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Light-induced transformations of 1,2-dihydroquinolines: opening of the heterocycle, radical formation and photoinduced proton transfer

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Abstract. Three types of light-induced photochemical reactions of 1,2-dihydroquinolines, opening of the heterocycle, formation of aminyl radicals upon the homolytic N—H bond cleavage and proton transfer in protic solvents, have been considered. Special attention has been focused on the photoinduced proton transfer reactions. The effect of the dihydroquinoline structure and solvent composition on the routes and kinetic parameters of photochemical reactions has been analyzed. The bibliography includes 108 references.

I. Introduction

1,2-Dihydroquinolines — heterocycles containing a nitrogen atom conjugated with the aromatic ring — are analogues of aromatic amines. Therefore, it seems probable that photolysis of secondary dihydroquinolines is analogous to photolysis of aromatic amines. Back in the early 1960s, Land and Porter [1,2] showed that flash photolysis of phenols and aromatic amines leads to the elimination of hydrogen atoms and formation of corresponding phenoxyl and aminyl radicals, which decay through recombination or (sometimes) disproportionation by a second-order process.

In the past five decades, a large body of experimental and theoretical data have been obtained concerning the photochemistry and photophysics of different aromatic amines,[3–7] including nitrogen-containing heterocycles. Since many of them turned out to be biologically active, researchers have focused special attention on studying the photochemical behaviour of these compounds in aqueous and micellar media.[8–14] Many heterocyclic compounds containing several nitrogen atoms in the ring (for example, azaindole) or a nitrogen atom and a hydroxy group (for example, 7-hydroxyquinoline) are capable of tautomerism in both the ground state and the excited singlet state. Reactions of these compounds have been intensively studied since the 1990s owing to the development of experimental pulse methods with pico- and femtosecond time resolution, matrix isolation and other methods, as well as quantum-chemical calculations.[15–24] For example, since indole is a functional group of tryptophan, the photochemical and photophysical processes that occur upon photoexcitation of this heterocycle and tryptophan *per se* are of great interest to both experimenters [23,25–27] and theorists.[28,29]

Studies of light-induced transformations of 1,2-dihydroquinolines have been developed in three directions:

1) in the late 1960s and early 1970s, the possibility of using some of dihydroquinoline derivatives as photochromic compounds was studied;

2) in the 1980s, photophysical and photochemical reactions of secondary † dihydroquinolines that occur in aprotic solvents and formation of aminyl radicals upon photolysis in hydrocarbons were intensively studied;

3) in the past decade, much attention was attracted by photophysical and photochemical transformations of dihydroquinolines in protic solvents, proton transfer reactions and carbocation formation upon photolysis of 1,2-dihydroquinolines.

This review addresses specific features of the photochemical behaviour of 1,2-dihydroquinolines in solutions as a function of their structure and solvent properties.

II. Opening of the heterocycle upon photolysis of 1,2-dihydroquinolines

In the early 1970s, Kolc and Becker [30,31] studied photochemical transformations of some 1,2-dihydroquinolines with the aim of revealing the photochromic properties of

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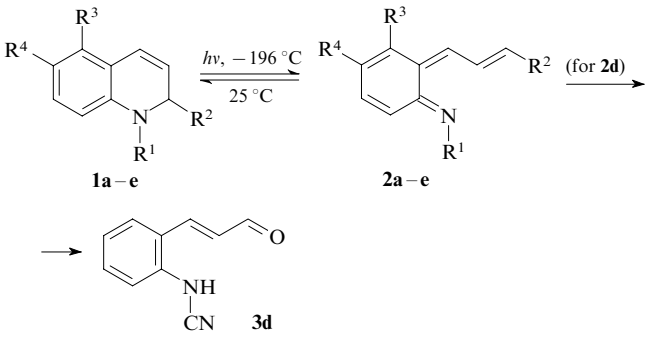
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† Dihydroquinolines with the free NH group are referred to as secondary (by analogy with secondary amines) and those with the substituted NH group, are called tertiary.

these compounds since they are structural analogues of chromenes, oxygen-containing heterocycles exhibiting photochromism.

It has been shown that N-substituted 1,2-dihydroquinolines **1a–e** with electron-withdrawing substituents in the 1- and/or 2-position under light irradiation undergo reversible N–C(2) bond cleavage in pentane–ethanol–ether glasses at −196 °C. As a result, the pyridine ring is opened to give imines **2a–e** (Scheme 1).

Scheme 1

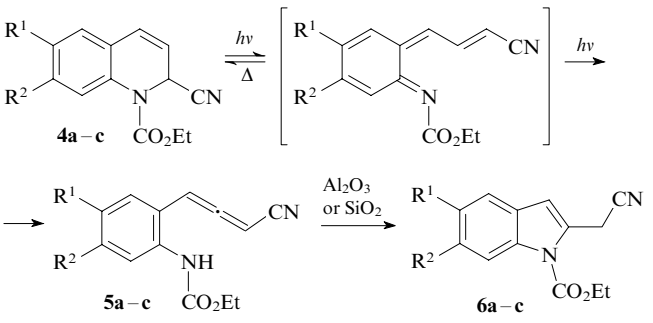


Compounds **1**, **2**	R^1	R^2	R^3	R^4
a	COPh	CN	H	H
b	COPh	CN	benzo	
c	CO_2Et	CN	H	H
d	CN	OH	H	H
e	CO_2Et	OEt	H	H

Heating the reaction mixture to room temperature leads to reversible discoloration. With *N*-cyano-2-hydroxy-1,2-dihydroquinoline (**1d**), the process becomes irreversible since product **2d** isomerizes to *N*-cyano-*o*-aminocinnamaldehyde (**3d**). The identification of **3d** is strong evidence in favour of the N–C(2) bond cleavage upon photolysis.[31] Coloured intermediate products **2a–e** have a broad absorption band in the visible spectral range with a maximum at 450–490 nm depending on the nature of substituents.[30,31] However, inasmuch as 1,2-dihydroquinolines **1a–e** held little promise for use as photochromic compounds, these studies have not been extended.

