

Photoaddition of water and methanol to 2,2,4,6-tetramethyl-1,2-dihydroquinoline

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Products of the steady-state photolysis of 2,2,4,6-tetramethyl-1,2-dihydroquinoline (**1**) in water, methanol, and water–ethanol were isolated for the first time and identified by ¹H and ¹³C NMR spectroscopy, IR spectroscopy, and mass spectrometry. As a result of the photolysis, the molecule of the solvent is added to the double bond of the heterocycle with formation of 4-hydroxy- (**2**) or 4-methoxy-2,2,4,6-tetramethyl-1,2,3,4-tetrahydroquinoline (**3**) in water and methanol, respectively. Compounds **2** and **3** are converted gradually into **1** in the dark. The rate of the back reaction depends on the solvent and the concentration of the product. Comparison of the products of the photolysis in methanol and hexane at 45 °C and of the azoisobutyronitrile-initiated oxidation of **1** at the same temperature has shown that unlike the photolysis in hexane, aminyl radicals are not precursors of the product of the photolysis in methanol. The reaction proceeds via an excited singlet state.

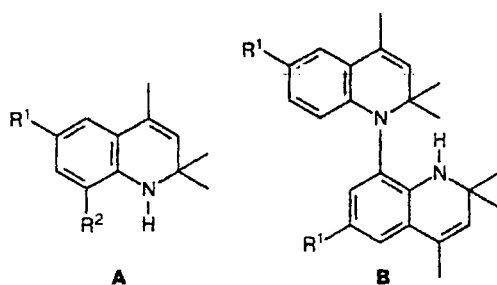
Key words: 1,2-dihydroquinolines, photoaddition to the double bond, steady-state photolysis, effect of a solvent, ¹H and ¹³C NMR.

Effect of the medium on the mechanism and kinetics of chemical transformations is one of the key problems of modern physical chemistry. The polarity of medium and hydrogen bonding between a reagent and a solvent play the most important role in this phenomenon. We have found earlier that the nature of the solvent affects the direction and the kinetics of photolysis of 2,2,4,6-tetramethyl-1,2-dihydroquinoline (**1**).¹

6-Substituted and partly hydrogenated quinolines of general formula **A**, especially ethoxyquin ($R^1 = \text{EtO}$ and $R^2 = \text{H}$), are widely used as antioxidants and antiozonants for rubbers,² as stabilizers for vitamin A and β -carotene in feed, and as a post-harvest dip for apples.^{3,4} Upon photolysis of these compounds in organic solvents (alkanes, benzene, toluene, and propan-2-ol), the hydrogen atom is split out from the molecule of dihydroquinoline and an aminyl radical is formed, which decays

at the ambient temperature predominantly in recombination reaction⁵ giving a 1-8'-dimer **B**.^{6,7} The rate constants of the recombination of the transient radicals measured by flash-photolysis⁵ and by ESR⁷ are close and vary from 10^6 to 10^7 L mol⁻¹ s⁻¹ depending on the substituent in position 6 and the solvent character. If the parent 1,2-dihydroquinoline has a substituent $R^2 \neq \text{H}$ in position 8, the rate constant for radical decay dramatically decreases and becomes equal to 10^2 L mol⁻¹ s⁻¹.⁷

The photolysis of aqueous solutions of compound **1** (**A** with $R^1 = \text{Me}$ and $R^2 = \text{H}$) gives a product the absorption spectrum of which significantly differs from that of the dimer.¹ The kinetics of the decay of the transient species changes crucially: it follows the first-order law with the rate constant depending on pH and varying from 25 s⁻¹ in acidic and neutral solutions to 3.9 s⁻¹ in alkaline solutions¹ at the pH range corresponding to the value of pK_a 10.4 measured for the transient species.⁸ These experiments pose a number of questions concerning the mechanism of the reaction in aqueous solutions; as well as the nature of the transient species and the final product. In this work, we tried to answer some of them: we identified the product of the photolysis of **1** in water and showed that the photolysis in methanol and water–alcohol mixtures occurred in a similar way. We carried out experiments that allowed us to make preliminary conclusions about the nature of transient species.



Experimental

2,2,4,6-Tetramethyl-1,2-dihydroquinoline (**1**), m.p. 42 °C (Voikov Plant for Chemical Reagents, Reakhim, Russia), was sublimed *in vacuo*. Methanol for spectroscopy (Merck) and bidistilled water were used. Azobisisobutyronitrile (AIBN) was successively recrystallized from benzene and ethanol.

