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Products and Mechanisms of Photochemical Transformations of *o*-Quinones

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Abstract—The photochemical transformations of quinones by the action of light at $\lambda > 500$ nm, namely, the photodecarbonylation and photoreduction reactions were studied with the use of a series of *o*-benzoquinones and 9,10-phenanthrenequinone as examples. The two-stage mechanism of the decarbonylation reaction of *o*-benzoquinones was established. At the first stage, rearrangement of a photoexcited quinone molecule into a bicyclic compound that spontaneously decomposes in the dark reaction into cyclopentadienone and CO takes place. It has been found that the formation of the photoreduction products of both *o*-benzoquinones and 9,10-phenanthrenequinone in the presence of various H donors (*N,N*-dimethylanilines and polymethylbenzenes) follows the same mechanism. In the first step, a phenol ether is produced, which subsequently undergoes quantitative transformation into pyrocatechol or ketol via the heterolytic mechanism. The stability of phenol ethers is determined by the structure and redox properties of the reactants.

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Under the action of light, quinones experience numerous transformations involved in important processes, such as photosynthesis of green plants and photodegradation of vat dyes [1]. Photoreactions of *o*-quinones form the basis for many systems used to initiate radical photopolymerization [2, 3]. *o*-Quinones exhibit absorption bands in the range of 400 to 650 nm and can act as photosensitizers [4] or can undergo various transformations; namely, they are capable of degradation with elimination of CO [5] or entering into the photoreduction reaction with various hydrogen donors [3, 5, 6]. The Razuvaev Institute of Organometallic Chemistry possesses a unique collection of sterically hindered *o*-benzoquinones, which allowed us to perform a systematic study of the products and mechanisms of photochemical transformations of *o*-quinones, namely, the photodecarbonylation and photoreduction reactions.

PHOTODECARBONYLATION REACTION OF *o*-BENZOQUINONES

The studies devoted to the photolysis of quinones have been basically limited to investigation into the kinetics or products produced by the action of UV radiation only [7–12]. It is known that 3,6- [7, 8] and 3,5-di-*tert*-butyl derivatives [9] of *o*-benzoquinone are decomposed by UV irradiation ($\lambda < 405$ nm) into cyclopentadienones, ejecting CO. This reaction can be considered a method for the synthesis of cyclopentadienones, which are used as ligands for organometallic compounds.

In our works, the photolysis of benzene solutions of a series of sterically hindered *o*-benzoquinones (1a–1f) (Scheme 1) with light of $\lambda > 520$ nm was studied [10]. The NMR study of the photoreaction of *o*-benzoquinones revealed the existence of an intermediate compound (2) containing three- and five-membered cycles. The intermediate quantitatively degrades already at room temperature to the single final product (main product for 1d), the corresponding 3,4-disubstituted 2,5-di-*tert*-butylcyclopentadienone (3) (Scheme 1). All cyclopentadienones 3a–3g were isolated and were characterized by instrumental techniques.

X = H(**a**); F (**b**); Cl (**c**); OCH₃ (**d**);
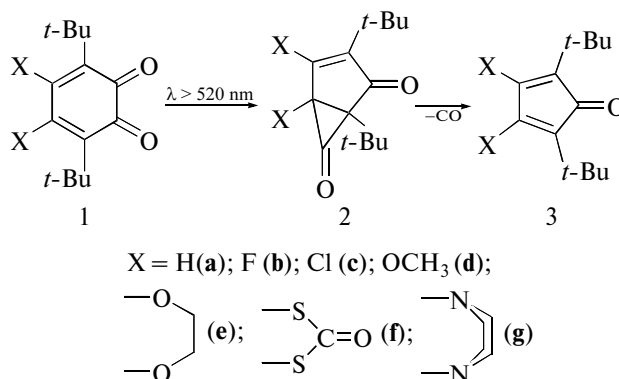
Scheme 1.

