheme 2). The protons of methylene

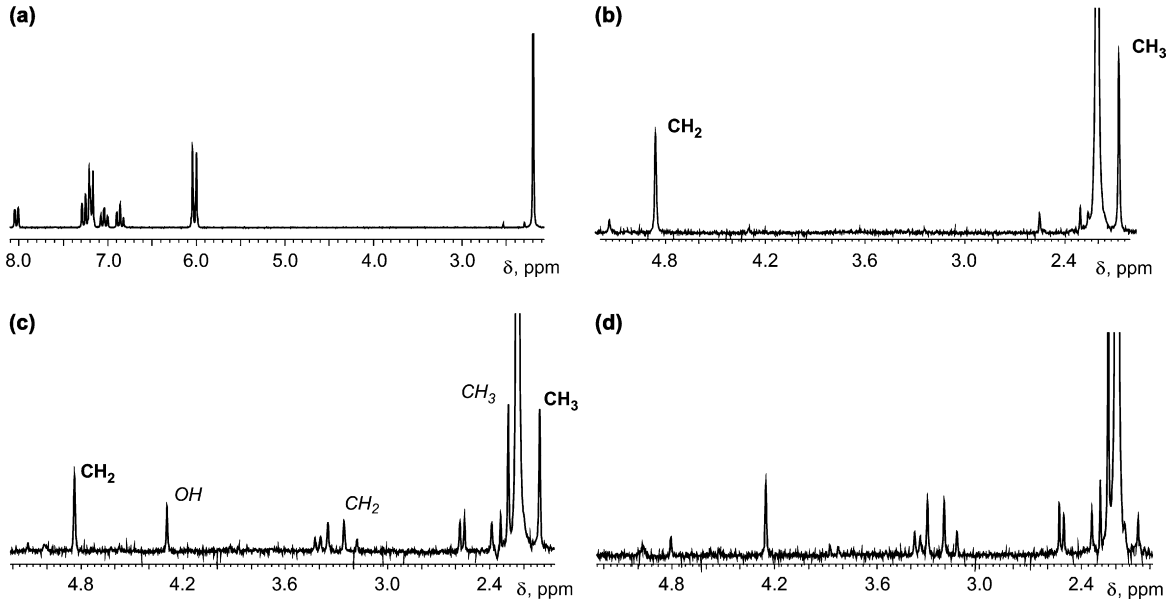
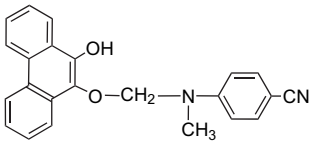
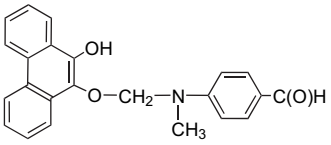
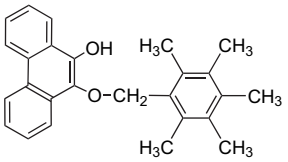
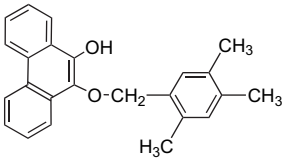
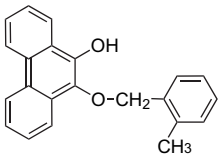
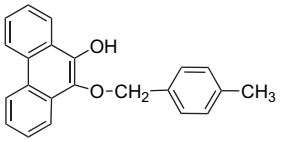
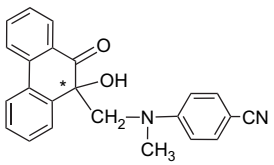
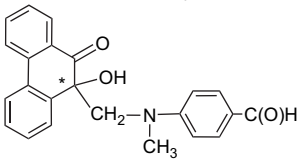


Figure 1. The changes in ^{1}H NMR spectrum of solution of 9,10-phenanthrenequinone (4×10^{-2} M) in the presence of *p*-cyano-*N*,*N*-dimethylaniline (4×10^{-2} M) in C_6D_6: (a) before irradiation; (b) 5 min after irradiation; (c) 35 min after irradiation; (d). 120 min after irradiation (irradiation by the light $380<\lambda<430$ nm, T=298 K). (Labels: bold for the protons of methyl group and methylene group of phenolether; italic for the protons of methyl group, methylene group and hydroxyl group of ketol.)

group of ketol **2a** are nonequivalent because they are coupled with the asymmetric carbon atom (in Scheme 2,this atom is marked by asterisk). Therefore they appear in the ^{1}H NMR spectrum as AB-spin system with spin–spin interaction constant 13–15 Hz attributed to geminal protons; this is typical for all ketols. During 2 h of shielding from light phenolether **1a** quantitatively gets converted to ketol **2a** (Fig. 1d).

