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Photoreduction of *o*-benzoquinones in the presence of *p*-bromo-*N*,*N*-dimethylaniline*

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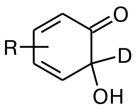
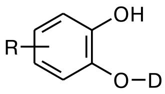
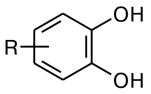
Photoreduction of *o*-benzoquinones in the presence of *p*-bromo-*N*,*N*-dimethylaniline under irradiation ($\lambda > 500$ nm) affords the corresponding pyrocatechols and hydroxyphenyl ethers. The latter are unstable and, in turn, decompose in the dark reaction to pyrocatechols. The ratio between pyrocatechol and hydroxyphenyl ether formed upon the photoreaction is determined by the structure of *o*-quinone, namely, the presence and bulk of substituents in positions 3 and 6 of the ring. The yield of pyrocatechol is maximal (60—65%) if the substituents are the same (H and H, Bu^t and Bu^t) or insignificantly differ (Pr^i and Bu^t), regardless of its bulk.

Key words: *o*-benzoquinone, symmetry, *p*-bromo-*N*,*N*-dimethylaniline, photoreduction, radical pair.

o-Quinones (A) efficiently enter into the photoreduction reaction in the presence of appropriate H-donating compounds (DH).[1,2] The process includes the formation of triplet radical pairs (RP) $^3[AH^\bullet, D^\bullet]$, whose transformation affords addition products at one (**I**) or both carbonyl groups (**II**) or pyrocatechol (**III**).[3,4]


I


II


III

The study of photoreduction of 9,10-phenanthrenequinone (PQ)[3,5] and 1,2-naphthoquinone[4] shows that the predominant formation of one or another product is determined by the nature of the donor DH. For example, in the presence of alkenes[1] or alkylarenes,[6] PQ is reduced under irradiation to the corresponding ketols **I**. Photoreduction in the presence of ethers (dialkyl[4] or alkyl aryl[3]) and aldehydes[2] proceeds *via* the mechanism of α-hydrogen elimination to give hydroxyphenyl ether **II**. Pyrocatechol, which was isolated as quinhydrone,[2,4] was also identified among the reaction products. The photoreduction of camphorquinone (1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-dione) in the presence of xylenes and lower alcohols affords ketols **I**,[7] and the corresponding pyrocatechol[8] **III** is the main product in the presence of tertiary amines.

The photoreduction of *o*-benzoquinones (Q) is studied to a lesser extent. It is known that these compounds are reduced under irradiation with visible and UV light in the presence of such H-donors as tertiary amines (AmH_2) to form intermediate radical products.[9] It is established that, unlike the quinones listed above, the direction of photoreduction of Q is determined by the structure of quinone itself.[10] As shown for two *o*-benzoquinones, hydroxyphenyl ether **II** or pyrocatechol **III** are the final reaction products, depending on the molecular structure of quinone. Perhaps, for different quinones, the $^3[QH^\bullet, AmH^\bullet]$ radical pairs either decompose with exit of free radicals from the solvent cage (disproportionation of the $QH^\bullet$ semiquinone radicals should form pyrocatechol), or undergo recombination to form hydroxyphenyl ethers **II**.

The progress in the synthesis of new *o*-benzoquinones[11] made it possible to perform more detailed studies of the influence of the molecular geometry of quinones on the direction of photoreduction. The present work is devoted to the solution of this problem.

Experimental

NMR spectra were recorded on a Bruker DPX-200 spectrometer. IR spectra were obtained on a Specord M 80 spectrophotometer.

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A KGM-24-150 lamp with a focusing device was used as the light source. Radiation with λ ≥ 500 nm was separated from the luminous flux of the lamp using the light filter. Solutions of *o*-quinone and *p*-bromo-*N*,*N*-dimethylaniline in a ratio of 1 : 5 in C_6D_6 were deaerated, saturated with Ar, placed in an NMR tube, and exposed at a distance of 15 cm from the focusing device for 3—5 min, selecting irradiation conditions in such a way that the conversion of quinone would be ~50%.