A steady-state photolysis of solutions of amine **1** and other 1,2-dihydroquinolines ($\sim 10^{-4}$ mol L $^{-1}$) was carried out with a DRS-1000 mercury lamp in quartz cells with a path length of 1 cm at the ambient temperature and at 45 °C. The long-wave band of compound **1** was excited ($\lambda_{\max}(\text{H}_2\text{O})$ 335 nm and $\lambda_{\max}(\text{MeOH})$ 343 nm) with the use of a UFS-5 filter transparent in the range 290–400 nm. In order to isolate and identify the product, a preparative-scale photolysis of solutions of compound **1** in the concentration of $(1-3) \cdot 10^{-3}$ mol L $^{-1}$ (~ 10 mg in 20 mL) was carried out. The solubility of **1** in water is $\sim 3 \cdot 10^{-4}$ mol L $^{-1}$; that is why to synthesize the product formed in water, we used water–ethanol mixtures. By ^1H NMR, it was shown that in the H_2O – EtOH 3 : 1 (vol/vol) mixture the same product was formed that did in water. Therefore, this mixture was used for the synthesis of this compound. When the concentration of ethanol in the mixture was higher, two products were formed (see Results and Discussion). The preparative-scale photolysis was carried out in a Pyrex flask with the use of a magnetic stirrer by the full light of the mercury lamp. In this case, Pyrex served as a light filter. The reaction was controlled by spectrophotometry in quartz cells with a path length of 0.2 cm, taking the samples periodically. Isobestic points in the spectra following the phototransformation indicate the quantitative formation of the one product in the course of the photolysis. Under these conditions, the duration of conversion of compound **1** into the product in the water–alcohol and methanol solutions is about 2 h. When the reaction was accomplished, the solvent was removed by distillation *in vacuo* at the ambient temperature, and the solid residue was analyzed without purification or in some cases (for compound **3**) after sublimation *in vacuo*. The products isolated were white fine-crystalline powders. The NMR and IR spectra before and after sublimation coincided completely. Identification of the compounds obtained in water, methanol, and ethanol was

carried out by ^1H and ^{13}C NMR and mass spectrometry and IR spectroscopy.

^1H and ^{13}C NMR spectra were recorded with a Bruker WM-250 NMR spectrometer. CDCl_3 , CD_3OD , and $(\text{CD}_3)_2\text{SO}$ were used as solvents. Tetramethylsilane served as a standard. IR spectra were recorded with a Perkin–Elmer 1720X FTIR spectrometer by the diffuse reflection-absorption technique⁹ using a PEDR device.

Mass spectra were obtained on a Varian MAT-311A GLC–MS instrument under standard conditions: the energy of ionizing electrons 70 eV, cathodic emission current 1 mA, accelerating voltage 3 kV, and resolution $M/\Delta M = 2000$. Absorption spectra in UV and visible regions were recorded with a Specord UV-VIS spectrophotometer in quartz cells with a path length of 1 and 0.2 cm depending on the initial concentration of compound **1**.

Thermal generation of the radicals from **1** was carried out in thermostatically controlled quartz cells with a path length of 1 cm in a cell compartment of a Specord UV-VIS spectrophotometer in the presence of the initiator of free radicals AIBN. The rate of initiation was $2.5 \cdot 10^{-8}$ mol L $^{-1}$ s $^{-1}$, initial concentration [**1**] $2 \cdot 10^{-4}$ mol L $^{-1}$, the temperature 45 °C, and the reaction time 2 h. The consumption of **1** and the formation of reaction products were followed by spectrophotometry. A solution of AIBN of the same concentration as in the working cell was used as a reference. When the reaction was accomplished, the reaction mixture was analyzed by TLC on Silufol using a hexane–ether mixture 3 : 1 (vol/vol) as an eluent and was compared with the mixture obtained upon photolysis.

