Photochemical transformations of 1-arylcyanomethyl-9,10-anthraquinones

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Photochemical transformations of 1-arylcyanomethyl-9,10-anthraquinones were studied. It was established that under irradiation, the hydrogen atom of the substituted methyl group is transferred to a *peri*-quinoid oxygen atom to form the corresponding 9-hydroxy-1,10-anthraquinone-1-arylcyanomethides. Dark transformations of photoinduced quinonemethides result from three competing parallel processes: intramolecular transfer of the hydrogen atom, a reaction with a solvent (alcohol), and oxidation by dissolved oxygen. The kinetics of these reactions were studied.

Key words: photochemical transformations, 1-arylcyanomethyl-9,10-anthraquinones, nucleophilic addition, oxidation, kinetics, quantum-chemical calculations.

It is known[1—4] that 1-alkyl-9,10-anthraquinones undergo photoenolization under the action of light to form dark-colored 9-hydroxy-1,10-anthraquinone-1-methides. These compounds are unstable at room temperature and restore their original structure by a dark process. The lifetime of photoproducts depends on the nature of substituents in the anthraquinone nucleus and at the carbon atom of the methide group, and it increases as the π-electron density at the carbon atom of the methide group decreases and bulky substituents are introduced at the methide group.[2,3]

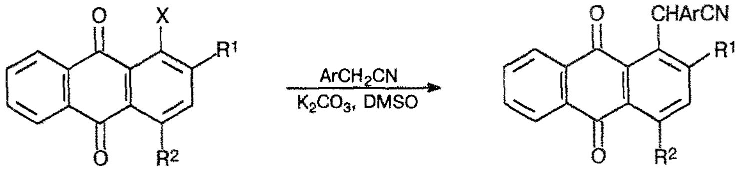
It was interesting to substantially modify the reaction center by introducing the electron-accepting and rather bulky cyano group for stabilizing the photoinduced form at room temperature. To achieve this goal, we synthesized a series of substituted 1-arylcyanomethyl-9,10-anthraquinones (**1—6**) and studied their photochemical properties.

Results and Discussion

Compounds **1—6** were obtained by reactions of the corresponding anthraquinone derivatives with phenylacetonitrile and pentafluorophenylacetonitrile in DMSO in the presence of a base[5] (Scheme 1).

The irradiation of 1-arylcyanomethyl-9,10-anthraquinones **1—6** was carried out both at room and reduced temperatures (77 and 175 K). Irradiation of solutions of compounds **1—6** with UV light results in the formation

Scheme 1



1—6

X = Cl, F, NO_2

1: $R^1 = R^2 = H$, Ar = Ph
2: $R^1 = R^2 = H$, Ar = C_6F_5
3: R^1 = OMe, R^2 = H
4: R^1 = H, R^2 = OMe
5: R^1 = H, R^2 = Cl
6: R^1 = H, R^2 = NO_2

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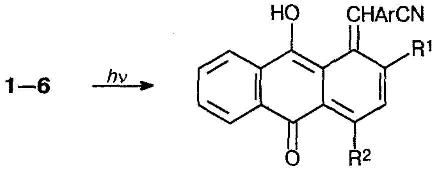
of photoproducts, which have long-wave absorption maxima in the region of 580—630 nm (Table 1). The quantum yield of phototransformations of compounds **1—6** is significantly (up to 2 orders of magnitude) lower than that of 1-methylanthraquinone. The spectral changes observed during the photolysis of substituted 1-arylcyanomethyl-9,10-anthraquinones at 77 K are completely identical to those for previously studied 1-alkyl- and 1-benzylanthraquinones.[1,4] Thus, in our case, substituted 9-hydroxy-1,10-anthraquinone-1-methides (**1a—6a**) are also the products of photolysis.



1a—6a

Alcohols were used as solvents. It is known[2,3] that the lifetime of 9-hydroxy-1,10-anthraquinone-1-methide is significantly higher in polar proton-donor solvents and varies from 350 ns in hexane to 200 μs in methanol at room temperature. The lifetime of photo-products **1a**, **2a**, **5a**, and **6a** in alcohols at room temperature does not exceed 10 s (see Table 1); therefore, their reactions were studied by pulse excitation of compounds **1**, **2**, **5**, and **6**. Compound **4a** appeared to be rather stable, which allowed us to study its transformations under conditions of stationary photolysis of **4**.