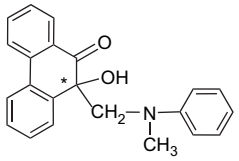
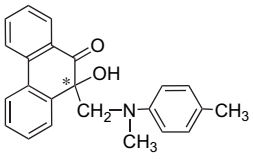
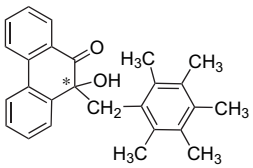
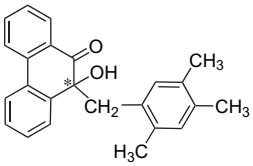
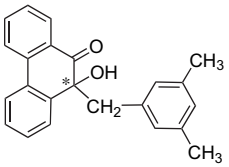
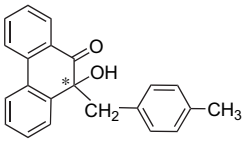
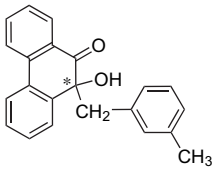
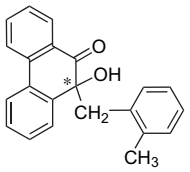
Photoreduction of PQ in the presence *p*-*N*,*N*-dimethylamino-benzaldehyde proceeds similarly. Typical signals in the ^{1}H NMR spectrum of all formed compounds including the signals of phenolether (**1b**) and ketol (**2b**) are listed in Table 2 (in the third column). Investigation of the kinetics in the absence of light allows us to calculate the rate constants for the conversion of phenolethers **1a** and **1b** (from the decreasing intensities of typical signals in NMR). In both cases the rates of rearrangement of phenolether occur according to first order. Increasing of the electron-donor properties of the amine from $E_{1/2}$=1.12 V (CN-DMA) to $E_{1/2}$=0.84 V (H(O)C-DMA) leads to the increase of rate constants of rearrangement from 3.3×10^{-4} s^{-1} (**1a**) to 5.3×10^{-4} s^{-1} (**1b**). It was previously described[24] that the stability of analogous phenolethers, which were formed upon photoreduction of *o*-benzoquinone by

Table 2
The chemical shifts of typical signals in the ^{1}H NMR spectra of products of photoreduction of 9,10-phenanthrenequinone in the presence *p*-substituted *N*,*N*-dimethylanilines and polymethylbenzenes of phenolethers (**1a**–**1f**) and ketols (**2a**–**2j**) (C_6D_6, δ (ppm), *J* (Hz), *T*=298 K)

Name of compounds	Structure	No	^{1}H NMR (δ (ppm), *J* (Hz))
4-(((10-Hydroxyphenanthren-9-yloxy)-methyl)(methyl)amino)benzonitrile		**1a**	2.07 (s, 3H, CH_3); 4.81 (s, 2H, OCH_2N); 5.28 (s, 1H, OH)
4-(((10-Hydroxyphenanthren-9-yloxy)-methyl)(methyl)amino)benzaldehyde		**1b**	2.21 (s, 3H, CH_3); 4.94 (s, 2H, OCH_2N); 6.20 (s, 1H, OH); 9.82 (s, 1H, C(O)H)
10-(2,3,4,5,6-Pentamethylbenzyloxy)-phenanthren-9-ol		**1c**	2.03–2.14 (m, 3H, CH_3); 5.27 (s, 2H, CH_2); 6.13 (s, 1H, OH)
10-(2,4,5-Trimethylbenzyloxy)-phenanthren-9-ol		**1d**	1.93 (s, 3H, CH_3); 4.96 (s, 2H, CH_2); 6.18 (s, 1H, OH)
10-(2-Methylbenzyloxy)-phenanthren-9-ol		**1e**	2.23 (s, 3H, CH_3); 4.88 (s, 2H, CH_2); 6.01 (s, 1H, OH)
10-(4-Methylbenzyloxy)-phenanthren-9-ol		**1f**	2.10 (s, 3H, CH_3); 4.84 (s, 2H, CH_2); 6.00 (s, 1H, OH)
4-(((9-Hydroxy-10-oxo-9,10-dihydrophenanthren-9-yl)-methyl)(methyl)amino)benzonitrile		**2a**	2.24 (s, 3H, CH_3); 3.17 (d, 1H, CH_2, *J*=15); 3.34 (d, 1H, CH_2, *J*=15); 4.25 (s, 1H, OH)
4-(((9-Hydroxy-10-oxo-9,10-dihydrophenanthren-9-yl)-methyl)(methyl)amino)-benzaldehyde		**2b**	2.41 (s, 3H, CH_3); 3.34 (d, 1H, CH_2, *J*=15); 3.49 (d, 1H, CH_2, *J*=15); 4.36 (s, 1H, OH); 9.86 (s, 1H, C(O)H)