Results and Discussion

As shown elsewhere,¹ the absorption spectrum of the product of the photolysis of amine **1** in water differs significantly from that of the parent compound. In this work, we have found that the photolysis of compound **1** in anhydrous methanol and ethanol containing water occurs similarly. However, despite the closeness of the absorption spectra in the UV–VIS region (see Table 1), different products are formed in water and methanol,

Table 1. Melting points, R_f , and UV, IR, and mass spectra of compounds **1**–**3**

Compound	M.p. / °C	R_f	UV spectrum (MeOH), λ/nm ($\epsilon/10^{-3}$ mol $^{-1}$ L cm $^{-1}$)	IR spectrum, ν/cm^{-1}	Mass spectrum, m/z (I_{rel} (%))*
1	42	0.53	232 (25.03), 270 (sh. 2.15), 343 (1.89)	3360, 2961, 2918, 2856, 1655, 1609, 1581, 1500, 1479, 1435, 1374, 1364, 1305, 1275, 1261, 1241, 1199, 1153, 879, 805	187(13) – $[\text{M}]^+$, 173(15), 172 (100), 171(20), 157(5), 156(5), 128(6), 115(6), 77(5)
2	149–151	0.18	214 (13.36), 246 (8.52), 305 (1.79)	3322, 3309, 3258, 2962, 2925, 2919, 2867, 1618, 1504, 1473, 1451, 1438, 1395, 1382, 1366, 1333, 1285, 1246, 1231, 1180, 1163, 1144, 1128, 1079, 1050, 1007, 933, 924, 885, 812	206(6), 205(43) – $[\text{M}]^+$, 191(8), 190(61), 187(7), 173(14), 172(100), 171(13), 157(8), 148(18), 132(6), 91(5), 77(5)
3	78–80	0.37	210 (24.00), 245 (9.24), 308 (1.71)	3330, 2963, 2928, 2918, 2861, 2858, 2825, 1618, 1505, 1474, 1456, 1438, 1371, 1363, 1300, 1283, 1256, 1232, 1143, 1127, 1071, 1050, 887, 838, 814	219(8) – $[\text{M}]^+$, 204(6), 187(5), 173(14), 172(100), 171(13), 157(8), 156(6), 148(6), 132(5), 128(5), 115(6), 77(5)

*The peaks of ions with intensity $\geq 5\%$ of I_{max} are given.

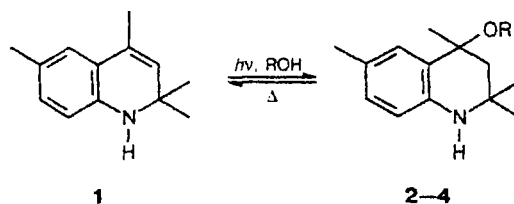
compounds **2** and **3**, respectively. During the conversion of **1** into the product, isobestic points are observed in the absorption spectra, indicating quantitative transformation. Similar changes in the absorption spectra were also observed during photolysis in water, methanol, and water–ethanol of other dihydroquinolines **A** with different substituents in position 6 ($R^1 = H, EtO, OH$).

It is worth noting that unlike methanol, the phototransformation in anhydrous ethanol occurs as in other organic solvents with the formation of the dimer. As water is added, the reaction of recombination of the transient aminyl radical turns into decay of the transient species giving a mixture of products **2** and **4** with **2** predominating. Therefore, in contrast to compounds **2** and **3**, compound **4** can be synthesized only as a mixture with **2** and even at low concentrations of water in the solvent its yield does not exceed 40%. In the water–ethanol mixture 3 : 1 (vol/vol), only compound **2** is formed. We did not separate compounds **2** and **4** because of their low stability (see below), and the 1H NMR spectrum of compound **4** was obtained from the spectrum recorded for the mixture of products **2** and **4**.

The analysis of the structures of compounds **2–4** (see Tables 1 and 2) indicates that in the photolysis of **1** the solvent molecule is added to the double bond of the heterocycle to give a corresponding tetrahydroquinoline. The phototransformation of **1** in water, methanol, and water–ethanol mixtures may be described by Scheme 1.

The 1H NMR spectra of the products synthesized in water (**2**), methanol (**3**), and water–ethanol solutions (**2** + **4**) strongly differ from the spectrum of starting **1** (see Table 2). In position 3 of the products, there appear two geminal hydrogen atoms with a difference between the shifts of protons H_a and H_b and their spin-

Scheme 1



$R = H$ (**2**), Me (**3**), Et (**4**).

spin coupling constants growing as the steric effect of the substituent OR in position 4 increases. Unlike the spectrum of amine **1**, in the product of photolysis, the signals of the protons of two methyl groups in position 2 become nonequivalent, as is typical of saturated cycles of this kind. In DMSO, we observed two signals belonging to mobile protons in compound **2** and only one signal of a mobile proton in compounds **3** and **4**; new groups, Me and Et, respectively, were registered in compounds **3** and **4**.