Solvents (benzene, hexane) were purified using standard procedures.[12] *o*-Benzoquinones **1a**—**e** and corresponding pyrocatechols were synthesized using previously described procedures.[11] *p*-Bromo-*N*,*N*-dimethylaniline (**2**) (Aldrich) was recrystallized from aqueous MeOH.

3,6-Di-*tert*-butylpyrocatechol. ^{1}H NMR (C_6D_6), δ: 1.36 (s, 18 H, Bu^t); 4.78 (s, 2 H, OH); 6.82 (s, 2 H, C(4)H, C(5)H).

6-*tert*-Butyl-3-isopropylpyrocatechol. ^{1}H NMR (C_6D_6), δ: 1.04 (d, 6 H, Me_2CH, J = 6.8 Hz); 1.49 (s, 9 H, Bu^t); 2.51 (sept, 1 H, $CHMe_2$, J = 6.8 Hz); 3.90 and 5.48 (both s, 1 H each, OH); 6.64 and 6.78 (both d, 1 H each, C(4)H, C(6)H, J = 8.3 Hz).

6-*tert*-Butyl-3-methylpyrocatechol. ^{1}H NMR (C_6D_6), δ: 1.50 (s, 9 H, Bu^t); 1.61 (s, 3 H, Me); 2.10 (s, 2 H, OH).

3,5-Di-*tert*-butylpyrocatechol. ^{1}H NMR (C_6D_6), δ: 1.27 and 1.55 (both s, 9 H each, Bu^t); 3.61 and 5.42 (both s, 1 H each, OH); 6.23 (d, 1 H, C(6)H, J = 2.3 Hz); 7.07 (d, 1 H, C(4)H, J = 2.3 Hz).

4,5-Dimethoxypyrocatechol. ^{1}H NMR (C_6D_6), δ: 3.39 (s, 6 H, MeO); 4.57 (s, 2 H, OH).

2-(*N*-*p*-Bromophenyl-*N*-methylamino)methoxy-4,6-di-*tert*-butylphenol (3d). 3,5-Di-*tert*-butyl-1,2-benzoquinone (**1d**) (0.44 g) and *p*-bromo-*N*,*N*-dimethylaniline (**2**) (2 g) were dissolved in benzene (20 mL). A glass cylindrical tube 30 mm in diameter filled with the solution was irradiated using the ZhS-17 light filter for 3 h at a distance of 18 cm from the focusing device, and the solvent was removed *in vacuo*. The residue was washed with hot hexane, and compound **3d** was isolated from the hexane solution as white crystals with m.p. 122—124 °C. Found (%): C, 62.8; H, 7.1; Br, 19.1. $C_{22}H_{30}NO_2Br$. Calculated (%): C, 63,41; H, 7.31; Br, 19.00. IR (KBr), ν/cm^{-1}: 810 (H(3), H(5)); 855, 875 (H(2´), H(3´), H(5´), H(6´)); 1300 (CO_{aryl}); 3490 (OH). ^{1}H NMR (C_6D_6), δ: 1.32 (s, 9 H, Bu^t); 1.57 (s, 9 H, Bu^t); 2.37 (s, 3 H, MeN); 4.67 (s, 2 H, OCH_2N); 5.85 (s, 1 H, OH); 6.27—6.35 (m, 2 H, C(2´)H, C(6´)H); 6.69 (d, 1 H, C(6)H, J = 2.1 Hz); 7.15—7.26 (m, 3 H, C(3´)H, C(5´)H, C(4)H)).

The products of photoreduction of 3,6-di-*tert*-butyl- (**1a**), 3-*tert*-butyl-6-isopropyl- (**1b**), 3-*tert*-butyl-6-methyl- (**1c**), and 4,5-dimethoxybenzoquinone-1,2 (**1e**) in the presence of *p*-bromo-*N*,*N*-dimethylaniline (**2**) were qualitatively and quantitatively analyzed and the reaction course was monitored by the NMR method.