Table 1. Positions of maxima of long-wave bands (λ_{max}) in EAS of derivatives **1—7** before and after irradiation at 77 K and rate constants (*k*) of dark transformations of the photoproduct at room temperature in ethanol

Compound	λ_{max}/nm		k/s^{-1} (±10 %)
	before irradiation	after irradiation	
1	333	635	0.1
2	327	631	—
3	371	622	—
4	388	610	0.0021
5	339	636	0.11
6	335	632	0.06

The photolysis of 1-arylcyanomethyl-4-methoxy-9,10-anthraquinone (**4**) was carried out at room temperature in methanol, ethanol, 2-propanol, and *tert*-butanol. The changes in the electron absorption spectrum (EAS) of compound **4** at room temperature occur with retention of the isobestic point (Fig. 1, *a*). The spectrum of the compound formed is close to those of the previously studied products of photolysis of 1-alkyl- and 1-benzylanthraquinones.[1—4] However, unlike substituted 9-hydroxy-1,10-anthraquinone-1-methides,[1,4] which recover the starting compounds when melted, this process is observed for compound **4a** only in isopropanol and *tert*-butanol (Fig. 2, *a*). The photochemical transformations in methanol and ethanol are irreversible (Fig. 2, *b*).

In the case of two different substituents at the carbon atom of the methide group, the formation of two struc-

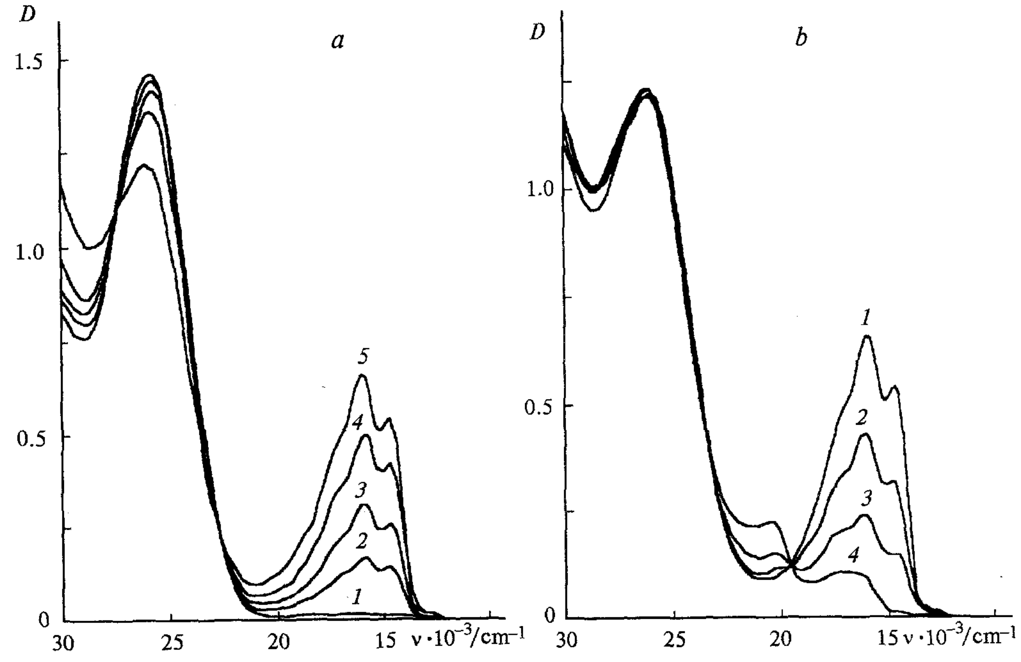


Fig. 1. *a* — *1*, Absorption spectrum of 4-methoxy-1-phenylcyanomethyl-9,10-anthraquinone (**4**) and its variation after irradiation for 1 (*2*), 2 (*3*), 4 (*4*), and 10 s (*5*); *b* — spectrum (*5*) in Fig. 1,*a* and its variation during storage in the dark for 8 (*2*), 20 (*3*), and 40 min (*4*) in 2-propanol at room temperature in the presence of oxygen ($C = 4 \cdot 10^{-4}$ mol L^{-1}).