Thus, the photodecarbonylation reaction of *o*-benzoquinones is a two-step process. In the first step, the rearrangement of the cyclohexadienone ring of a photoexcited *o*-benzoquinone molecule into the corre-

sponding bicyclic compound takes place. The second stage comprises the elimination of CO from the cyclopropane moiety and the formation of the final product cyclopentadienone with a yield close to quantitative.

PHOTOREDUCTION REACTION OF QUINONES

The photoreduction reaction of carbonyl compounds consists in the abstraction of a hydrogen atom from an H-donor molecule by a photoexcited acceptor molecule to give radicals, which yield various products via their subsequent transformations [11]. It has been found that the formation of one or another pre-
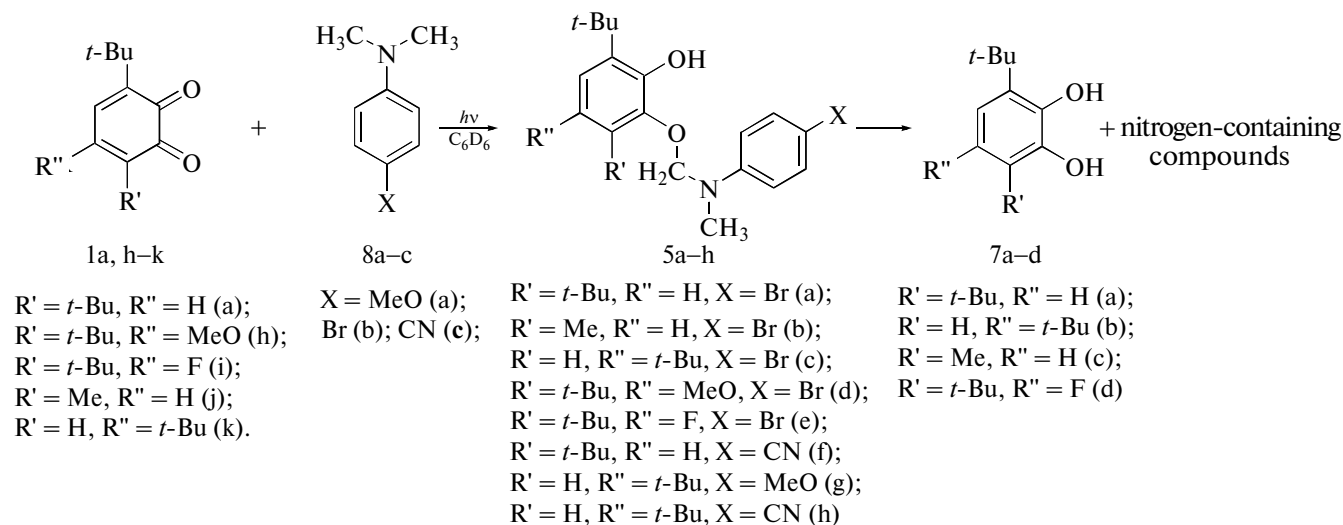
ferred product for 9,10-phenanthrenequinone (4) [12−14] is determined by the nature of the hydrogen donor. For example, 9,10-phenanthrenequinone in the presence of alcohols [15], ethers [12], and aldehydes [11] is reduced to corresponding phenol ethers (Scheme 2, product 5) As a result of the photoreaction of 4 in the presence of hydrocarbons [15−18], corresponding ketols are produced (Scheme 2, product 6). Earlier, we have found [19] that some o-benzoquinones in the presence of tertiary amine are effectively photoreduced with UV and visible light, yielding a mixture of products: phenol ether 5 and pyrocatechol (Scheme 2, compound 7).
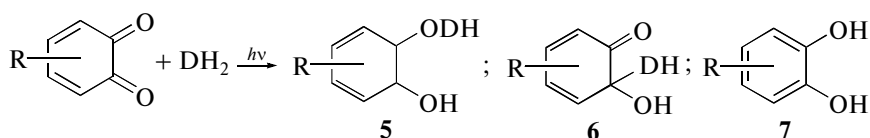
Scheme 2.