The light-induced opening of the heterocyclic ring in substituted 1,2-dihydroquinoline-1-carboxylates **4a–c** has been used for synthesizing indole derivatives.[32–35] It has been suggested that a two-quantum process leads to allene derivatives **5a–c**. These derivatives have been identified by ^{1}H NMR and IR spectroscopy after photolysis; however, attempts to isolate them by thin layer chromatography have led to their conversion to indole derivatives **6a–c** (Scheme 2).[32]

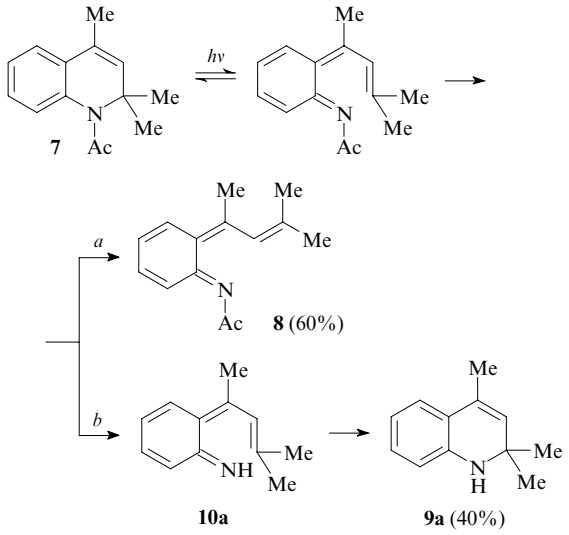
Scheme 2



$R^1 = R^2 = H$ (**a**); $R^1 = Me$, $R^2 = H$ (**b**); $R^1 = H$, $R^2 = Me$ (**c**)

The dihydropyridine ring is also opened upon photolysis of 1-acetyl-2,2,4-trimethyl-1,2-dihydroquinoline (**7**) in dioxane at room temperature (Scheme 3).[36]

Scheme 3

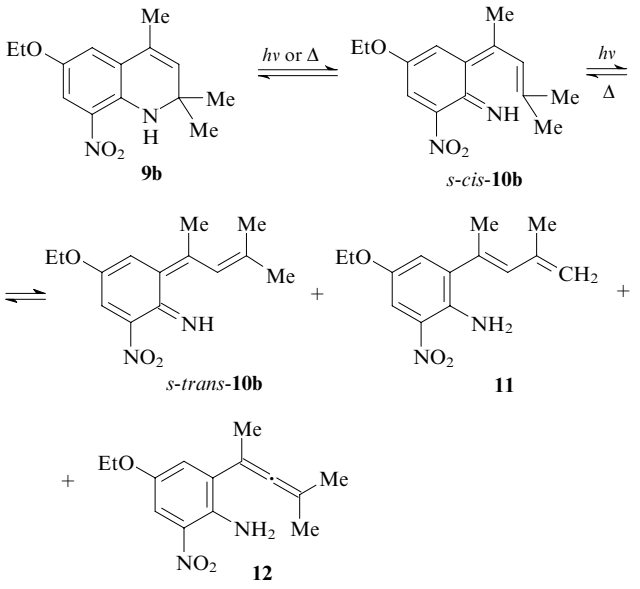


Two stable products have been isolated from the reaction mixture. One of them (compound **8**, yield 60%) is a coloured compound with the absorption maximum (λ_{max}) at 420 nm. The second product is 2,2,4-trimethyl-1,2-dihydroquinoline (the product of condensation of acetone with aniline, acetone anil **9a**). The authors have suggested a scheme in which compound **8** results from rotation of the dimethylallyl group after the opening of the heterocycle at the N–C(2) bond and compound **9a** is formed upon ring closure in intermediate **10a**, formed after elimination of the acetyl group.

Study of photochemical transformations of 2,2,4-trimethyl-8-nitro-6-ethoxy-1,2-dihydroquinoline (**9b**) by the flash photolysis has demonstrated an unusual dependence of the photochemical reaction on the excitation light wavelength.[37] Excitation in the long-wavelength absorption band in the range 400–490 nm initiates a reversible reaction. Spectral and kinetic characteristics of three transient species observed upon photolysis have been studied. These species in acetonitrile have absorption maxima at 390, 400 and 420 nm and are characterized by decay rate constants (k) of 97, 500 and 2000 s^{-1}, respectively. The absorption spectra are nearly independent of the medium polarity and the presence of oxygen in the system. Upon photoexcitation in the short-wavelength absorption band ($290 < \lambda_{ex} < 350$ nm) no transient species are observed. A mechanism of a reversible photochemical reaction has been suggested implying the opening of the heterocycle at the N–C(2) bond upon photoexcitation in the long-wavelength absorption band and the dark back reaction (Scheme 4).

It is assumed that formation of compounds *s-trans*-**10b**, **11** and **12** is a two-quantum process: after the opening of the heterocycle, intermediate *s-cis*-**10b** absorbs a second light quantum and transforms to *s-trans*-**10b** through rotation about the C(3)–C(4) bond and to amine **11** or **12** when the nitrogen atom detaches a hydrogen atom either from the methyl group in the 2-position or from the carbon atom in

Scheme 4

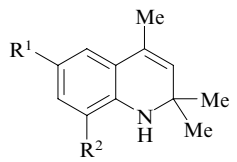


the 3-position of the parent molecule. As mentioned above, the formation of allene derivatives has been observed upon photolysis of *N*-carboxylates (see Scheme 2).[32–34]

The sequence of transformations in Scheme 4 is analogous to the mechanism accounting for the formation of intermediate products upon photolysis of chromenes.[38] It is worth noting that 1,2-dihydroquinolines with a nitro group in the 6- or 7-position undergo analogous reversible transformations upon excitation in the long-wavelength absorption band in the visible range and are photostable when exposed to UV light. These compounds are currently the only example of 1,2-dihydroquinolines with the free NH group in which the opening of the heterocycle occurs.