We failed to isolate compounds **3a**—**c**,**e** because of their instability. The NMR data for these compounds in the reaction mixture are presented below.*

2-(*N*-*p*-Bromophenyl-*N*-methylamino)methoxy-3,6-di-*tert*-butylphenol (3a). ^{1}H NMR (C_6D_6), δ: 1.39 (s, 9 H, Bu^t); 1.53 (s, 9 H, Bu^t); 2.33 (s, 3 H, MeN); 4.47 (s, 2 H, OCH_2N).

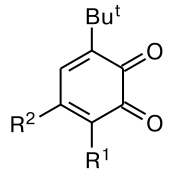
2-(*N*-*p*-Bromophenyl-*N*-methylamino)methoxy-6-*tert*-butyl-3-isopropylphenol (3b). ^{1}H NMR (C_6D_6), δ: 1.34 (d, 6 H, Pr^i, J = 6.8 Hz); 1.42 (s, 9 H, Bu^t); 4.57 (s, 2 H, OCH_2N).

2-(*N*-*p*-Bromophenyl-*N*-methylamino)methoxy-6-*tert*-butyl-3-methylphenol (3c). ^{1}H NMR (C_6D_6), δ: 1.47 (s, 9 H, Bu^t); 2.07 (s, 3 H, Me); 2.33 (s, 3 H, MeN); 4.57 (s, 2 H, OCH_2N).

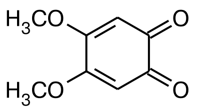
2-(*N*-*p*-Bromophenyl-*N*-methylamino)methoxy-4,5-dimethoxyphenol (3e). ^{1}H NMR (C_6D_6), δ: 2.38 (s, 3 H, MeN); 3.30 (s, 3 H, MeO); 3.47 (s, 3 H, MeO); 4.64 (s, 2 H, OCH_2N).

Results and Discussion

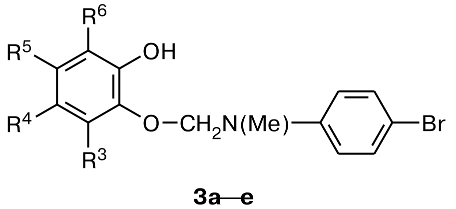
Colored organic solutions of mixtures of *o*-benzoquinones **1a**—**e** with *p*-bromo-*N*,*N*-dimethylaniline (**2**) become colorless upon irradiation with visible light. A change in the spectral characteristics of the solutions is related to the transformation of *o*-benzoquinone into pyrocatechol and its derivatives, which is confirmed by the NMR data. For example, the ^{1}H NMR spectrum of the initial solution of **1d** and **2** (1 : 5) in C_6D_6 contains high-field signals. They are assigned to protons of the methyl groups in compound **2** (δ = 2.31) and nonequivalent *tert*-butyl groups in compound **1d** (δ = 1.13 and 0.74). The irradiation (λ ≥ 500 nm) of the solution results in a decrease in the intensities of signals for the protons of the *tert*-butyl groups in **1d** and the appearance of new signals attributed to protons of the *tert*-butyl groups in 3,5-di-*tert*-butylpyrocatechol (δ = 1.29 and 1.55) and protons of two *tert*-butyl groups, methyl group, and methylene group of hydroxyphenyl ether 2-(*N*-*p*-bromophenyl-*N*-methylamino)methoxy-4,6-di-*tert*-butylphenol (**3d**) (δ = 1.32, 1.57, 2.38, and 4.68, respectively) (Fig. 1). Compound **3d**



1a—d



1e



3a—e

Compound	R	a	b	c	d	e
1	R^1	Bu^t	Pr^i	Me	H	H
	R^2	H	H	H	Bu^t	OMe
3	R^3	Bu^t	Pr^i	Me	H	H
	R^4	H	H	H	Bu^t	MeO
	R^5	H	H	H	H	MeO
	R^6	Bu^t	Bu^t	Bu^t	Bu^t	H

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* Signals for aromatic protons are not presented because they overlap with signals of the starting compounds.