This reaction was studied in detail [20, 21] with the use of a number of o-benzoquinones (1a, 1h−1k) (Scheme 3) in the presence of p-substituted N,N-dimethylanilines (8a−8c).Owing to the detailed NMR study of the evolution of the process, it has been found

that the only product, corresponding phenol ether (5a−5h), is formed, which subsequently degrades in the dark to yield pyrocatechol (7a−7d) and a set of nitrogen compounds (Scheme 3) [21].

1a, h–k

R' = t-Bu, R" = H (a);
R' = t-Bu, R" = MeO (h);
R' = t-Bu, R" = F (i);
R' = Me, R" = H (j);
R' = H, R" = t-Bu (k).

8a–c

X = MeO (a);
Br (b); CN (c);

5a–h

R' = t-Bu, R" = H, X = Br (a);
R' = Me, R" = H, X = Br (b);
R' = H, R" = t-Bu, X = Br (c);
R' = t-Bu, R" = MeO, X = Br (d);
R' = t-Bu, R" = F, X = Br (e);
R' = t-Bu, R" = H, X = CN (f);
R' = H, R" = t-Bu, X = MeO (g);
R' = H, R" = t-Bu, X = CN (h)

7a–d

R' = t-Bu, R" = H (a);
R' = H, R" = t-Bu (b);
R' = Me, R" = H (c);
R' = t-Bu, R" = F (d)

Scheme 3.

We have revealed the factors that affect the stability of phenol ethers. One of them is the structure of o-benzoquinone. The replacement of the *tert*-butyl with the methyl group or hydrogen atom in the 3-position

of the quinone ring considerably reduces the rate of degradation of phenol ethers. The degradation rate constant (k_d) decreases by two orders of magnitude from 3.30×10^{-3} (5a) to 2.2×10^{-5} s^{-1} (5b) or 2.6 ×