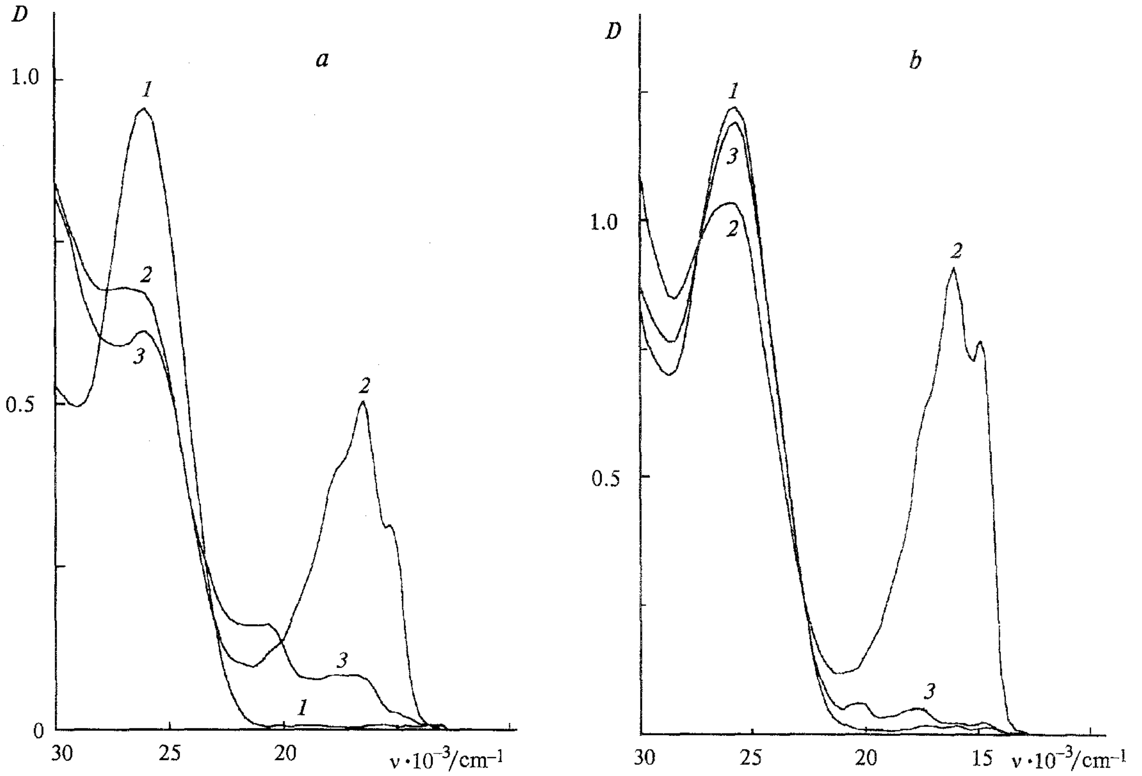
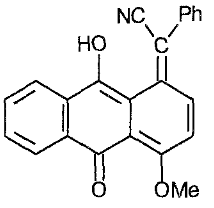
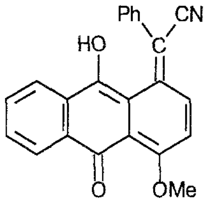


Fig. 2. *1*, Absorption spectrum of 4-methoxy-1-phenylcyanomethyl-9,10-anthraquinone (**4**) and, *2*, its changes after irradiation for 3 s and after dark transformations for 1 h in ethanol ($C = 1.75 \cdot 10^{-4}$ mol L^{-1}) (*a*) and in *tert*-butanol ($C = 2.25 \cdot 10^{-4}$ mol L^{-1}) (*b*) in the absence of oxygen.

tural isomers was detected.[4] In our case, one may also expect the formation of a mixture of two isomers. According to the calculations by the AM1 method (see Ref. 6), the enthalpy of formation of isomer **A** is 3.3 kcal mol^{-1} lower, which indicates that this compound is thermodynamically more stable.



A



B

The dark process of destruction of **4a** at room temperature is described by a first-order equation. The absorption recorded under stationary conditions probably belongs to one isomer, most likely, an **A** type compound. For this compound one should expect a substantially longer lifetime than for isomer **B** due to the significant steric hindrance for reverse migration of the H atom. It was shown earlier[4] that the phenyl substituent does not create steric hindrance for thermal migration of the H atom. With pulse excitation of **4**, the absorption of an intermediate, probably a **B** type isomer, with a much shorter lifetime (5±1 ms) is also observed. However, the absorption of this isomer is significantly less. In this work we paid primary attention to the study of long-lived isomer **A**. All the results of kinetic studies presented below deal with isomer **A**.