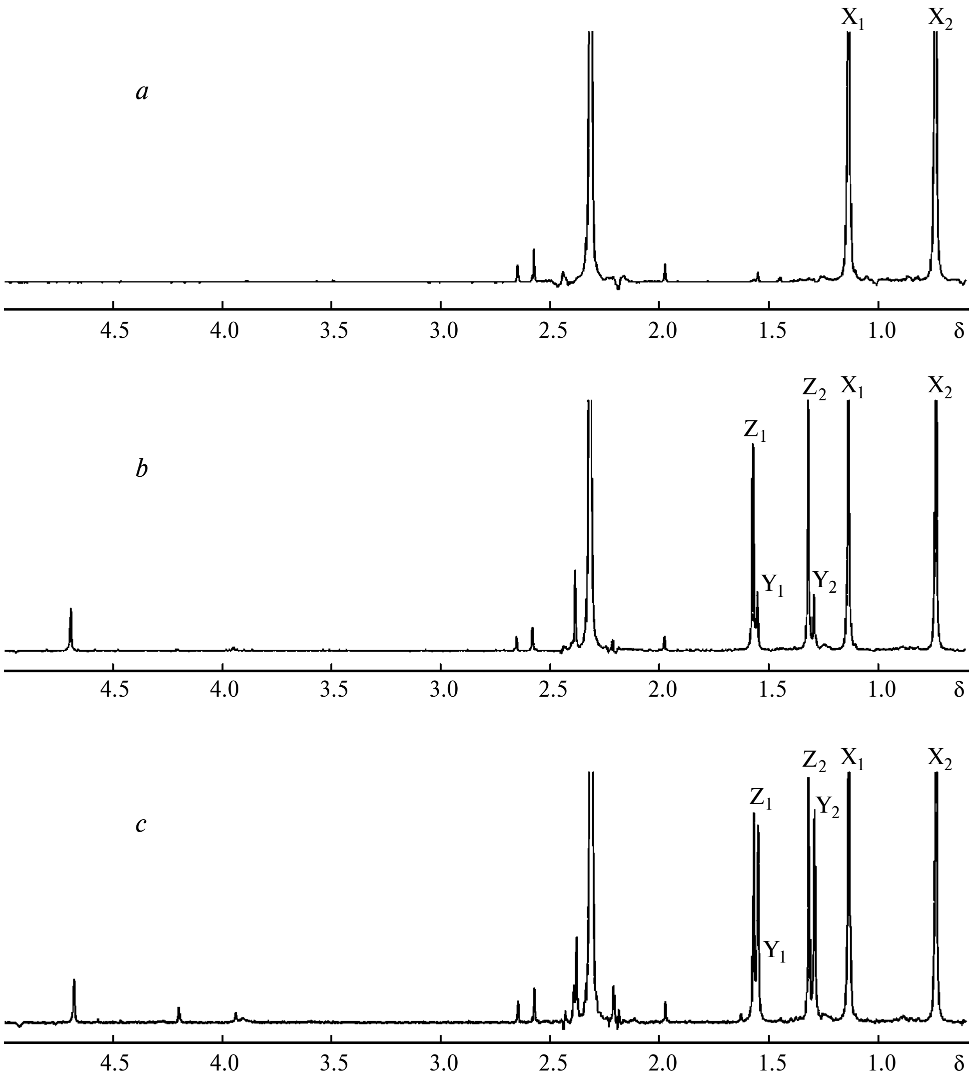


Fig. 1. NMR spectra of a solution of 3,5-di-*tert*-butyl-1,2-benzoquinone (**1d**) and *p*-bromo-*N,N*-dimethylaniline (**2**) (1 : 5) in C_6D_6 before irradiation (*a*), immediately after irradiation (*b*), and 60 min after irradiation (*c*). The signals for protons of the *tert*-butyl groups of quinone (X_1 and X_2), pyrocatechol (Y_1 and Y_2), and hydroxyphenyl ether (Z_1 and Z_2) are denoted.

is unstable and decomposes in air to pyrocatechol (the product formed from the nitrogen-containing moiety of **3d** was not identified). In a solution, the rate of transformation of **3d** into pyrocatechol is much higher. The ratio of content of ether **3d** and pyrocatechol in the reaction mixture immediately after irradiation and after 60-min storage in the dark changes from 3.5 : 1 to 1 : 1.