(*continued on next page*)

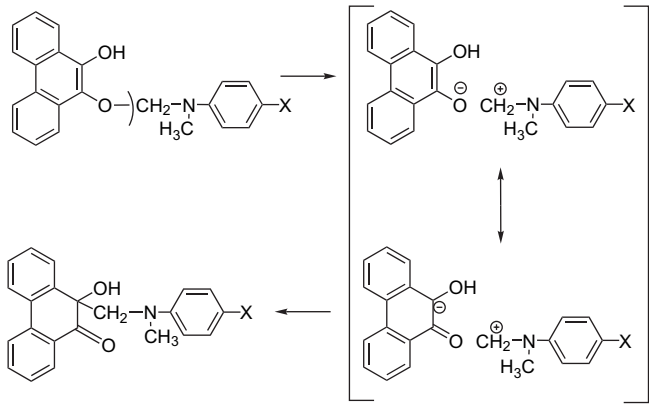
Table 2 (*continued*)

Name of compounds	Structure	No	^{1}H NMR (δ (ppm), J (Hz))
10-Hydroxy-10-((methyl(phenyl)-amino)methyl)-phenanthren-9(10*H*)-one		**2c**	2.55 (s, 3H, CH_3N); 3.47 (d, 1H, CH_2N, J=15); 3.62(d, 1H, CH_2N, J=15); 4.53 (w. s, 1H, OH)
10-Hydroxy-10-((methyl(*p*-tolyl)-amino)methyl)-phenanthren-9(10*H*)-one		**2d**	2.25 (s, 3H, CH_3N); 3.49 (d, 1H, CH_2N, J=15); 3.64 (d, 1H, CH_2N, J=15); 4.62 (s, 1H, OH)
10-Hydroxy-10-(2,3,4,5,6-pentamethylbenzyl)-phenanthren-9(10*H*)-one		**2e**	2.03–2.14 (m, 3H, CH_3); 3.37, 3.45 and 3.52 (two d, 1H, CH_2, J=15); 6.13 (s, 1H, OH)
10-Hydroxy-10-(2,4,5-trimethylbenzyl)-phenanthren-9(10*H*)-one		**2f**	2.10 (s, 3H, CH_3); 3.03 (d, 1H, CH_2, J=13.5); 3.24 (d, 1H, CH_2, J=13.5); 4.13 (s, 1H, OH)
10-(3,5-Dimethylbenzyl)-10-hydroxyphenanthren-9(10*H*)-one		**2g**	2.19 (s, 6H, CH_3); 2.92 (d, 1H, CH_2, J=13); 3.00 (d, 1H, CH_2, J=13); 3.99 (s, 1H, OH); 6.43 (s, 2H, CH(2′), CH(6′)); 6.81 (s, 1H, CH(4′)); 7.38–7.95 (m, 8H, CH(1,2,3,4,5,6,7,8))
10-Hydroxy-10-(4-methylbenzyl)-phenanthren-9(10*H*)-one		**2h**	2.15 (s, 3H, CH_3); 2.99 (d, 1H, CH_2, J=13); 3.11 (d, 1H, CH_2, J=13); 4.28 (s, 1H, OH)
10-Hydroxy-10-(3-methylbenzyl)-phenanthren-9(10*H*)-one		**2i**	2.14 (s, 3H, CH_3); 3.01 (d, 1H, CH_2, J=13); 3.12 (d, 1H, CH_2, J=13); 4.29 (s, 1H, OH)
10-Hydroxy-10-(2-methylbenzyl)-phenanthren-9(10*H*)-one		**2j**	1.95 (s, 3H, CH_3); 3.01 (d, 1H, CH_2, J=13); 3.23 (d, 1H, CH_2, J=13); 4.25 (s, 1H, OH)

p-substituted *N*,*N*-dimethylaniline, also diminishes with the increase of the electron-donor ability of the substituent in the amine fragment of the phenolether.