III. Photochemical processes in alkyl-, alkoxy- and hydroxy-substituted 1,2-dihydroquinolines in aprotic solvents

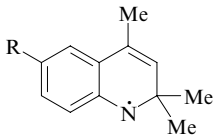
2,2,4-Trimethyl-1,2-dihydroquinolines (**9a–g**) containing different substituents in the 6- and 8-positions of the aromatic ring[39–42] are efficient inhibitors of chain oxidation of organic compounds, especially unsaturated ones. Under different trademarks, these compounds have been long and widely used in many countries worldwide as efficient antioxidants and antiozonants for stabilization of rubbers, propellants and lubricating oils.[43–47] They are nearly nontoxic;[48–51] therefore, they are used for stabilization of β-carotene, vitamin A and other polyunsaturated substances in fodder and for pre-storage treatments of fruits and vegetables.[52] Many dihydroquinolines are biologically active and have been explored as potential drugs.[53–59]



9a–g

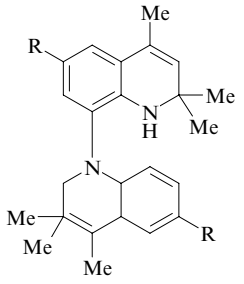
R^2 = H: R^1 = H (**a**), Me (**c**), OEt (**d**), OH (**e**);
R^1 = H: R^2 = OMe (**f**), OH (**g**); R^1 = OEt, R^2 = NO_2 (**b**)

Studies of photochemical transformations of dihydroquinolines with antioxidant properties were pioneered in 1980.[60,61] The authors determined the recombination rate constants of aminyl radicals **13d**, which form in oxidized hydrocarbon systems from the most efficient antioxidant ethoxyquin (**9d**). It has been suggested that these radicals can be generated upon illumination of solutions of compound **9d**. (An analogous behaviour is typical of anilines and other aromatic amines.) It has been unambiguously demonstrated that, upon steady-state photolysis of compounds **9a** and **9d** in hexane, benzene and absolute propanol, corresponding aminyl radicals **13a** and **13d** are generated.[60,61]



13a,d

R = H (**a**), OEt (**d**)



14a,c,d

R = H (**a**), Me (**c**), OEt (**d**)

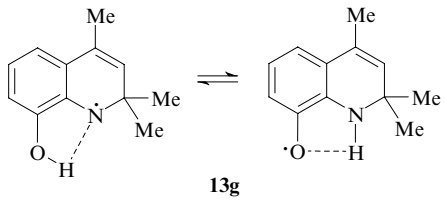
Later, Walton and co-workers[62] have obtained aminyl radical **13d** from dihydroquinoline **9d** upon *in situ* irradiation of sealed evacuated ampoules containing a heptane solution at room temperature in the cavity of an EPR spectrometer. The EPR spectrum of radical **13d** with a resolved fine structure has been recorded, hyperfine coupling constants have been determined, and the theoretical spectrum has been calculated. The latter is consistent with the experimental spectrum. The major conclusion drawn by the authors on the basis of these data is that the unpaired electron in radical **13d** is strongly delocalized, and most of the electron density is distributed between the 1- and 8-positions of the quinoline ring. This accounts for the fact that recombination of aminyl radical **13d** leads to dimer **14d** at the 1- and 8-positions. The absorption spectrum of the dimer is close to that of initial compound **9d**. Dimer **14d** has been identified among the products of photolysis[62] and oxidation of compound **9d**.[63,64]

Yet another piece of evidence supporting formation of radicals **13a,c,d,f** from dihydroquinolines **9a,c,d,f** is provided by the EPR study of the products formed upon photolysis in the presence of spin traps: nitrosodurene, *C*-phenyl-*N*-*tert*-butylnitrone and *tert*-butylmethylenenitrone.[65]

A more complicated problem is to identify the generated radical in the case of hydroxydihydroquinolines **9e,g**, since both aminyl and phenoxyl radicals can form. As is known, it is precisely the phenoxyl radical that is formed upon oxidation of compound **9e** in hydrocarbons,[66] which is explained by the lower O–H bond energy as compared with the N–H bond energy.[67,68] Detailed study of the spectral and kinetic properties of the intermediate and ultimate products formed upon photolysis of compound **9e**[69] demonstrates that the aminyl radical is generated. The close proximity of the hydroxy and amino groups in compound **9g** is responsible for that radical **13g** can behave itself as both the aminyl and phenoxyl radical owing to the

formation of a hydrogen bond between the neighbouring moieties (Scheme 5).

Scheme 5



13g

Under pulsed photoexcitation of solutions of compounds **9a**,**c**–**g** in benzene and hexane, a transient product has been observed that absorbs in the visible range at $\lambda_{max} = 380-440$ nm depending on the solvent and the structure of the initial dihydroquinoline.[60,61,70] The decay of the intermediate follows second-order kinetics. The $2k/\varepsilon$ values, where k is the bimolecular rate constant for the reaction of intermediate species and ε is the molar extinction coefficient at the wavelength of recording, have been obtained from the time-dependence of the absorbance of the transient species by flash photolysis. In order to find the extinction coefficient, it is necessary to determine the concentration of radicals that are formed after the excitation light pulse by an independent method.

To determine ε, the yield of radicals formed upon photolysis has been studied as a function of the excitation pulse energy.[60] With increasing the pulse energy, the radical concentration ceases to depend on it. With the assumption of the lack of the cage effect for the H atoms in the liquid phase[71] and the lack of the back photoreaction, the change in the absorbance is caused only by the formation of radicals, and their concentration in the range of limiting absorptions is equal to the initial concentration of dihydroquinoline. The extinction coefficients at $\lambda = 400$ nm thus calculated are in the range 300–600 litre mol^{-1} cm^{-1} depending on the nature of the solute and solvent, which gives the recombination rate constant on the order of 10^7 litre mol^{-1} s^{-1}.[60,61] It is worth noting that this estimate of the recombination rate constant for the aminyl radicals generated from compound **9d** is close to the value $(5 \pm 3) \times 10^6$ litre mol^{-1} s^{-1} obtained for the same radicals in hexane at 0 °C by EPR.[62] This is indirect evidence of the adequacy of determination of the extinction coefficient ε_{400}.

In this context, the extinction coefficients for aminyl radicals **13a** and **13c** (7500 and 5000 litre mol^{-1} cm^{-1}, respectively) reported by Malkin *et al.*[70] seem to be overestimated. These values were obtained upon photolysis of dihydroquinolines **9a**,**c** in methylcyclohexane glasses at 77 K, and it was assumed that the buildup of absorption at $\lambda = 400$ nm was determined only by the amount of the generated radical, which was measured from the EPR spectra of the samples under stationary irradiation. The authors ignored the fact that the stable products of dihydroquinoline phototransformation, for example, dimers resulting from recombination in the solid phase, absorbed in the same range.

Primary photophysical and photochemical processes involved in the photolysis of dihydroquinolines **9** in hydrocarbon solvents have been considered by Malkin *et al.*[70,72,73] Spectral characteristics of the initial compounds and generated radicals have been determined; excitation decay pathways have been studied; and the quantum yields of fluorescence, intersystem crossing, and photochemical dissociation of the N–H bond under excitation by light with different wavelengths have been measured. It has been shown that the quantum yields of the aminyl radicals are low (0.01–0.02) under excitation in the long-wavelength absorption band, whereas the fluorescence quantum yield is high (0.2–0.4). An unusual behaviour of the reaction and fluorescence quantum yields as a function of excitation energy has been observed: upon excitation in the short-wavelength absorption band, the reaction quantum yield increases by an order of magnitude, while the fluorescence quantum yield decreases almost twofold.