The results of irradiation of solutions of other *o*-benzoquinones in the presence of **2** are analogous: the NMR spectra exhibit a superposition of signals of the corresponding pyrocatechols and hydroxyphenyl ethers. Then the intensity of signals for protons of ethers decreases, and that for protons of pyrocatechols increases. The kinetics of disappearance of hydroxyphenyl ethers suggests that the rate of transformation of **3d** is by approximately an order of magnitude lower than that of other compounds of this type. Therefore, an attempt to synthesize hydroxyphenyl ethers **3a—c** and **3e** in preparative amounts was unsuccessful, and their formation was detected only *in situ* by the NMR method. The low stability of hydroxyphenyl ethers explains the fact that no formation of compound **3a** has been found previously[10] when studying the products of photoreduction of quinone **1a**.

The transformation products of aniline **2** were studied in its reaction with **1a**. The reaction was carried out at the 1 : 1 ratio of the reactants in benzene in an argon atmosphere under irradiation with λ > 500 nm. The solution was irradiated until discoloration, after which benzene was removed, and the residue was recrystallized from hexane, dissolved in $CDCl_3$, and analyzed by NMR. The ^1H, ^{13}C, and DEPT NMR spectra showed that the mixture contained compounds bearing four different methyl groups

(δ_H = 2.81, 2.85, 3.01, and 3.04; δ_C = 30.7, 36.4, 38.6, and 39.0), three methylene groups (δ_H = 4.71, 4.78, and 4.95; δ_C = 57.6, 70.1, and 81.0), and aromatic fragments (δ_H = 6.4, 6.7, and 7.3; δ_C in regions of 110, 115, 131.5, and 148, groups of four signals each). The presence of cross-peaks of δ_H signals 2.85/4.71, 3.01/4.78, and 3.04/4.95 in the COSY spectra implies that the corresponding pairs of methyl and methylene groups exist in the same molecule. All groups listed above have cross-peaks with protons in the aromatic region. Based on the chemical shifts, integral intensities, and correlation experiments, one can suppose that a mixture of four products is formed, of which three products contain the —(Me)NCH$_2$— fragment and one product contains the —NH—Me fragment. The chemical shift of the methylene groups indicates that they are situated near an electron acceptor (for example, nitrogen or oxygen atoms). Presumably, these are the following compounds: *p*-BrC$_6$H$_4$NHMe, whose formation is deduced from the presence of the methyl group (δ_H = 2.81, δ_C = 30.1) bound to none of the methylene groups; *p*-BrC$_6$H$_4$N(Me)CH$_2$N(Me)(*p*-BrC$_6$H$_4$), whose formation is evidenced by two methyl groups (δ_H = 2.85, δ_C = 36.5) per methylene group (δ_H = 4.71, δ_C = 70.1) and signals for the aromatic carbon atoms δ_C 110.0 (CBr), 115.2 (CH), 131.8 (CH), and 147.9 (CN), their chemical shifts being in good accordance with those expected for such a structure. Similarly, based on the chemical shifts of the methylene groups of other products in the ^{1}H and ^{13}C NMR spectra, the formation of compounds containing the ArN(Me)CH$_2$Br fragments and amine oxidation products including the ArN(Me)CH$_2$O fragments can be assumed.

A half of quinone **1a** is photoreduced when **1a** reacts with **2** in a molar ratio of 2 : 1. This means that pyrocatechol (as well as hydroxyphenyl ether) is formed in the reaction of quinone and amine in a ratio of 1 : 1. In other words, in the formation of pyrocatechol one amine molecule formally donates two hydrogen atoms for the reduction of one molecule of quinone **1a**. Benzophenone and fluorenone are similarly photoreduced in the presence of amines.[13] These processes are described by the scheme in which the first molecule of a carbonyl-containing compound is reduced owing to the dehydrogenation of the amine molecule to the AmH$^{\bullet}$ radical, and the second molecule is reduced due to hydrogen elimination from AmH$^{\bullet}$. The formation of pyrocatechol from *o*-benzoquinones is described by the Scheme 1.