Further increasing the donor properties of amines up to $E_{1/2}$=0.71 V (*N*,*N*-dimethylaniline) and $E_{1/2}$=0.65 V (*p*-methyl-*N*,*N*-dimethylaniline), apparently, leads to a decrease of stability of corresponding phenolethers such that they were not observed, possibly because the first ^{1}H NMR spectra were registered 90–120 s after the end of irradiation. The ^{1}H NMR spectra of irradiated mixtures: PQ–DMA and PQ–CH_3-DMA show only signals attributed to the corresponding ketols (**2c**) and (**2d**). Analogous to the mechanism of decomposition of phenolether formed from *o*-benzoquinones and *p*-X-DMA described in Ref. 25, it can be suggested that the conversion path of phenolether obtained from PQ-*p*-X-DMA into ketol is as follows (see Scheme 3).

First is the heterolytic cleavage of the O–C ether bond of phenolether followed by formation of an ion-pair. Then the addition of cation to carbon-centred anion and ketol formation occur. The greater the number of substituents in amine fragment that can stabilize cation in the intermediate ion-pair, the faster the cleavage of O–C ether bond of phenolether proceeds, and consequently, the phenolether is less stable.

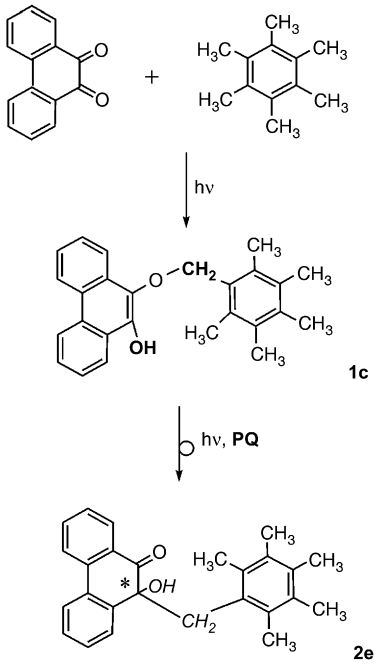


Scheme 3.

So, the mechanism of formation of products of photoreduction of 9,10-phenanthrenequinone in the presence *p*-substituted *N*,*N*-dimethylanilines involves two consecutive reactions. First is the photoreaction, which results in the formation of phenolether, second is the process which consists of the quantitative rearrangement of phenolether into ketol.

2.2. The products of photoreduction of 9,10-phenanthrenequinone in the presence polymethylbenzene

Short-term irradiation (λ>500 nm, 1 min) of a reaction mixture of PQ and hexamethylbenzene (Fig. 2a) results in the appearance of new signals in ^{1}H NMR spectrum attributed to phenolether (**1c**) (Fig. 2b, Scheme 4), namely to protons of the methyl groups (m, δ=2.03−2.14 ppm), methylene group (δ=5.27 ppm) and hydroxyl group (δ=6.13 ppm). Exposition of the irradiated solution in the dark during 24 h doesn't lead to changes in ^{1}H NMR spectrum. However, upon following the irradiation of the reaction, the appearance and accumulation of new signals attributed to ketol (**2e**) (Fig. 2c and d, Scheme 4) are observed; namely to protons of the methylene group (δ=3.45 ppm) and hydroxyl group (δ=4.22 ppm). Protons of the methylene group have various chemical shifts and give AB-type ^{1}H NMR spectrum (geminate constant J=15 Hz). After total decolouration of reaction mixture (irradiation during 40 min, Fig. 2d) the ratio of products of photoreduction of PQ by HMB, namely phenolether and ketol becomes 1:1 and does not change further.



Scheme 4.

Photoreduction of PQ in the presence of durene proceeds similarly. The irradiation during 1 min of the reaction mixture