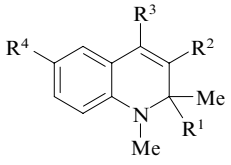
On the basis of experimental data and CNDO/S calculations (complete neglect of differential overlap), an energy level diagram for 1,2-dihydroquinolines has been suggested.[74] As is known, the repulsive term of the dissociating bond is triplet;[75] *i.e.*, the N–H bond dissociation can occur with a noticeable yield only from the triplet state. According to the energy level diagram and experimental data, the energy of the lowest triplet state of 1,2-dihydroquinoline (2 eV) is considerably lower than the N–H bond cleavage energy (~3.4 eV). Therefore, on excitation in the long-wavelength absorption band, photodissociation occurs from the lowest excited singlet state S_1 by a nonadiabatic mechanism with low quantum yield.[70,74] Upon excitation in the short-wavelength absorption band when the excited molecule is in the S_3 or S_4 state, the photodissociation of the N–H bond in dihydroquinolines presumably occurs from the higher antibonding triplet state formed through intersystem crossing from the S_3 or S_4 state.

Recent studies have shown that the yield of the triplet state upon photoexcitation of 1,2-dihydroquinolines can be increased by complicating the structure of a compound. In particular, furodihydroquinolines with the furan ring annelated to the benzene ring show a high yield of the triplet state upon photoexcitation in the long-wavelength absorption band.[76]

IV. Photophysical and photochemical processes in alkyl-, alkoxy- and hydroxy-substituted 1,2-dihydroquinolines in protic solvents

1. Products of photolysis of 1,2-dihydroquinolines in water and alcohols

The pathways of photochemical transformations of secondary (**9a**,**c**–**g**) and tertiary (**15a**–**e**) 1,2-dihydroquinolines strongly depend on the type of solvent (protic or aprotic) and the nature and position of the substituents in the heterocyclic and aromatic rings.

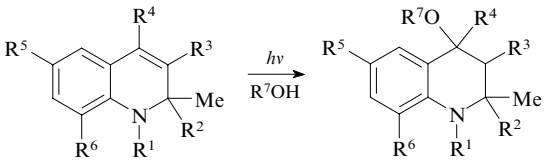


15a–**e**

Compound **15**	R^1	R^2	R^3	R^4
a	Me	H	Me	H
b	Me	H	Me	Me
c	Me	H	Me	OEt
d	Me	Me	H	H
e	H	H	H	Me

Upon photolysis of dihydroquinolines **9a**,**c**–**g** and **15a**–**e** in water or methanol, the solvent is attached to the double bond of the heterocycle to give 4-hydroxy- or 4-methoxy-1,2,3,4-tetrahydroquinolines **16** (Scheme 6).[77–82]

Scheme 6



9, **15** **16**

R^1, R^2, R^3, R^4 = H, Me; R^5 = H, Me, OH, OEt; R^6 = H, OH, OMe; R^7 = H, Me, Et, CH_2CF_3, Pr^n

Except the reaction of compound **9e**,[80] the other reactions occur almost quantitatively. Figure 1 shows the change in the absorption spectra of compound **15d** upon steady-state photolysis in MeOH.

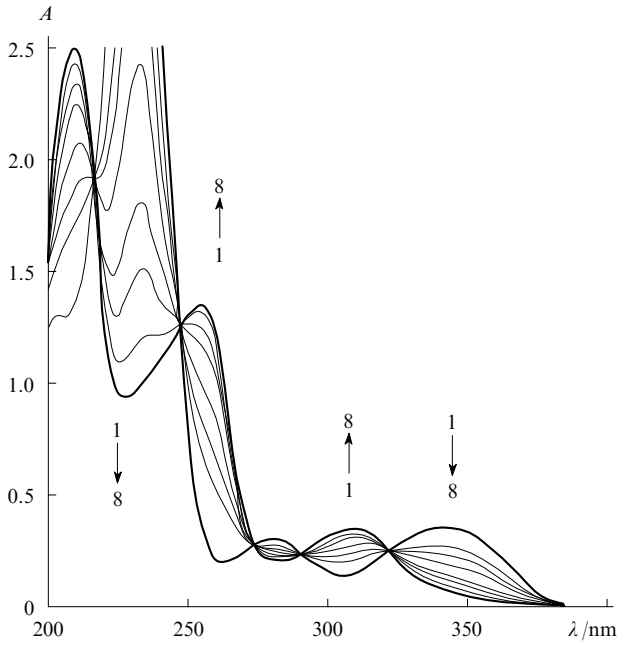


Figure 1. Evolution of the absorption spectra of compound **15d** upon stationary photolysis in MeOH.[82]
Time interval/min: 0 (*1*), 5 (*2*), 7 (*3*), 10 (*4*), 15 (*5*), 20 (*6*), 30 (*7*), 45 (*8*); [**15d**] = 2×10^{-4} mol litre^{-1}, $300 < \lambda_{ex} < 400$ nm.

Under these conditions, a protic solvent does not add in the case of nitro-substituted dihydroquinoline **9b**; rather, as noted above, light exposure leads to the reversible opening of the heterocycle (see Scheme 4).[37]

The photoreaction of 2,2,4-trimethyl-substituted dihydroquinolines **9a**,**c**–**g** in anhydrous ethyl and propyl alcohols occurs as in other organic solvents, *i.e.*, with formation of corresponding dimer **14**, whereas *N*-methyl-substituted analogues **15a**–**c** in these solvents are almost not subjected to photolysis. The addition of water or methanol results in the formation of a mixture of alkoxy and hydroxy adducts or of two alkoxy adducts rather than of the products of aminyl radical recombination.[83] Thus, the ethoxy and propoxy derivatives can be obtained only in mixture with the hydroxy and methoxy adducts. In dihydroquinolines **15d**,**e**, having no substituent in the 4-position, photolysis also occurs according to Scheme 6 in other normal alcohols, including 2,2,2-trifluoroethanol (TFE).[81,82] Isopropyl alcohol forms adducts with none of the studied dihydroquinolines because of steric hindrance.