Scheme 1

$$\mathrm{Q + AmH_2 \longrightarrow QH^{\bullet} + AmH^{\bullet}}$$

$$\mathrm{Q + AmH^{\bullet} \longrightarrow QH^{\bullet} + Am}$$

$$\mathrm{2\,QH^{\bullet} \longrightarrow Q + QH_2}$$

$$\overline{\mathrm{Q + AmH_2 \longrightarrow QH_2 + Am}}$$

Analysis of the NMR spectra of the photoreduction products of quinones **1a—e** shows that the ratios of hydroxyphenyl ethers to pyrocatechols are determined by the nature of *o*-benzoquinone. Below we present the yields (*P*) of pyrocatechols upon the photoreduction of quinones **1a—e** after 3-min irradiation, which corresponds to ~50% conversion.

Starting *o*-benzoquinone	**1a**	**1b**	**1c**	**1d**	**1e**
P (%)*	60	65	25	20	60

* *P* is the yield of the corresponding pyrocatechol.

A comparison of the yields of pyrocatechols upon photoreduction of quinones **1a** and **1d** shows that the *P* value changes threefold, although the only difference between these quinones is the position of one Bu^t group in the quinonoid ring. The yield of pyrocatechol upon the photoreduction of quinone **1c** almost coincides with that for quinone **1d**. The main photoreduction products of quinones **1b** and **1c**, as well as of **1a**, are the corresponding pyrocatechols.