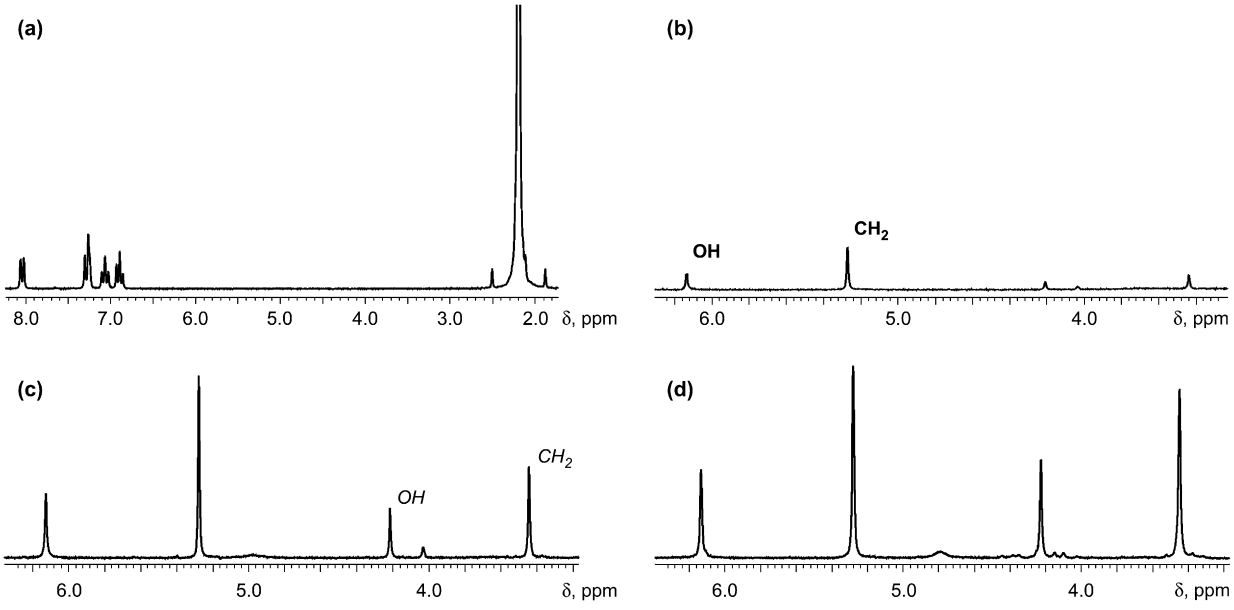
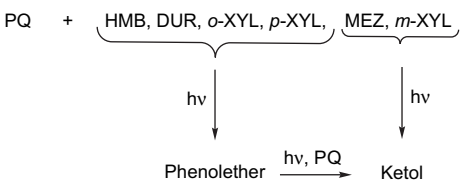


Figure 2. The changes in the ^{1}H NMR spectrum of a solution of 9,10-phenanthrenequinone (4×10^{-2} M) in the presence of hexamethylbenzene (2×10^{-1} M) before irradiation (a); 1 min of irradiation (b); 7 min of irradiation (c); 40 min of irradiation (d) (C_6D_6, irradiation by light λ>500 nm, T=298 K). (Labels: the protons of methylene group and hydroxyl group of phenolether are in bond; the protons of methylene group and hydroxyl group of ketol are in italic.)

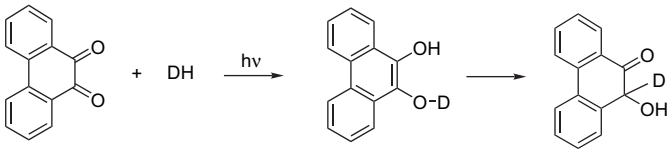
of PQ and DUR in C_6D_6 results only in the appearance in the ^{1}H NMR spectrum of signals attributed to phenolether (**1d**). Irradiation of the reaction mixture leads to the appearance and accumulation of signals attributed to ketol (**2f**). This, the phototransformation of phenolether **1d** to ketol occurs faster than **1c**. So, after total decolouration of reaction mixtures PQ–HMB and PQ–DUR, the ratios **1c**:**2e** and **1d**:**2f** become 1:1 and 1:3, respectively, and does not change further. Upon further diminution of the electron-donor properties of polymethylbenzene from $E_{1/2}$=1.46 V (HMB) and $E_{1/2}$=1.59 V (DUR) to $E_{1/2}$=1.85 V (mesitylene) the formation of corresponding phenolether was not observed. The ^{1}H NMR spectrum shows signals of the single product of the reaction - ketol (**2g**). Ketol **2g** was isolated and described.[12] The difference in stability of phenolethers can't be explained in the context of the earlier proposed mechanism for the conversion of phenolethers formed from *N*,*N*-dimethylanilines. The diminishing of electron-donor ability of polymethylbenzenes should cause increasing of stability of phenolether but not vice versa.