The rate of dark transformation of **4a** depends on the nature of the alcohol. When passing from methanol to ethanol, the rate constant (k/s^{-1}, accuracy determination: ±10 %) decreases by a factor of 3, and when passing from ordinary to branched alcohols, this constant decreases by more than an order of magnitude:

	1a	**4a**
MeOH	0.75	$6.2 \cdot 10^{-1}$
EtOH	0.10	$2.1 \cdot 10^{-1}$
Pr^{i}OH	0.03	$3.0 \cdot 10^{-4}$
Bu^{t}OH	0.05	$1.2 \cdot 10^{-3}$

A similar effect of the nature of the alcohol was observed previously[7] for the reaction of nucleophilic 1,4-addition of an alcohol molecule to 9-aryloxy-1,10-anthraquinones. We specially checked whether the nature of the alcohols used influences the rate constant of dark migration of the hydrogen atom in unsubstituted 9-hydroxy-1,10-anthraquinone-1-methide. The rate constants of dark transfer of the hydrogen atom were equal in all alcohols used (methanol, ethanol, 2-propanol, and *tert*-butanol).

Based on the dependence of the dark transformation rate on the nature of the alcohol, one may assume that

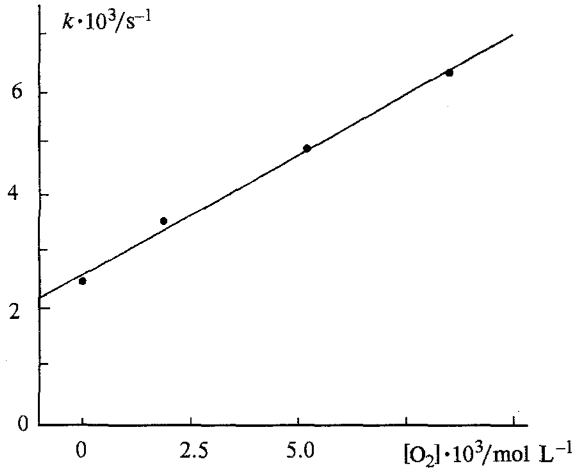


Fig. 3. Dependence of the rate constant of the destruction of 9-hydroxy-4-methoxy-1,10-anthraquinone-1-phenylcyanomethide (**4a**) in ethanol at 298 K on the concentration of dissolved oxygen.

photoinduced quinone-methide **4a** can react with alcohols. The reaction with 2-propanol and *tert*-butanol is sterically hindered and does not compete with the reaction of reverse thermal transfer of the H atom. The main contribution to the measured reaction rate probably comes from the transfer of the H atom.

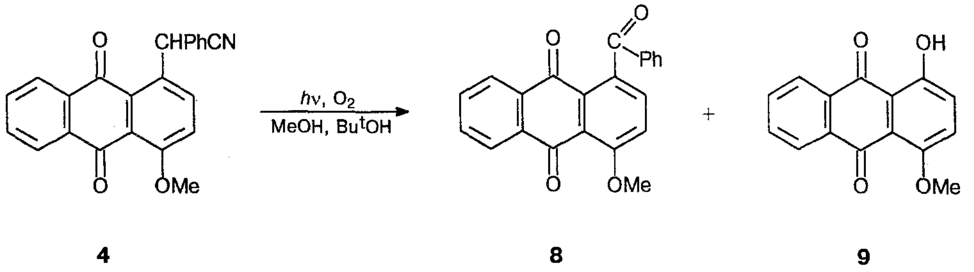
The lifetime of **4a** depends not only on the nature of the alcohol but also on the content of oxygen in solution. The dependence of the rate constant of the destruction of photoproducts **4a** on the content of O_2 in solution was studied (Fig. 3). The experimental points are well described by a linear dependence. Using the data on the solubility of O_2 in ethanol,[8] we obtained a second order rate constant for the reaction of **4a** with oxygen (0.42 ± 0.02 L (mol s)$^{-1}$).

Preparative photolysis of compound **4** in methanol in the presence of oxygen resulted in 1-benzoyl-4-methoxy-(**8**) and 1-hydroxy-4-methoxyanthraquinones (**9**) as the main products. However, the same main products **8** and **9** are formed in the photolysis of **4** in methanol preliminarily purged with argon. Compound **8** was obtained in an independent synthesis by oxidation of compound **4** with alcoholic alkali[5] (Scheme 2).