The products of photolysis of dihydroquinolines in alcohols have been isolated and identified on the basis of UV and IR absorption spectroscopy, ^{1}H and ^{13}C NMR and mass spectrometry data. Physicochemical characteristics and spectra of 20 newly synthesized tetrahydroquinolines with HO, MeO, EtO, CF_3CH_2O and Pr^nO groups in the 4-position, as well as of the adduct with azide ion, have been reported.[78–82,84] Comparison of the photolysis products obtained in MeOH with the products of initiated thermal oxidation of dihydroquinolines in the same solvent unambiguously demonstrates that no aminyl radicals are generated in the photolysis in MeOH.[77]

2. Spectral and kinetic behaviour and photolysis mechanism of 1,2-dihydroquinolines in protic solvents

The kinetic behaviour of photoinduced water and methanol addition to 1,2-dihydroquinolines have been studied by the flash photolysis in a wide range of acid and base concentrations at different temperatures.[79–88]

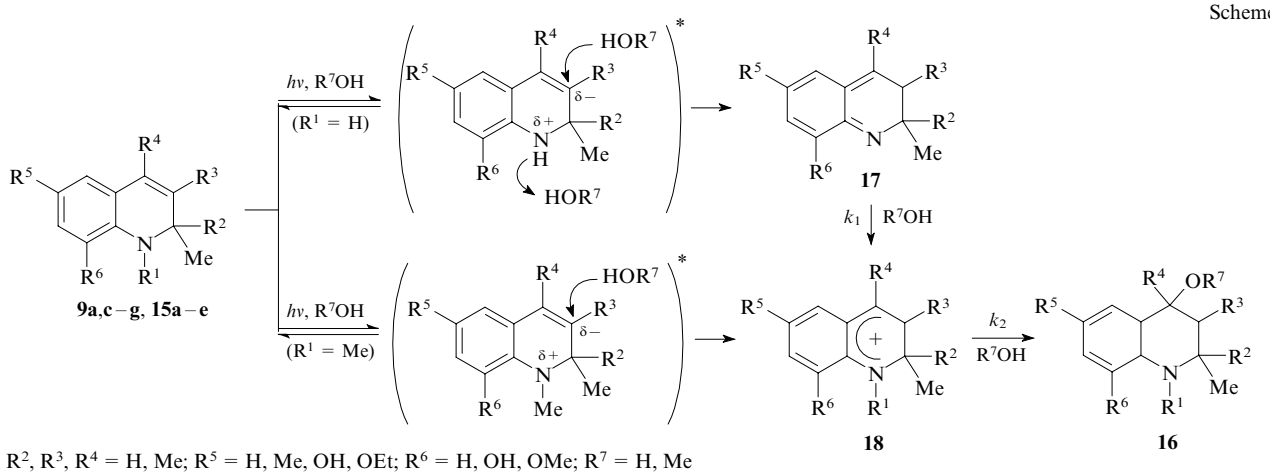
Photoexcitation in the long-wavelength absorption band of the initial dihydroquinoline (λ_{max} = 360–330 nm depending on the nature of the initial heterocycle and solvent) induces a single-quantum process originated from the S_1 excited state. Two transient species are formed successively in the photolysis in MeOH with λ_{max} at 410–420 and 480–500 nm, respectively. The introduction of an acid promotes the formation of the second intermediate, while only the first intermediate is formed in strong alkaline solutions.

On the basis of the kinetic analysis of experimental data and analysis of the reaction products, a mechanism of photolysis of dihydroquinolines **9a**,**c**,**d**,**f** and **15a**–**c** has been suggested,[85,86] which is also valid, with some variations, for the other studied dihydroquinolines (Scheme 7).

According to this mechanism, the primary intermediate in the case of secondary 1,2-dihydroquinolines is corresponding 2,3-dihydroquinoline **17** with the *o*-quinomethanimine structure (λ_{max} = 410–420 nm), which is protonated by the solvent to give carbocation **18** (R^1 = H) with λ_{max} = 480–500 nm. For tertiary dihydroquinolines, photolysis directly leads to carbocation **18** (R^1 = Me) followed by the nucleophilic addition of the solvent to yield 4-hydroxy- or 4-alkoxy-1,2,3,4-tetrahydroquinolines **16**.

The rate constants k_1 and k_2 obtained by the flash photolysis are presented in Table 1. The kinetic isotope effects (KIEs) of reactions measured in MeOD and MeOH confirm the suggested mechanism.[85,86] The KIE is 2 for k_1, which is typical of proton transfer reactions by the AS_E2 mechanism, and 1.2–1.3 for k_2, which is typical of the reactions of nucleophilic addition of the solvent to the carbocation.[91] According to the suggested mechanism, the introduction of electron-donating substituents into the aromatic ring stabilizes intermediate 2,3-dihydroquinoline (Table 1). For a series of compounds with a substituent in the 6-position, this effect is more clearly pronounced than for compounds with a substituent in the 8-position (cf. k_1

Scheme 7



R^1, R^2, R^3, R^4 = H, Me; R^5 = H, Me, OH, OEt; R^6 = H, OH, OMe; R^7 = H, Me

Table 1. Rate constants and activation energies for the reaction of intermediate species formed upon photolysis of 1,2-dihydroquinolines in water, methanol and TFE at 20 °C (error of measurements ±10%).

Compound	Solvent	k_1 /s^{-1}	k_2, /s^{-1}	E_1^a (see [a])	E_2^a (see [a])	Ref.
9a	H_2O	–	90	–	–	83
	MeOH	1400	2000	–	–	86
9c	H_2O	> 1000	22	0	49	85
	MeOH	310	600	0	31	85
	MeOD	155	390	–	–	85
9d	H_2O	–	5	–	–	83
	MeOH	22	80	0	38	86
9e	MeOH	28	78	–	–	80
9f	H_2O	> 1000	65	–	49	79
	MeOH	900	1830	15	30	79
9g	MeOH	–	870	–	–	80
15a	H_2O		100			83
	MeOH		1400			88
15b	H_2O		13		–	83
	MeOH		790		52	85
	MeOD		650		–	83
15c	H_2O		5.6		–	89
	MeOH		90		34	90
15d	H_2O		300		42	82
	MeOH		1.5×10^5		–	82
	TFE		1		25	82
15e	H_2O		3000		–	81
	MeOH		$> 10^5$		–	81
	TFE		81		–	81

[a] The E_1^a and E_2^a values are in kJ mol^{-1}.

for 2,3-dihydroquinolines **9a**, **9d** and **9f** in Table 1). Correspondingly, the lifetimes of transient species increase with an increase in the electron-donating ability of substituents in the aromatic ring. The maximal lifetime of 2,3-dihydroquinoline in a neutral MeOH solution is observed for compound **17** ($R^1 = R^3 = R^6 = H$, $R^2 = R^4 = Me$, $R^5 = OEt$) and the minimal lifetime, for compound **17** ($R^1 = R^3 = R^6 = R^5 = H$, $R^2 = R^4 = Me$). For compounds with substituents in the 6-position, the activation energy of the first reaction (E_1^a) is close to zero, whereas for dihydroquinoline **9f** E_1^a = 15.0 kJ mol^{-1}.