It should be mentioned that not only do the electron-donor properties of polymethylbenzenes in examined row (HMB, DUR, MES) decrease, but also the steric protection of ether bond of phenolether decreases. It is possible that the absence of a substituent in *ortho*-position of the methylene group of the phenolether somehow facilitates its rearrangement to ketol. Then, steric factors will be determinative in the photoreduction of PQ in the presence of xylenes with close values of $E_{1/2}$: in the case of *o*-xylene the ^{1}H NMR spectrum should show phenolether, while in the cases of *m*- and *p*-xylenes only the signals of corresponding ketols should be observed. In reality, the irradiation of PQ during 1 min in the presence of *o*-xylene leads to the appearance of superposition signals in ^{1}H NMR spectrum attributed to phenolether (**1e**) and ketol (**2h**) in the ratio 1:2. But irradiation of PQ and *m*-xylene (during 1 min) results only in ketol (**2i**). However, the presence of *p*-xylene (the irradiation during 1 min) produces not only ketol (**2j**) but also phenolether (**1f**) (ratio of **2j**:**1f** is 2:1). The obtained results are summarized in Scheme 5.

It was established here that the photoreduction of 9,10-phenanthrenequinone by HMB, DUR, *o*- and *p*-XYL affords the corresponding phenolethers as initial products. Unfortunately, the attempts to isolate the formed phenolethers were failed. The resulting phenolethers are involved in a secondary photoreaction with PQ to give the corresponding ketols. In the course of photoreaction of PQ with MES and *m*-XYL the existence of phenolethers is not registered. The ^{1}H NMR spectra contain only signals of the corresponding ketols. We suggest that photoreduction of 9,10-phenanthrenequinone in the presence of both polymethylbenzenes and tertiary amines occurs as a two-stage reaction (Scheme 6).



Scheme 5.



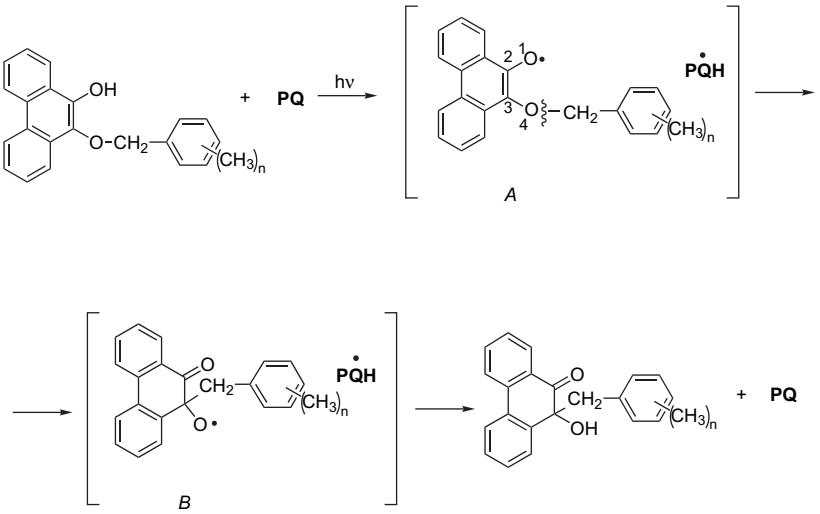
Scheme 6.

In the first stage a photoexcited molecule of PQ interacts with the H-donor resulting in the formation of a phenolether. In the second stage, under light and in the presence of the second molecule 9,10-phenanthrenequinone formed phenolether transforms into ketol. The weaker the electron-donor properties of the polymethylbenzene, the greater the probability of phototransformation of the phenolether into ketol. Apparently, mesitylene and *m*-xylene during initial photoreaction with PQ also form corresponding phenolethers. But due to the fast second stage, the formed phenolethers are rapidly converted into ketols.

Based on the aforementioned data, the following scheme of transformation of phenolether where PQ is 'phototransfer' of hydrogen can be suggested.