Fully decoupled and off-resonance ^{13}C NMR spectra of compound **2** in DMSO- d_6 confirm the proposed structure. In high fields, four signals of methyl groups (20.58, 28.65, 30.72, and 32.35 ppm), a signal of methylene carbon at 50.90 ppm, and two signals of quaternary carbon atoms in positions 2 and 4 (48.70 and 66.90 ppm) are observed. In the range of the signals of aromatic carbon atoms, signals of three CH groups at 114.55, 127.15, and 128.06 ppm and of three quaternary atoms at 123.87, 127.37, and 141.51 ppm are observed. In a mixture of H- and D-methanol the signal of the carbon atom in position 4 splits in two signals at 69.27 and 69.15 ppm with an isotopic effect of 0.12 ppm

Table 2. Proton chemical shifts (δ) and spin-spin coupling constants (J) of compounds **1–4** in DMSO- d_6

Compound	δ									J/Hz		
	N(1)H	C(2)Me ₂	C(3)H _a H _b	C(4)Me	C(4)OR	C(5)H	C(6)Me	C(7)H	C(8)H	H _a ,H _b	H(5),H(7)	H(7),H(8)
1	5.50 (1 H)	1.16 (6 H)	5.24 (1 H)*	1.87 (3 H)		6.75 (1 H)	2.12 (3 H)	6.68 (1 H)	6.35 (1 H)	—	2.1	8.1
2	5.09 (1 H)	1.13 (3 H) 1.18 (3 H)	1.68 (1 H) 1.84 (1 H)	1.38 (3 H)	4.39 (1 H)	7.09 (1 H)	2.14 (3 H)	6.69 (1 H)	6.37 (1 H)	13.7	2.1	8.1
3	5.32 (1 H)	1.12 (3 H) 1.17 (3 H)	1.49 (1 H) 2.05 (1 H)	1.40 (3 H)	2.94 (3 H)	6.96 (1 H)	2.14 (3 H)	6.74 (1 H)	6.40 (1 H)	14.1	2.1	8.1
4	5.29 (1 H)	1.15 (3 H) 1.19 (3 H)	1.50 (1 H) 2.06 (1 H)	1.41 (3 H)	0.98 (3 H) 3.19 (2H)	6.97 (1 H)	2.14 (3 H)	6.73 (1 H)	6.40 (1 H)	14.3	2.1	8.1

*The far constants of spin-spin coupling J with C(4)Me (1.3 Hz) and NH (1.9 Hz) for the signal of the C(3)—H vinyl proton are found.

typical of alcohols. The signal in the lowest field is attributed to the carbon atom in position 10, which is bound to the amino group, and in the mixture of H- and D-methanol it also gives an isotopic effect (142.47 and 142.32 ppm).

The masses of molecular ions ($[M^+]$) of compounds 2 and 3 m/z 205 and 219, respectively, correspond to the products of addition of water and methanol to the starting 1. In the initial step of the fragmentation of amine 1, the methyl radical is split away from the quaternary carbon atom giving quinolinium cation; then elimination of the H atom and the methyl group occurs giving corresponding radical ions of trimethyl- and dimethylquinoline. Similar processes have been described in detail.^{10,11} In the mass spectra of the products of the photolysis in water and methanol (see Table 1), similar aromatization of the cycle occurs only after elimination of the neutral molecules H₂O and MeOH from M^+ (ion with m/z 187). The distinguishing feature of the tetrahydroquinoline structure of compounds 2 and 3 is a retrodiene decay that takes place for M^+ . As a result, a CH₃C(OR)CH moiety splits out accompanied by a migration of the hydrogen atom into the benzene ring to give a fragment with m/z 148.¹²

Significant changes were also observed in the IR spectra of the products in comparison with compound 1 (see Table 1). The band of the stretch mode of the NH group shifts from 3360 cm⁻¹ in the initial amine 1 to 3330 cm⁻¹ in compound 3, and in compound 2 two bands attributed to the alcohol and amine moieties are observed: a strong band at 3257 cm⁻¹ and a weaker one in the form of a doublet at 3350 and 3340 cm⁻¹. It is worth mentioning for comparison that in 2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline (5) this band is at 3350 cm⁻¹. Instead of styrene absorption in the parent amine 1 at 1665, 1609, and 1581 cm⁻¹, in products 2 and 3 one strong band appears at 1618 cm⁻¹. In tetrahydroquinoline 5 two bands at 1603 and 1581 cm⁻¹ are observed in this range. In the range from 1200 to 1000 cm⁻¹, the bands characteristic of bend and stretch modes of the C—O group in alcohols and ethers appear.