10^{-5} s^{-1} (5c). Another factor affecting the stability of phenol ether is the donor–acceptor properties of its substituents. The enhancement of the electron-withdrawing properties of the substituent in the quinine moiety and the donating properties in the amine moiety of phenol ether reduces its stability. This fact can be explained in terms of the assumption that the degradation of phenol ether follows the heterolytic mechanism (Scheme 4).
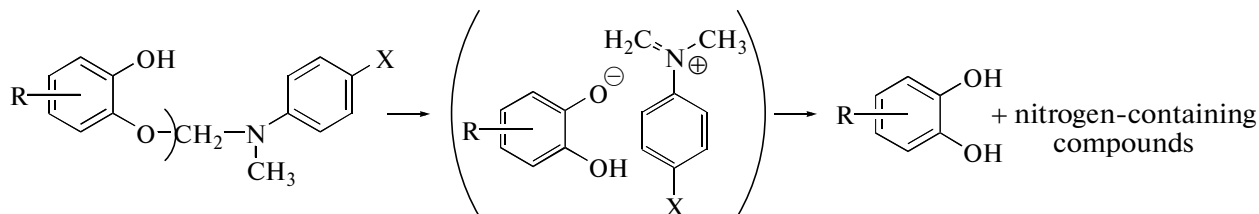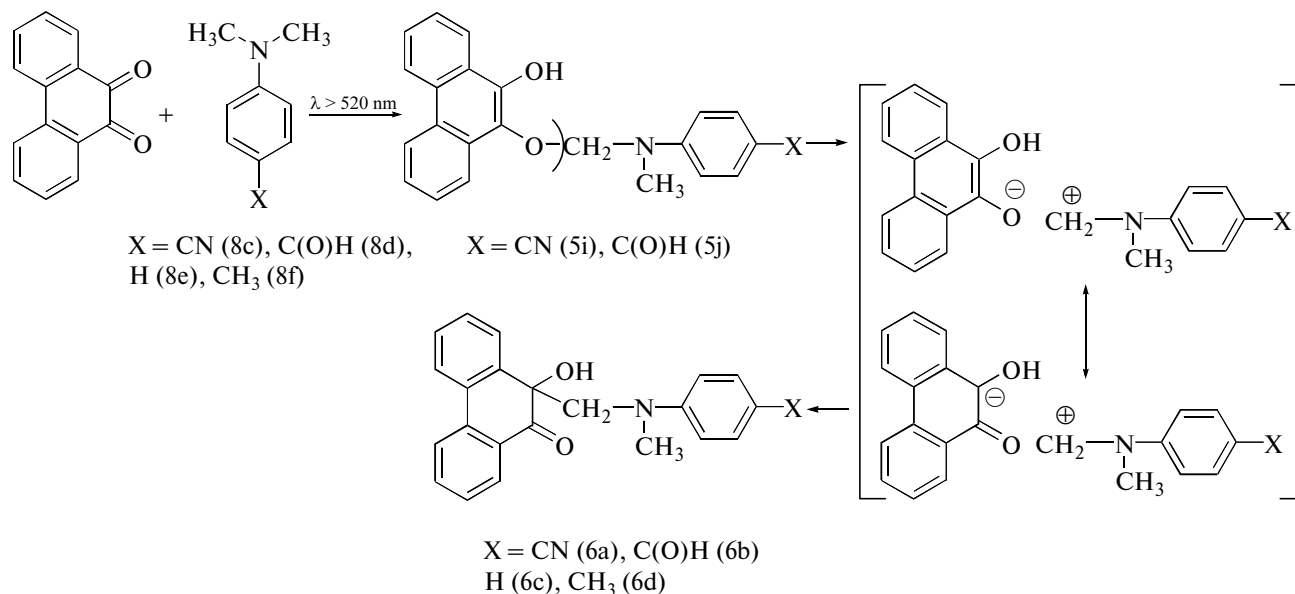

Scheme 4.

An additional support for the assumption on the heterolytic degradation is the response of the degradation rate to a change in the solvent polarity. When deuterated benzene is replaced with deuterated chloroform, the degradation rate increases by an order of magnitude from 3.1×10^{-7} to 4.1×10^{-8} s^{-1}. Thus, the photoreduction of o-benzoquinones in the presence of N,N-dimethylanilines leads to the formation of the only product phenol ether in the first step, which experiences degradation via the heterolytic mechanism yielding pyrocatechol.

The photoreduction products of 9,10-phenanthrenequinone have been studied to the greatest extent. It is known [22] that p-substituted N,N-dimethylanilines effectively photoreduce 9,10-phenanthrenequinone during irradiation with visible light. As hydrogen donors, a number of anilines (8d–8f) were taken. An analysis of proton NMR spectra has shown [23] that irradiation of 9,10-phenanthrenequinone in the presence of anilines 8c and 8d results in the formation of the corresponding phenol ether alone (Scheme 5), as in the case of o-benzoquinones. An increase in the electron-donating power of amines from $E_{1/2} = 1.12$ V (8c) to 0.84 V (8d) destabilizes the phenol ether in this case. The values of the phenol ether degradation rate constant increases from 3.3×10^{-4} (5i) to 5.3×10^{-4} s^{-1} (5j). During they dark reaction, phenol ether is quantitatively rearranged into ketol (6a, 6b) following the first-order rate law.

X = CN (8c), C(O)H (8d),
H (8e), CH$_3$ (8f)

X = CN (5i), C(O)H (5j)

X = CN (6a), C(O)H (6b)
H (6c), CH$_3$ (6d)

Scheme 5.