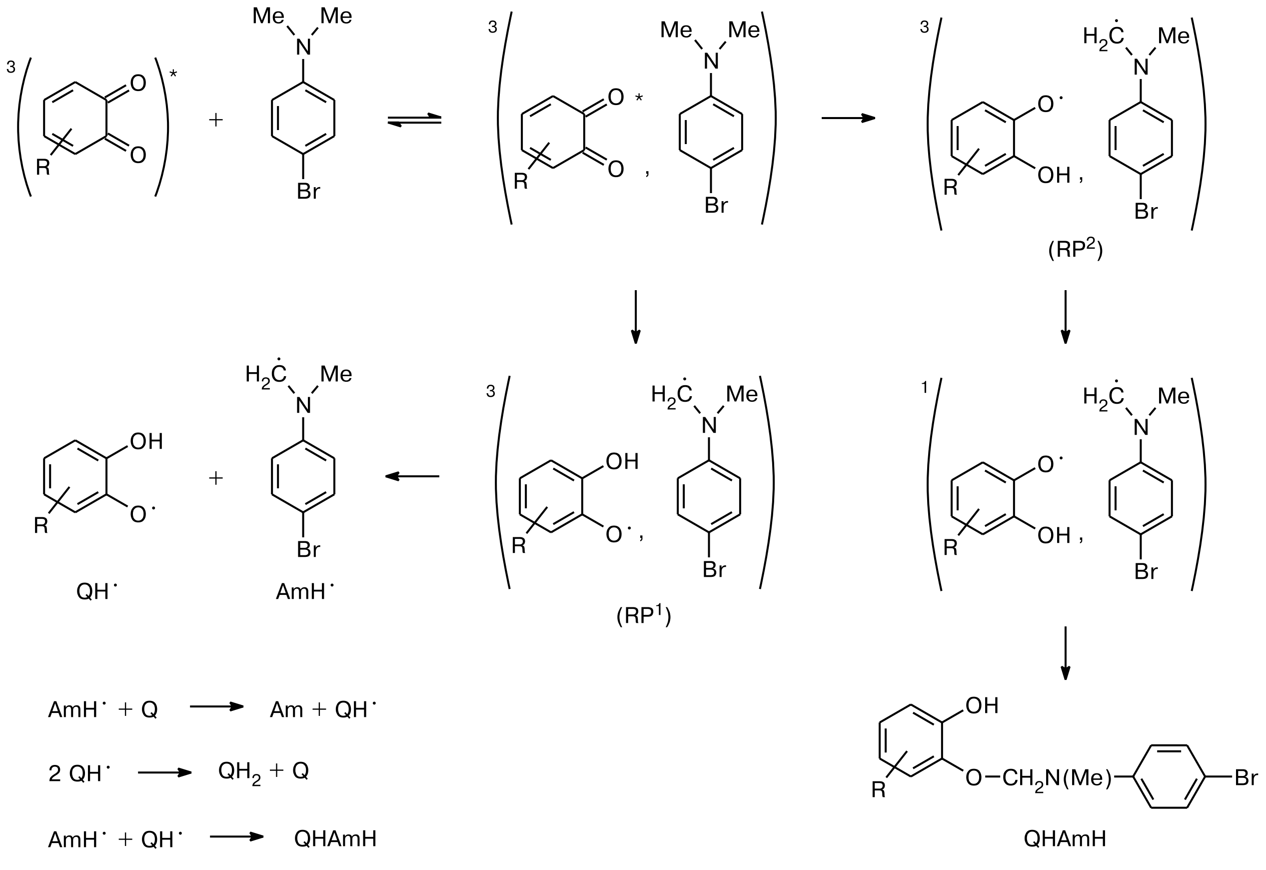
As in the case of other carbonyl-containing compounds,[13] the process of photoreduction of *o*-benzoquinones is the interaction of the *o*-benzoquinone molecule excited to the lowest $n\pi^*$-triplet state with the amine molecule[9] to form the triplet exciplex ("collision complex" [14]) ^{3}(Q*, AmH$_2$), which is transformed into the triplet radical pair ^{3}(QH$^{\bullet}$, AmH$^{\bullet}$) after the transfer of hydrogen atom. It is known that the main products of benzophenone photoreduction are the corresponding pinacones,[13] which are the recombination products of ketyl radicals formed, in turn, upon the decomposition of the triplet RP. At the same time, PQ photoreduction in the presence of aryl-containing hydrogen donors mainly affords the products of geminal recombination of the radicals, *viz.*, ketols or hydroxyphenyl ethers.[3,15] This indicates that, in the case of PQ, the triplet RP is transformed into the singlet RP with a high probability followed by radical recombination. *o*-Benzoquinones studied in this work afford products of both disproportionation of two semiquinone radicals (pyrocatechol) and recombination of the QH$^{\bullet}$ and AmH$^{\bullet}$ radicals (hydroxyphenyl ether), and the ratio between the products is determined by the quinone structure. We believe that the triplet RP formed upon the photoreduction of *o*-benzoquinones: both decomposes to radicals with formation of pyrocatechol and amine dehydrogenation products and transforms into the singlet RP followed by radical recombination to hydroxyphenyl ether. The predominant direction of triplet RP transformation is determined by the quinone structure.

To explain the observed effects, let us consider changes that can occur in the ^{3}(QH$^\bullet$, AmH$^\bullet$) radical pair when varying substituents in the QH$^\bullet$ radicals. It follows from the equality of the P values for pyrocatechols obtained upon reduction of quinones **1a** and **1e** that shielding of the radical center in QH$^\bullet$ does not determine the direction of transformation of the triplet RP. It is known that hydrogen is transferred to the quinone molecule and the RP forms when quinones **1a** and **1d** are photoreduced in the presence of hydrogen donors (sterically hindered phenols,[16] pyrocatechol **1a**,[17] and diphenylamine[18]) in glassy solutions. The RP structure and the distance between the radical centers are also determined by the nature of *o*-benzoquinone. For example, irradiation of **1a** in the presence of 2,4,6-tri-*tert*-butylphenol[16] and diphenylamine[18] results in the formation of the RP with the distance between unpaired electrons $<r> \sim 6.3$ Å. When **1d** is irradiated in the presence of diphenylamine,[18] two types of an RP are formed: with $<r>$ ~5.3 and 6.3 Å; those with the lower $<r>$ value are mainly formed. Although the RP states in a solution and solid matrix are not identical in the general case, it can be assumed that the photoreduction of **1a**—**e** in the presence of **2** in a solution also affords two types of a triplet RP with different geometries and distances between the radical centers. Triplet RPs of the first type (RP^1) (with a higher $<r>$ value) decompose to component radicals, one of the transformation products being pyrocatechol. Triplet RPs of the second type (RP^2) (with lower $<r>$) undergo the $T \to S$ transition followed by the rapid recombination of the radicals with the singlet RP to form hydroxyphenyl ether (Scheme 2). According to the assumed mechanism, the quantitative ratio between both types of an RP is determined by the symmetry of the initial *o*-benzoquinone. The lower the difference in bulks of the substituents in positions 3 and 6 the greater the fraction of the RPs of the first type and, correspondingly, the higher the content of pyrocatechol in the reaction products.