Photoexcited PQ molecule abstracts a proton from the hydroxyl or methylene group of the phenolether forming a radical pair consisting of protonated semiquinone radical PQ$^{\bullet}$H and radical *A* (Scheme 7). Radical *A* then transforms into radical *B* (Scheme 7). Interaction of *B* with radical PQ$^{\bullet}$H gives ketol and a molecule of initial PQ. The inner contradiction of suggested mechanism is the fact that relatively stable radical *A* spontaneously transforms into the certainly less stable radical *B*. A possible explanation is that transformation of the phenolether proceeds simultaneously with energy-favourable reaction of dehydrogenation of PQ$^{\bullet}$H with the formation of ketol; the whole process occurs in the cell of solvent. Consequently, the rate of reaction is determined by the probability of conversion of radical *A* and stability of radical *B*, respectively. Decreasing of the number of methyl groups in the benzyl fragment (in *A* and *B*) increases its acceptor property. The increasing of the electron-acceptor properties of the benzyl fragment, in turn enhances the stability of radical *B* and accelerates the photoreaction of phenolether with PQ. Analyzing the difference in behaviour of *m*- and *p*-xylenes, it is necessary to mention the following: according to values of Taft's constants,[26] fragment $CH_2C_6H_4CH_3$-*meta* appears to be a stronger acceptor than fragment $CH_2C_6H_4CH_3$-*para* (σ^*=0.20 and 0.17, respectively). Apparently, it is because of the less probability of a secondary reaction of phenolether which was formed from *p*-XYL, in comparison with phenolether formed from *m*-xylene, and, consequently, the possibility to observe phenolether which was formed upon photoreduction of PQ with *p*-XYL in reaction mixture.

Thus, on the basis of experimental and literature data it can be concluded that the mechanism of formation of products of photoreduction of 9,10-phenanthrenequinone and *o*-benzequinone is the same. The first stage of photoreaction results in the formation of a 1,4-addition product—phenolether. And only in a secondary reaction (photo- or dark reaction) is phenolether converted into the 1,2- addition product (ketol in the case of PQ). The range of products of photoreduction of *o*-quinones



Scheme 7.

is determined by the ratio of irradiation light and reaction in the absence or irradiation reactions and the nature of the reagents, namely, redox properties and structure of the reagents.

3. Experimental

3.1. Equipment

NMR spectra were recorded on a Bruker DPX-200 spectrometer.

3.2. Materials

9,10-Phenanthrenequinone (PQ) (Aldrich) was recrystallized from methanol. *p*-Cyano-*N*,*N*-dimethylaniline (Fluka) was doubly sublimed. *p*-*N*,*N*-Dimethylamino-benzaldehyde (Fluka) was recrystallized from hexane. *N*,*N*-Dimethylaniline (Aldrich) and *p*-methyl-*N*,*N*-dimethylaniline (Aldrich) were distilled under low pressure. Hexamethylbenxene (Aldrich), 1,2,4,5-tetramethylbenzene (durene) (Reachem), 1,3,5-trimethylbenzene (mesitylene) (Reachem), 1,2-dimethylbenzene (*o*-xylene) (Reachem), 1,3-dimethylbenzene (*m*-xylene) (Reachem), 1,4-dimethylbenzene (*p*-xylene) (Reachem) and benzene were purified using standard procedures.[27]

Photoreduction of PQ in the presence of H-donors was monitored by NMR spectrometry. Solutions (1 mL) of 9,10-phenanthrenequinone (4×10^{-2} M) and H-donors (4×10^{-2} M (*p*-substituted *N*,*N*-dimethylanilines); 4×10^{-1} M (polymethylbenzenes)) in C_6D_6 were degassed in an NMR tube, sealed and exposed at a distance of 7 cm from the focusing device. The reaction mixture was irradiated with a KGM-24-150 lamp as the light source. Radiation with $380<\lambda<430$ and $\lambda>500$ nm was separated from the luminous flux of the lamp using an SS-5 (for amines) and YGS-5 (for polymethylbenzenes) filters, respectively.

The apparent rate constants of rearrangement of phenolethers (**1a**) and (**1b**) were determined graphically from slope of the linear portion of the $\ln([I]_0/[I]_t)$ vs time curve (where $([I]_0$ and $[I]_t$ are the initial (calculated from the first spectrum) intensities of the typical signals of phenolethers after irradiation and at instant t, respectively; t is dark reaction time). The reaction mixture irradiation times were varied taking efficiency of reaction pair photoreduction into account. First ^{1}H NMR spectra were registered 90–120 s after irradiation. Further ^{1}H NMR spectra were registered after specified time periodically. In both cases the rates of rearrangement of phenolethers **1a** and **1b** occurred according to first order. The presented data are the average of results based on calculations performed on at least three kinetic curves obtained from the same system. The telemetry error lies within the 15–20% range.

The products of photoreduction of PQ in the presence H-donors—phenolethers (**1**) and ketols (**2**) were monitored only by NMR (excluding ketol (**2g**)). Signals for aromatic protons are not presented because they overlap with signals of the starting compounds. Table 2 shows the chemical shifts of typical signals of phenolethers and ketols.