The further enhancement of the electron-donating ability of amine on passing from 8e and 8f ($E_{1/2} = 0.71$ and 0.65 V, respectively) apparently lowers the stability of the corresponding phenol ethers to such an extent that they become undetectable. The ^{1}H NMR spectra display only the signals of the corresponding ketols (6c, 6d). By analogy with the above-discussed mechanism of degradation of phenol ethers produced from *o*-benzoquinones (Scheme 4), it may be assumed that the rearrangement of phenol ethers due to 9,10-phenanthrenequinone and amine follows the heterolytic mechanism as well.

In the presence of polymethylbenzenes, the process occurs via another scheme. We studied the photoreaction of 9,10-phenanthrenequinone in the presence of a number of polymethylbenzenes (9a–9f). It has been found [23] that the primary products of the photoreduction reaction of 9,10-phenanthrenequinone with polymethylbenzenes 9a, 9b, 9d, and 9e are the corresponding phenol ethers (5k–5p) (Scheme 6). The phenol ethers produced in this reaction are stable in the dark and enter into a secondary photoreaction with 4 upon subsequent irradiation, yielding corresponding ketols.
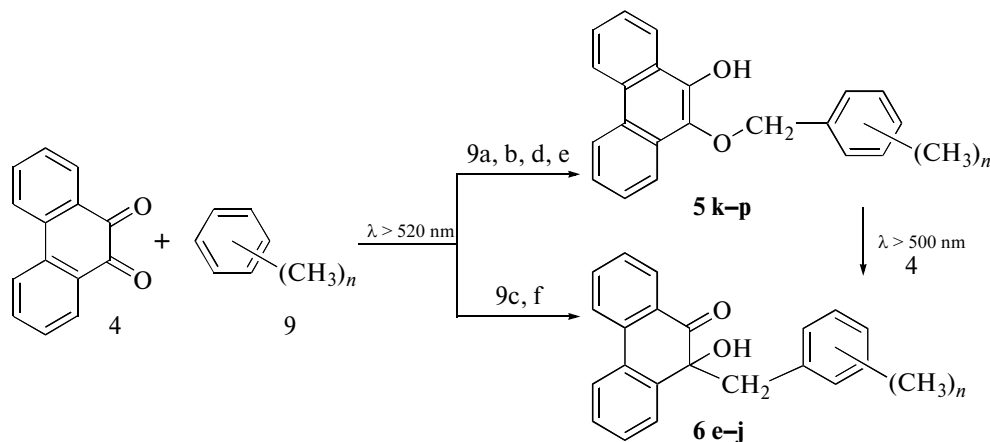
n = 6 (a), 4 (b), 3 (c), 2 (*o*–d, *n*–e, *m*–f)

Scheme 6.

During the photoreaction of 4 in the presence of 9c or 9f, the formation of only the corresponding ketols is manifested in the ^{1}H NMR spectra. All ketols 6a–6j were isolated in the individual form and were characterized by instrumental techniques. Thus, we assume that the photoreduction of 9,10-phenanthrenequinone in the presence of either polymethylbenzenes or tertiary amines is a two-step process, as in the case of the photoreaction of *o*-benzoquinones.

The results obtained in this work suggest that the formation of the photoreduction products of both *o*-benzoquinones and 9,10-phenanthrenequinone follows the same scheme at the first step. Namely, the only product (phenol ether) is produced, which subsequently transforms into pyrocatechol (in the case of *o*-benzoquinone) or ketol (in phenanthrenequinone reactions) depending on the nature of both reactants. The variety and controversy of published data on the products of phototransformations of quinones can be explained by several factors. The first is the difference in stability between phenol ethers; consequently, different product ratios will be observed depending on the time of isolation of the products. The second is the nature of the acceptor, which determines the structure of the final product of degradation of phenol ether. Phenol ether is rearranged into ketol in the case of phenanthrenequinone or pyrocatechol in the case of *o*-benzoquinones. Moreover, along with the photoreduction products, the products of the competing quinone decarbonylation process are formed, although the contribution of this process is insignificant since the reaction rates differ by more than an order of magnitude.

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