The influence of the symmetry of the *o*-benzoquinone molecule on the RP geometry can be formulated as follows. In the semiquinone radical formed upon the transfer of a hydrogen atom, the H atom migrates from one oxygen atom to another with a frequency of ~10^9 s^{-1},[19] *i.e.*, the semiquinone molecule exists in two isomeric forms (Scheme 3).

For symmetrical semiquinones (derivatives of **1a** and **1e**), these isomers are degenerate in energy, and the probability that the H atom is situated near each O atom

Scheme 2

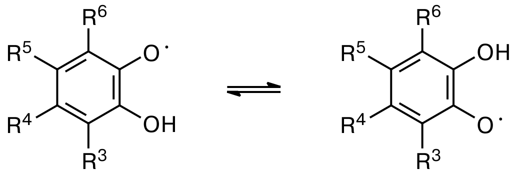


$$\mathrm{AmH^{\cdot} + Q \longrightarrow Am + QH^{\cdot}}$$

$$\mathrm{2\,QH^{\cdot} \longrightarrow QH_2 + Q}$$

$$\mathrm{AmH^{\cdot} + QH^{\cdot} \longrightarrow QHAmH}$$

Scheme 3



is the same. Therefore, the AmH$^•$ radical located near such a radical in the RP has not any predominant orientation with respect to one of the carbonyl groups of the semiquinone molecule. This should increase the distance between the radical centers in the RP, weaken the interaction between the radicals, and increase the probability of RP decomposition. In nonsymmetrical semiquinones, the degeneration in energy of the isomers is eliminated. One of the isomers is more stable than another, and the probabilities that the hydrogen atom is situated near one or another oxygen atom are different.[20] Therefore, the AmH$^•$ radical in the RP will take a certain orientation with respect to the semiquinone radical QH$^•$. The approach of the radical centers in the RP increases the probability of radical recombination for transitions from the triplet to singlet state of the RP. The higher reactivity of semiquinones of nonsymmetrical quinones is confirmed by the fact that the rate constant for disproportionation of semiquinone of nonsymmetrical quinone **1d** is threefold higher than the similar constant for symmetrical quinone **1a**.[21]

Thus, *o*-benzoquinones are photoreduced in the presence of *p*-bromo-*N*,*N*-dimethylaniline to the corresponding pyrocatechols and hydroxyphenyl ethers. The quantitative ratio between them is determined by the difference in bulks of the substituents in positions 3 and 6 of the quinonoid ring: the lower the ratio the higher the content of pyrocatechol. According to the proposed mechanism of the reaction, the phototransfer of a hydrogen atom results in the formation of triplet RPs, which can transform by two variants: decomposition to radicals (pyrocatechol is the final product of *o*-quinone photoreduction) or recombination of radicals after the triplet-singlet transitions of the RP to form hydroxyphenyl ether. The quantitative ratio between these directions of the reaction is determined, most likely, by the difference in energies of two isomeric forms of the semiquinone radical. This is manifested as a difference in bulks of the substituents in positions 3 and 6 of the ring. If, regardless of the bulk, the substituents are the same or the difference between them is small (for example, *tert*-butyl and isopropyl groups), then the RP mainly decomposes to radicals composing this RP. If the difference in volumes of the substituents is great (for example, the *tert*-butyl and methyl groups or the *tert*-butyl group and hydrogen atom), then the radicals mainly recombine in the $T \rightarrow S$ transitions of the RPs.

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