Acknowledgements

This study was financially supported by the Council on Grants of President of the Russian Federation (Program for State Support of Leading Scientific Schools of the Russian Federation, Grant NSh-4947.2006.3) and the Russian Foundation for Basic Research (Project nos 05-03-32706, 06-03-33061-a, 06-03-08186-ofi).

References and notes

1. Pierpont, C. G.; Buhaman, R. M. *J. Am. Chem. Soc.* **1975**, *97*, 4912–4917.
2. Razuvaev, G. A., Abakumov, G. A., Cherkacov, V. K., Muraev, V. A., Tichonov, V. D., Chesnokov S. A. **1985**, certificate no. 228673-01.11.1985.
3. Razuvaev, G. A., Abakumov, G. A., Cherkacov, V. K., Muraev, V. A., Tichonov, V. D., Chesnokov S. A. **1982**, certificate no. 943630-16.03.1982.-G 03 C1/733.
4. Merrill, R., Krreger, T. Fr. Demande 2,330,033, 1977.

5. Barltrop, J. A.; Coyle, J. D. *Excited States in Organic Chemistry*; John Wiley and Sons: London–New York–Sydney–Toronto, 1975.
6. Shigorin, D. N.; Ozerova, G. A.; Voznyak, V. M. *Zh. Fiz. Khim.* **1967**, *41*, 1238–1246 [*J. Phys. Chem. USSR* **1967**, *41* (Engl. Transl.)].
7. Kubogama, A.; Yaba, S. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2475–2479.
8. Wong, H. C.; Aruold, D. R. *Can. J. Chem.* **1979**, *57*, 1037–1048.
9. Calvert, J. G., Pitts, J. N. *Photochemistry*. New York–London–Sydney, 1968; p 671.
10. Carapllucci, P. A.; Wolf, H. P.; Weiss, K. *J. Am. Chem. Soc.* **1969**, *91*, 4635–4639.
11. El'zov, A. V.; Studzin'skii, O. P.; Greben'kina, V. M. *Usp. Khim.* **1977**, *46*, 185–227.
12. Shurygina, M. P.; Chesnokov, S. A.; Lopatin, M. A.; Cherkasov, V. K.; Abakumov, G. A. *Izv. Akad. Nauk, Ser. Khim.* **2004**, *11*, 2381–2385 [*Russ. Chem. Bull., Int. Ed.* **2004**, *53* (Engl. Transl.)].
13. *Einfuhrung in die photochemie*; Bekker, G. O., Ed.; VEB Deutscher sder Wissenschaften: Berlin, 1976; Von einem autorenkollektiv.
14. Maruyama, K.; Shindo, H.; Maruyama, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 585.
15. Maruyama, K.; Shindo, H.; Otsuki, T.; Maruyama, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2756–2760.
16. Shindo, H.; Maruyama, K.; Otsuki, T.; Maruyama, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2789–2794.
17. Shonberg, A. *Preparative Organische Photochemie*; Springer: Berlin–Gottingen–Heidelberg, 1958.
18. Patai, Saul *The Chemistry of the Quinonoid Compounds*; John Wiley and Sons: London–New York–Sydney–Toronto, 1974; p 616.
19. Maruyama, K.; Ono, K.; Osugi, J. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 3357–3359.
20. Maruyama, K.; Otsuki, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2885.
21. Maruyama, K.; Ono, K.; Osugi, J. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 847–851.
22. Maruyama, K.; Otsuki, T.; Shindo, H.; Maruyama, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2000.
23. Fukuzumi, S.; Itoh, S.; Komori, T.; Suenobu, T.; Ishida, A.; Fujitsuka, M.; Ito, O. *J. Am. Chem. Soc.* **2000**, *122*, 8435–8443.
24. Mann, Ch. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, NY, 1970.
25. Shurygina, M. P.; Kurskii, Yu. A.; Chesnokov, S. A.; Drujkov, N. O.; Fukin, G. K.; Abakumov, G. A.; Cherkasov, V. K. *Izv. Akad. Nauk, Ser. Khim.* **2006**, *9*, 1528–1535 [*Russ. Chem. Bull., Int. Ed.* **2006**, *55* (Engl. Transl.)].
26. Vereschagin, A. N. *Inductive Effect. Constants of Substituent for Correlation Analysis*; Nauka: Moscow, 1988.
27. Gordon, J.; Ford, R. A. *The Chemist's Companion*; A Wiley-Interscience Publication, John Wiley and Sons: New York–London–Sydney–Toronto, 1972.