In the case of N-substituted tertiary dihydroquinolines **15a–e**, the carbocation decays *via* a first-order reaction with the rate constant close to k_2 for the corresponding carbocation generated from a secondary dihydroquinoline (Table 1). For carbocations, the longest lifetime is also observed for compounds with the ethoxy group in the 6-position.[88,89] The lack of a substituent in the 4-position (**15d**,**e**) significantly increases the rate constant of the solvent addition to the carbocation ($k_2 = 1.5 \times 10^5$ s^{-1} for the reaction of addition of MeOH to the carbocation formed from compound **15d**). The activation energies of reactions of carbocations derived from dihydroquinolines **9a–c** with alcohols are 30–40 kJ mol^{-1}, and in water, the activation energy increases to 50 kJ mol^{-1}. For dihydroquinolines **15d**,**e**, the activation energy of the reaction of the carbocation with the solvent is noticeably lower (Table 1).

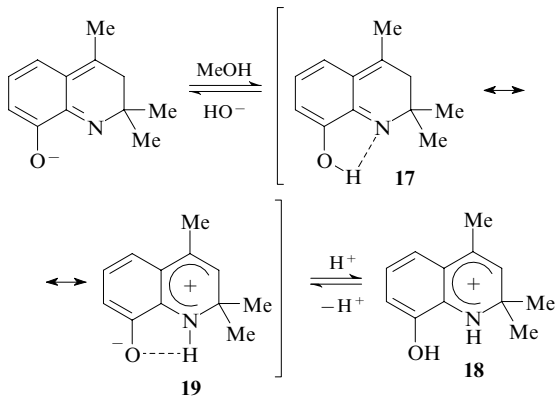
The rate constants for the reaction of 2,3-dihydroquinolines **9a**,**c**,**d**,**f** with AcOH are $(2-4) \times 10^8$ litre mol^{-1} s^{-1} (Ref. 86). The rate constants of the back reaction of the carbocations with alkali have also been determined: they are $2.5 \times 10^7 - 2.5 \times 10^8$ litre mol^{-1} s^{-1} for secondary dihydroquinolines **9a**,**c**,**d**,**f** and depend on the nature of substituents in the aromatic ring.[79,85,86] The rate constant of the reaction of the carbocation generated from N-substituted dihydroquinoline **15b** with alkali is 7×10^6 litre mol^{-1} s^{-1} (Ref. 92). It is worth noting that, for tertiary dihydroquinolines, this reaction is the interaction of the carbocation with the hydroxide anion resulting in 4-hydroxytetrahydroquinoline rather than acid–base equilibrium.[92] In neutral aqueous solutions, it is often impossible to register 2,3-dihydroquinoline by the lamp flash photolysis since its transformation to carbocation occurs on the microsecond time scale (Table 1): after a flash, the formation of the carbocation is immediately observed. In alkaline solutions, the lifetime of 2,3-dihydroquinoline increases to tens of milliseconds, so that its transformation to the carbocation can be detected by the flash photolysis.[78,82,84]

Study of photoinduced reactions that occur in solutions of hydroxyl-containing dihydroquinolines **9e**,**g** in methanol and water has shown that the direction and kinetic parameters of the reaction depend on the position of the hydroxy group in the aromatic ring. In MeOH, the major process for both compounds is still the photoinduced addition of a solvent molecule to the double bond of dihydroquinoline; however, the elevated acidity of the excited state leads to intermediates giving by-products upon transformations of

the excited phenolate ion. These processes are stimulated in aqueous solutions because of the possibility of acid–base transformations between intermediates generated from different forms of excited molecules **9e**,**g**.

As is known, intramolecular hydrogen bonding between the phenol group and the nitrogen atom changes the pK_a value and decreases the redox potential of compounds in which such a bond is present.[93] This is likely to account for the smaller contribution of side reactions in the case of dihydroquinoline **9g** as compared with compound **9e**, for which the intramolecular hydrogen bond between the phenol group and the nitrogen atom is impossible. Formation of the intramolecular hydrogen bond is responsible for the fact that, for compound **9g**, the corresponding intermediate 2,3-dihydroquinoline **17** exists as zwitterion **19** and is in acid–base equilibrium with carbocation **18** ($R^1 = R^3 = R^5 = H$, $R^2 = R^4 = Me$, $R^7 = OH$), which is the major intermediate not only in an acidic but also in a neutral medium (Scheme 8). The formation of zwitterion **19** manifests itself in the change in the absorption spectrum of the primary intermediate formed upon photolysis: λ_{max} is 600 nm as distinct from 420 nm for other secondary dihydroquinolines. The carbocation has a typical absorption spectrum with $\lambda_{max} = 500$ nm.

Scheme 8



The rate constants for the reactions of intermediate species with methanol increase by about an order of magnitude in going from compound **9e** to **9g**, analogously to other dihydroquinolines with substituents in the 6- and 8-positions.[80] For compound **9e**, the rate constants for the reactions of 2,3-dihydroquinoline and carbocation are close to the rate constants of these intermediates for derivative **9d** (Table 1), while for compound **9g**, the rate constant of the nucleophilic addition of MeOH to carbocation is nearly twice as low as the corresponding rate constant for the carbocation generated from dihydroquinoline **9f** (Table 1). It is worth noting that compound **9e** in water is involved in dark reactions yielding 5-hydroxy-3-methylindole as a major product; *i.e.*, the CMe_2 group is eliminated from the six-membered heterocyclic ring to give a five-membered ring, while the amino and phenol groups are retained.[80]