Compounds 2, 3, and 4 are relatively unstable and in the dark spontaneously are converted predominantly into the parent dihydroquinoline 1. The rate of the conversion depends on the solvent and the concentration of the product. In chloroform, the reaction can be followed by spectrophotometry and ¹H NMR. It is completed in a day. In methanol, it occurs in several days. When the conversion of compound 3 into the initial 1 is carried out in methanol, the intensity of the signal of the OMe group decreases and simultaneously the signal of the solvent (3.30 ppm) increases at the expense of liberating methanol. In DMSO, noticeable changes in the ¹H NMR spectrum are observed only in a week. The decomposition of compound 2 in water at 50 °C is close to a second-order reaction with a rate constant of 0.09 L mol⁻¹ s⁻¹. It is worth noting that the rate of this reaction depends weakly on

the temperature. In TLC on Silufol compounds 2 and 3 quantitatively turn into the starting amine 1 when not eluted immediately after application but in 15 min.

As mentioned above, in the photolysis of 1,2-dihydroquinolines in organic solvents, aminyl radicals are the primary products, which recombine giving dimeric products. The same products are formed when the reaction of hydrogen abstraction is initiated thermally with initiators of radical reactions, for example, AIBN. In order to identify the nature of the transient species of the photoreaction in water and methanol, we compared the composition of products of the steady-state photolysis of 1 in methanol and hexane at 45 °C and the products of the reactions of the radicals from 1, which were generated in methanol with the use of AIBN at the same temperature. Variations in the absorption spectra and TLC have shown that as a result of the photolysis in hexane and the thermal reaction with initiator in methanol, the dimer and a small amount of 2,4,6-trimethylquinoline, the product of high-temperature transformation of the aminyl radical mentioned, are formed. 2,4,6-Trimethylquinoline has a characteristic absorption band with fine structure in the range of 305–330 nm and thus can be easily identified.¹³ Compound 3 was found neither by spectrophotometry (Fig. 1, curves 1–7) nor by TLC. When the photolysis is carried out in methanol at 45 °C, the reaction proceeds as at ambient temperature, is completed in thirty minutes, and gives only compound 3 (Fig. 1, curve 8).

Compound 3 being an aromatic amine like the starting dihydroquinoline 1 might behave as an antioxi-

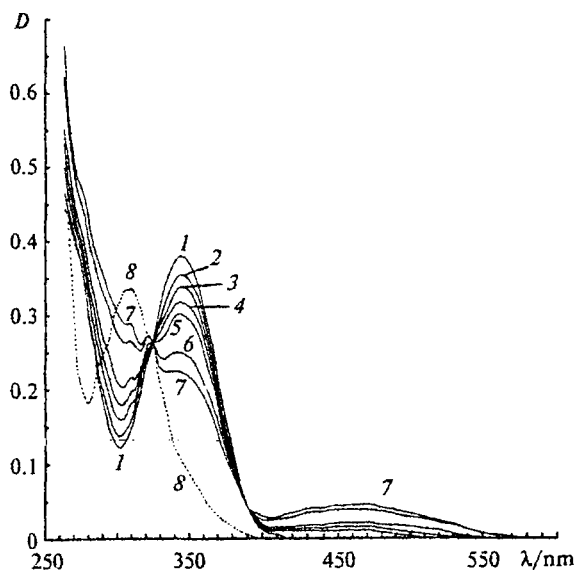
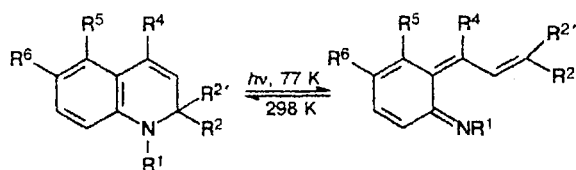