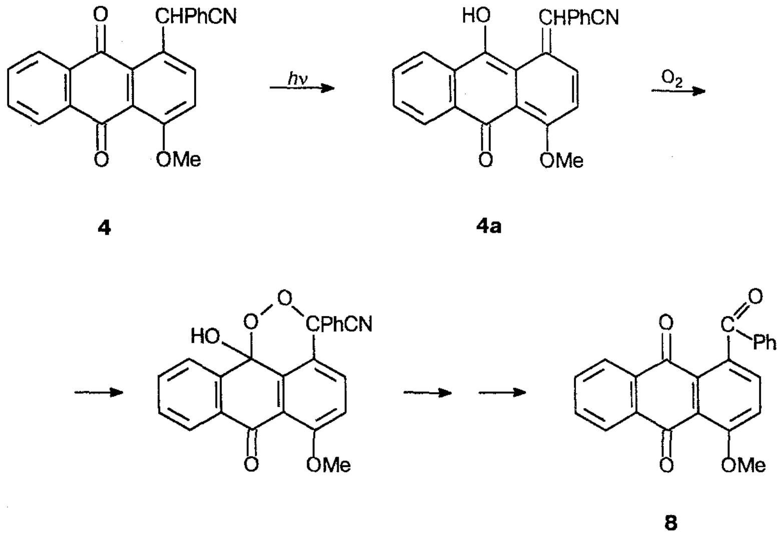
It is known from the literature[9] that 1-methyl-9,10-anthraquinone can undergo photooxidation. In our case, we also observed photooxidation accompanied by the loss of the cyano group, during irradiation of compound **4** in the presence of oxygen. According to the literature data,[9] the following scheme of formation of **8** may be suggested (Scheme 3).

Compound **9** can be obtained by deeper oxidation of **8** (see Ref. 9). The possible pathway leading to formation of **8** without participation of oxygen may be 1,4-addition

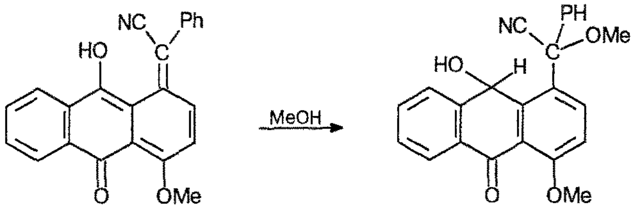
Scheme 2



Scheme 3



Scheme 4



4a **10**

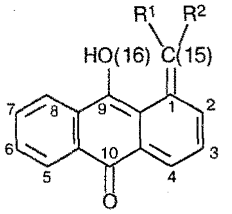
of an alcohol through intermediate adduct **10** (Scheme 4).

We rejected the possibility of addition of an alcohol to the double methide bond (1,2-addition) since 1,2-addition is 15 kcal mol^{-1} less thermodynamically favorable than 1,4-addition, according to AM1 calculations. The resulting adduct **10** contains a sterically strained substituted methoxy group and, probably, gives end product **8** in the course of subsequent transformations.

The possibility of 1,4-addition of an alcohol to compound **4a** is consistent with the results of quantum-chemical calculations. It is known[10,11] that the position with the largest partial electron density at the lowest unoccupied molecular orbital (LUMO) is the most favorable for the attack of nucleophilic agents. Quantum chemical calculations using the AM1 method (see Ref. 6) show that the most active atom for nucleophilic attack in 9-hydroxy-1,10-anthraquinone-1-arylcyanomethide is the carbon atom of the methide group (C(15)). This position has the highest partial electron density at the LUMO (0.16). For comparison, we present the distribution of the partial electron density (ρ) at the lowest unoccupied MO for 9-hydroxy-1,10-anthraquinone-1-methide as a function of substituents in the methide group calculated using the AM1 method:

	$R^1 = R^2 = H$	$R^1 = Ph, R^2 = CN$
ρ_1	0.10	0.05
ρ_2	0.10	0.08
ρ_4	0.16	0.10
ρ_9	0.10	0.14
ρ_{15}	0.13	0.16

It is evident that the partial electron density at the LUMO at C(15) of the methylene group is increased when passing from 1,10-anthraquinone-1-methide unsubstituted at the methide group to the arylcyano-substituted one.