Thus, upon photolysis of 1,2-dihydroquinolines **9a**,**c**–**g** and **15a**–**e** in protic solvents, the key intermediate product is carbocation. As compared with many carbocations studied by pulsed methods,[94–96] the carbocations generated upon photolysis of 1,2-dihydroquinolines do not decay in a primary contact ion pair, are formed in high quantum yield, have relatively long lifetimes, and absorb in the visible spectral range. This makes them convenient model compounds for studying the reactivity of carbocations with respect to different alcohols and ions. Specific features of reactions of carbocations generated from 1,2-dihydroquinolines under the action of molecular and ionic nucleophiles in various protic solvents and their mixtures have been described in detail.[83, 84, 90, 92, 97, 98]

Yet another feature of the photoinduced addition of alcohols to 1,2-dihydroquinolines is that the alcohol is always added in such a way that the 3-position is protonated, and the alkoxy or hydroxy group is attached to the 4-position independently of the presence and position of methyl substituents in the heterocycle.[78, 81, 82] Hence, the addition of an alcohol to 4-methyl-substituted dihydroquinolines occurs formally according to Markovnikov's rule, whereas the addition to 3-methyl-substituted dihydroquinolines is an anti-Markovnikov reaction without a change in the reaction mechanism. This is due to the fact that the structure of the ultimate product is determined by the route of the light-induced proton transfer reaction, which depends on the charge distribution in the excited singlet state S_1, the configuration of the complex between the dihydroquinoline and alcohol molecules in the ground state (see below) and the stability of the generated carbocation. According to quantum chemical calculations, the major negative charge in the excited singlet state (S_1) of 1,2-dihydroquinolines is distributed over the C(3) (−0.133), C(5) (−0.111) and C(7) (−0.167) atoms.[74] Recent calculations‡ of the molecular electrostatic potential (MEP) in the excited Franck–Condon and relaxed S_1 states for compound **15b** have shown that MEP minima are in the 3-, 5- and 7-positions, and the magnitude of these minima is larger in the unrelaxed state. Formation of intermediate compounds through proton transfer to the C(3) atom is evidence that all necessary conditions for this reaction are fulfilled only in this case.

3. Dynamics of proton transfer from a solvent to 1,2-dihydroquinolines in the excited state

A specific feature of the photophysical behaviour of the dihydroquinolines under consideration in some solvents is the violation of Kasha's rule, which states that the fluorescence quantum yield is independent of the excitation wavelength. In the solvents where proton transfer does not take place (hexane, isopropyl alcohol), the fluorescence quantum yield is independent of the excitation wavelength within the limits of the long-wavelength absorption band. At the same time, in water and methanol, the fluorescence quantum yield noticeably decreases with a decrease in the excitation wavelength[99] indicating that proton transfer occurs probably from the unrelaxed excited state S_1^{FC} of dihydroquinoline.

The dynamics of the process has been studied by femtosecond laser spectroscopy.[100] It has been shown that, in the case of compounds **9c** and **15b** in hexane, acetonitrile or isopropyl alcohol, transient species [absorption maxima at 700, 450 nm (**9c**) and 700, 470 nm (**15b**)] generated upon photoexcitation by light with $\lambda_{ex} = 308$ nm decay on the subnanosecond time scale. Their lifetimes are close to the fluorescence lifetimes obtained by the single-photon counting method (for compound **9c**, they are 3.5, 7.5 and 5.7 ns in

‡ Unpublished data of O K Bazyl', V Ya Artyukhov and G V Maier, Tomsk State University.

hexane, acetonitrile and isopropyl alcohol, respectively[99]). This data are unambiguous evidence that the observed transient species is the excited singlet state (S_1) of dihydroquinoline.

In MeOH, in a time interval of 200–250 fs, not only the formation of species with the absorption characteristic of the excited singlet state S_1 but also the formation of transient species with λ_{max} at 410 (**9c**) and 490 nm (**15b**,**d**) has been observed.[100, 101] At delay times >500 fs, the spectral patterns do not change, and only the absorption of the excited singlet state decays with the rate constant corresponding to the fluorescence lifetime in MeOH.

Figure 2 shows the normalized absorption spectra of the intermediate carbocation formed upon photolysis of compounds **15b**,**d** in different protic solvents. The spectra of the reaction in MeOH are shown in Fig. 2 *a*: results of lamp flash photolysis are shown by the solid line,[85] and the circls correspond to the spectrum calculated from the dynamics of the decrease in transient absorption in femtosecond laser photolysis.[100] The spectra for the carbocation generated from compound **15d** in TFE are shown in Fig. 2 *b*: the lamp flash photolysis data are shown by the solid line,[82] and the femtosecond laser photolysis data are shown by the circls.[101] The close similarity between the absorption spectra of the transient species formed on the femtosecond time scale and the spectra of the primary transient species observed by the nanosecond laser and conventional flash photolysis for compounds **15b**,**d** is strong evidence that these transient species are formed from the unrelaxed excited singlet state in a few hundreds of femtoseconds.

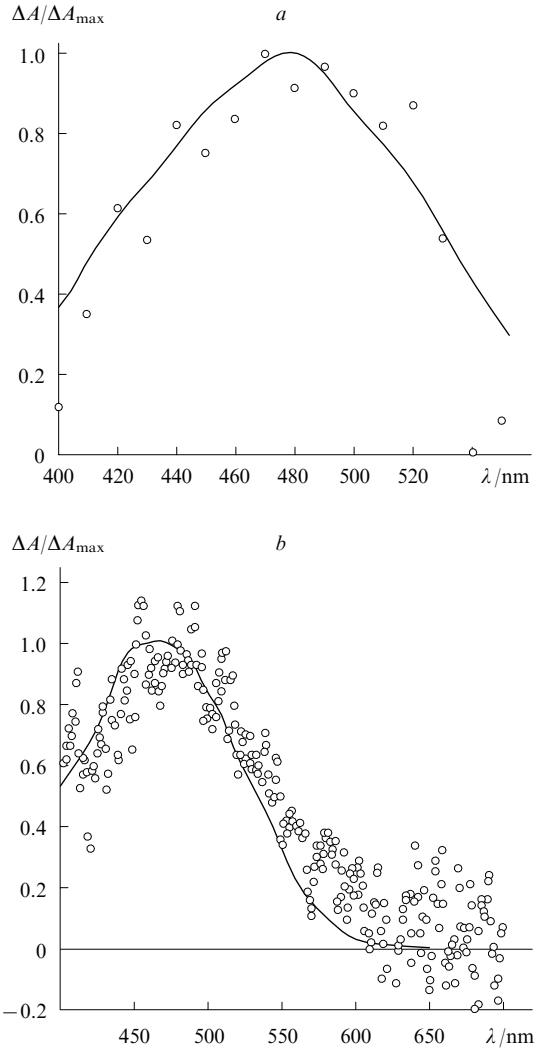


Figure 2. Normalized absorption spectra of the intermediate carbocation formed upon photolysis of compounds **15b** in MeOH (*a*) and **15d** in TFE (*b*).[82, 85, 100, 101]