Fig. 1. The changes in the absorption spectrum of compound 1 during initiated oxidation in methanol with AIBN as an initiator, w_i $2.5 \cdot 10^{-8}$ mol L⁻¹ s⁻¹, the reaction time/min: 0 (1), 15 (2), 30 (3), 45 (4), 60 (5), 90 (6), and 120 (7); the product of photolysis of 1 in methanol (8); [1] $2 \cdot 10^{-4}$ mol L⁻¹, 45 °C.

dant and be consumed in the reaction with free radicals in the presence of AIBN. However, upon incubation of the solution of this compound in methanol in the thermostatically controlled cells of the spectrophotometer at 45 °C in the presence of AIBN for two hours, the variations in the absorption spectrum were negligible, indicating relative stability of **3** under these conditions. The absence of **3** in the mixture of the products of the thermal reaction with initiator cannot also be rationalized in terms of a competition between the reaction of recombination of the aminyl radical and the reaction of formation of compound **3**. If this competition took place at the thermal initiation, it would also take place during the photolysis. Hence, the absence of compound **3** in the thermal reaction as well as the absence of the dimer and quinoline, the products of transformation of the aminyl radical, in phototransformation in methanol indicates that these reactions proceed *via* different transient species, although the absorption spectra of these species are close. This was the main reason for the incorrect assumption made in^{1,8} that the aminyl radical and radical cation are transient species in the reaction in aqueous solution. Currently, study of the nature of the active transient species formed in water and methanol is in progress.

The reaction found is characteristic for dihydroquinolines without substituents at the nitrogen atom. For the photolysis of *N*-substituted dihydroquinolines in a solid ether—*i*-pentane—ethanol matrix (5 : 5 : 2), a cleavage of the C(2)—N bond in the heterocycle was suggested^{14,15} to account for the formation of colored products at -196 °C (Scheme 2).

Scheme 2

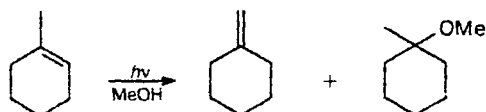


It is worth noting that in these works the photoproduct was not isolated and identified for the majority of dihydroquinolines under study because of its instability and conversion into the starting compound upon heating to ambient temperature. The structure was assumed by analogy with corresponding chromenes. Only for the compound with $R^1 = \text{CN}$, $R^2 = \text{OH}$, and $R^{2'} = R^4 = R^5 = R^6 = \text{H}$, was the product of the cleavage of the C(2)—N bond in the heterocycle, a stable *N*-cyano-*o*-aminocinnamic aldehyde, identified. As assumed by the authors¹⁵, this product was formed from the unstable colored product upon heating to the ambient temperature as the result of keto-enol tautomerization. Recently,¹⁶ the product of the scission of the C(2)—N bond upon the photolysis of *N*-acetyl-2,2,4-trimethyl-

1,2-dihydroquinoline in dioxane at room temperature was isolated and identified. The process occurs according to Scheme 2 for $R^1 = \text{Ac}$, $R^2 = R^{2'} = R^4 = \text{Me}$, and $R^5 = R^6 = \text{H}$.

The photoaddition of methanol and water to the double bond has been intensely studied for the last three decades.^{17–20} The closest to the transformation under consideration is the photoaddition of methanol to the double bond of 1-methylcyclohexene and related compounds upon irradiation in the presence of an aromatic sensitizer (benzene, toluene, or xylene).^{17,18} This reaction proceeds in parallel with the reaction of formation of exocyclic isomer (Scheme 3).

Scheme 3



The mechanism involving the formation of a carbonium ion, which either converts into the exocyclic isomer or adds the solvent, was suggested.¹⁷ In the photolysis of phenylbutadiene in methanol, along with a dimer and 2-phenylbutene, various isomers with the methoxy group are formed.¹⁹ Unlike these compounds, in the case of dihydroquinoline **1**, the photoaddition of water, methanol, and other alcohols proceeds practically quantitatively giving no side products. No sensitizer is needed for the reaction. Dihydroquinolines under study have two absorption bands in the UV range (see Table 1). The reaction under consideration proceeds immediately upon excitation of the long-wave band. The direction of the reaction and the yield of the products do not depend on the presence of oxygen. This indicates that the process occurs *via* the excited singlet rather than the triplet state.

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