Earlier[7] we discovered the reaction of 1,4-nucleophilic addition of alcohols to substituted 1,10-anthraquinones. Unlike the case considered now, position 9 in 1,10-anthraquinone is active toward nucleophiles, this position having also the largest partial electron density at the LUMO (see Ref. 12).

During pulse excitation of compounds **1—3**, **5**, and **6** at 298 K in ethanol, we observed the formation of products, whose spectra are similar to those obtained at 77 K and to the spectrum obtained by irradiation of compound **4** under stationary conditions. The kinetic curve of decreasing absorption of the intermediate at the absorption maximum of the intermediates (580—630 nm) is an exponent at times longer than 1 ms. This absorption also probably corresponds to intermediates with long lifetimes (A type compounds). Alcohols were used as solvents in pulse photolysis experiments since the lifetime of photoinduced products decreases significantly and becomes shorter than the time resolution of the instrument (20 μs) in other solvents. The rate constant of the decay of the photoproduct also depends on substituents at the anthraquinone nucleus. The values of the rate constants of the decay of quinone-methides **1a** and **4a** are given above. It can be seen from these data that the characteristic values of the constants differ by an order of magnitude, which may be explained by a stabilizing effect of the donor substituent at position 4 of a quinone-methide.

It was found that, unlike for compound **4a**, the rate of transformation of **1a** does not depend on the content of oxygen in solution. Hence, oxidation does not compete with other pathways of transformation of **1a**. The lifetime of **1a** decreases significantly in ethanol and methanol. The reaction with an alcohol may also be the main pathway for the destruction of **1a**.

The effect of temperature on the rate constant of dark transformations of **1a** in ethanol was studied. The temperature dependence is described by the Arrhenius law

$$k = 10^{7.9\pm0.4}\cdot\exp(-(6000\pm300)/T).$$

The preexponential factor obtained ($10^{7.9\pm0.4}$ s^{-1}) is substantially smaller than that for the transfer of the hydrogen atom in 9-hydroxy-1,10-anthraquinone-1-methide and its derivatives ($\sim10^{11}\div10^{12}$ s^{-1})[3,4] and is close to the preexponential factor of reactions of 1,4-addition of alcohols and amines to 1,10-anthraquinone derivatives ($\sim10^{6}\div10^{9}$).[12] Probably, the interaction with an alcohol may prevail in the process of dark transformations of compound **1a**.

Hence, the dark process of destruction of photoinduced products **1a—6a** involves not only the step of reverse transfer of the hydrogen atom of the methyl group but also the interaction of photoinduced quinone-methides with alcohols and dissolved oxygen. Hence, the introduction of arylcyano derivatives to the methyl group and donor substituents at anthraquinone nucleus increases the lifetime of the photoinduced form so strongly that the reactions of 9-hydroxy-1,10-anthraquinon-1-arylcyanomethides with oxygen and alcohols

Table 2. Physicochemical characteristics of compounds **2**—**6**

Compound	Yield (%)	M.p./°C $C_2H_5OH—C_6H_6$	M^+, *m/z* Found / Calculated	Empirical formula	IR, ν/cm^{-1} C≡N	IR, ν/cm^{-1} C=O	UV, λ_{max}/nm (log ε)
2	55	192—194	413.0472 413.0475	$C_{22}H_8F_5NO_2$	2245	1675	255 (4.63), 327 (3.74),
3	55	199—201	353.1049 353.1052	$C_{23}H_{15}NO_3$	2245	1665	268 (4.41), 333 (3.62), 371 (3.52)
4	70	199—201	353.1049 353.1052	$C_{23}H_{15}NO_3$	2245	1665	257 (4.51), 325 (3.47), 388 (3.70)
5	60	132—134	357.0548 357.0557	$C_{22}H_{12}ClNO_2$	2240	1675	256 (4.56), 339 (3.60)
6	30	168—170	368.0791 368.0797	$C_{22}H_{12}N_2O_4$	2240	1675	257 (4.58), 335 (3.64)

Table 3. Chemical shifts of protons (δ) and coupling constants (*J*/Hz) in the ^1H NMR spectra of compounds **1**—**6**