As already mentioned, for dihydroquinoline **15d**, photoinduced proton transfer occurs not only in methanol and water but also in other normal alcohols. The reaction of compound **15d** in TFE is a good model for studying the carbocation formation dynamics since the lifetime of the excited state S_1 in this alcohol is considerably shorter (115 ps) than in methanol owing to efficient internal conversion. Therefore, both the formation of the carbocation and the decay of the S_1 state can be observed during the registration time (500 ps).[101]

In secondary dihydroquinolines, double proton transfer occurs: from the heterocyclic nitrogen atom to an alcohol molecule and from the alcohol molecule to the 3-position of the heterocycle; *i.e.*, there is formally the ene–imine rearrangement (see Scheme 7). In the ground state, this process does not occur. The proton is transferred along a bridge of several hydrogen-bonded MeOH molecules, as in the case of 7-hydroxyquinoline.[16, 17, 20, 22]

Comparison of changes in the fluorescence spectra of compound **9c** as a function of the composition of binary solvents in mixtures of methanol with hexane and pentane with the results of studying the photochemical reaction in these mixtures has shown that the proton transfer reaction occurs in a complex containing at least six alcohol molecules.[101, 102] This is consistent with theoretical and experimental results according to which formation of a hydrogen bond between the π system of aromatic compounds and water, ammonia or alcohol involves large clusters (no less than six molecules) since proton transfer in such systems is facilitated by cooperative interactions.[103–106] In the case of tertiary dihydroquinolines, single proton transfer occurs from an alcohol molecule to the C(3) atom of the heterocycle. Figure 3 shows major photophysical and photochemical processes that occur upon photoexcitation of dihydroquinoline **9c** in different solvents (PT is proton transfer, IC is internal conversion, ISC is intersystem crossing).

Proton transfer in the unrelaxed excited state means that the substrate–solvent complex in which the reaction occurs is formed in the ground state, and conformational and relaxation changes have no time to take place in the course of reaction.[19] Therefore, such processes are very sensitive to the nature of the medium. This fact accounts for many trends in the photolysis of 1,2-dihydroquinolines and the critical dependence of the process on the nature of the medium. In particular, for 4-methyl-substituted dihydroquinolines, the replacement of methanol by ethanol, which has close polarity, proton-donating ability and proton affinity values, leads to crucial changes in the reaction mechanism. The increase in the volume of the alkyl substituent in photolysis in ethanol prevents the formation of a complex with hydrogen bonds in the configuration necessary for the proton transfer reaction in the excited state.

The observed decrease in the proton transfer quantum yield in water is caused by the higher protonating ability of

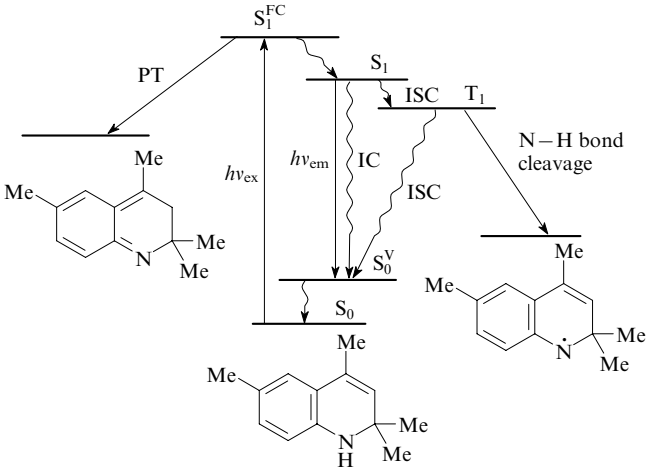


Figure 3. Major photophysical and photochemical processes that occur upon photoexcitation of dihydroquinoline **9c** in different solvents (see text).

this solvent as compared with MeOH. The small size of the water molecule is responsible for the formation of a complex in which the nitrogen atom of the heterocycle is mainly protonated. This configuration of the complex is unfavourable for proton transfer to the 3-position in the excited state. Thus, the size of the methanol molecule and its amphiphilicity are optimal for the proton transfer reaction in the complex with the excited 1,2-dihydroquinoline molecule. As distinct from water, in TFE, which also strongly protonates the nitrogen atom of the heterocycle, the quantum yield of proton transfer to the C(3) atom for compound **15d** is almost equal to the quantum yield in methanol. In addition, in TFE, the fluorescence quantum yield decreases by more than an order of magnitude and, as mentioned above, the lifetime of the S_1 excited state decreases by almost an order of magnitude. These observations point to strong internal conversion $S_1 \rightarrow S_0$ caused by the formation of a complex with strong hydrogen bonds between the hydrogen atom of TFE molecules and both the nitrogen atom of the heterocycle and the π system of the aromatic ring and heterocycle.[101, 107]

A fundamental difference of the proton transfer reaction in the case of 1,2-dihydroquinolines from most of the known tautomeric equilibria, also occurring on the femtosecond time scale, is its irreversibility. This transformation involving the solvent is one of few examples of nonadiabatic reaction that occurs on the femtosecond time scale.

* * *

1,2-Dihydroquinolines are unique compounds for which the photolysis direction, mechanism and kinetic behaviour are extremely sensitive to the nature of substituents in the aromatic ring and heterocycle, as well as to the nature of the medium in different transformations ranging from primary photophysical and photochemical processes to thermal reactions of key intermediate products, aminyl radicals and carbocations. The effect of the microenvironment of 1,2-dihydroquinoline molecules is especially clearly pronounced in micellar solutions. As is known, in cationic micelles of cetyltrimethylammonium bromide (CTAB), the 1,2-dihydroquinoline molecules are mainly located in the hydrophobic micelle core, whereas in anionic micelles of sodium dodecylsulfate (NaDDS), they are located in the Stern layer.[108] This is responsible for the fact that photolysis of 1,2-dihydroquinolines in NaDDS micelles occurs analogously to photolysis in aqueous solutions, *i.e.*, with formation of carbocations, whereas in CTAB micelles, there is independent formation of aminyl radicals in the hydrophobic micelle core and of carbocations in the Stern layer.[89]

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