Compound	HCR^1R^2(s)	C_6H_5 (m)	H-2 (d)	H-3 (d)	H-4 (d)	H-6,7 (m)	H-5,8 (m)
1	7.13	7.27	7.91 (*J* = 8)	7.80 (t, *J* = 8)	8.41 (*J* = 8)	7.78	8.24
2	6.97		8.20 (*J* = 8)	7.90 (t, *J* = 8)	8.49 (*J* = 8)	7.79	8.22
3	7.53	7.25—7.43	3.90 (s, OCH_3)	7.32 (*J* = 9)	8.46 (*J* = 9)	7.77	8.26
4	6.92	7.27—7.39	7.79 (*J* = 9)	7.35 (*J* = 9)	4.02 (s, OCH_3)	7.72	8.14
5	6,97	7.32—7.40	7.80 (*J* = 8)	7.75 (*J* = 8)	Cl	7.78	8.16
6	7.09	7.28—7.45	7.73 (*J* = 8.5)	7.99 (*J* = 8.5)	NO_2	7.83	8.21

compete with the reverse transformation into the starting compound. This allowed us to estimate the rate constants of these reactions. The studied photochemical reaction of 1-arylcyanomethyl-9,10-anthraquinones in alcohols is a new method for the preparation of hardly accessible 1-benzoylanthraquinones.

Experimental

IR spectra were recorded on a UR-20 spectrophotometer in KBr pellets; electron absorption spectra (EAS) were obtained on a Specord UV-VIS spectrophotometer. ^1H NMR spectra were measured on a Bruker AC-200 instrument in $CDCl_3$. Chemical shifts are given in the δ scale. $SiMe_4$ was used as the internal standard. Mass spectra were obtained on a Finnigan MAT-8200 instrument; *m/z* values are given for molecular ions [M^+]. Chromatography was carried out on silica gel columns (L 100—250 μm); TLC was carried out on Silufol UV-254 plates.

Photolysis was carried out by the light from a DRSh-500 lamp with a UVS-1 filter (280—400 nm) and from a full-spectrum hydrogen lamp. The absorption spectra of the products of photolysis of compounds **1**—**7**, which are unstable at room temperature, were recorded at 77 K similarly to the previously described procedure[1,4] or at the temperature of melting isopropanol (−89.5 °C).[13] Kinetic curves of destruction of the photoproducts with lifetimes longer than 1 min were recorded spectrophotometrically after pleliminary irradiation of the samples. When the lifetimes of photoproducts were within the range from milliseconds to seconds, a pulse photolysis device with a flash energy of 1000 J and a 20 μs flash duration was used. Kinetic curves were recorded using a MERA-60-KAMAK computer complex connected to a lamp pulse photolysis device.[14] Kinetic parameters were determined using the nonlinear regression mean square method.[15] The accuracy of determination of constants was ±10 %. All solvents were purified by known procedures.[16]

Quantum-chemical calculations of geometry, electron density distribution, and enthalpy of formation of compounds under study and proposed intermediates were carried out by the AM1 method (see Ref. 6) using a modified MNDO-85 program (see Ref. 17). The standard Davidon—Fletcher—Powell[18,19] procedure was used for geometric optimization.

1-Arylcyanomethyl-9,10-anthraquinones (1—6) were obtained by the previously described procedure.[5] The yields, m.p., molecular masses, IR spectra, and EAS are given in Table 2. ^1H NMR spectral data are presented in Table 3.

The photolysis of 1-arylcyanomethyl-4-methoxy-9,10-anthraquinone (4) was carried out both with and without preliminary purging of the solutions with argon for 20 min. A solution of compound **4** (0.7 g) in methanol (*tert*-butanol) was irradiated by a hydrogen lamp (full spectrum) or by sunlight for 5—6 h. Photolysis was carried out at room temperature until the starting compound disappeared (TLC monitoring). The reaction mixture was diluted with water, and the precipitate that formed was filtered off, washed with water, dried, and chromatographed on a column using benzene as the eluent. 1-Methoxy-4-hydroxy-9,10-anthraquinone (**9**) (0.12 g, 23 %), which was identical to an independently synthesized sample, was obtained from the first zone. 1-Benzoyl-2-methoxyanthraquinone (**8**) (0.41 g, 60 %) was obtained from the second zone. M.p. 257—258 °C (from EtOH). Found, *m/z*: M 342.0891. $C_{22}H_{14}O_4$.

Calculated: 342.0892. IR, ν/cm^{-1}: 1670, 1655 (C=O). EAS in *tert*-butanol, λ_{max}/nm (lg ε): 380 (3.59).

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