Dual reactivity of an intermediate cation formed in the photolysis of dihydroquinolines in methanol

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Photolysis of 2,2,4,6-tetramethyl- (**1**) and 1,2,2,4,6-pentamethyl-1,2-dihydroquinoline (**2**) in methanolic alkali yields only 4-methoxy-2,2,4,6-tetramethyl-1,2,3,4-tetrahydroquinoline in the former case and a mixture of 4-methoxy- and 4-hydroxy-1,2,2,4,6-pentamethyl-1,2,3,4-tetrahydroquinoline in the latter case. This result was rationalized by the existence of two resonance structures of an intermediate cation, *viz*., carbocationic and *ortho*-quinomethaneiminium species. The cation from **1** reacts with an alkali in the *ortho*-quinomethaneiminium form, and the cation generated from **2** reacts in the carbocationic form.

Key words: 1,2-dihydroquinolines, photoaddition to double bond, steady-state photolysis, ^{1}H NMR spectroscopy, reactivity of a carbocation, resonance structures.

It has previously[1—4] been shown that the photolysis of 2,2,4-trimethyl-1,2-dihydroquinolines (DHQ) with different substituents in positions 1, 6, and 8 in methanol or water resulted in the Markownikoff addition of a solvent molecule to the double bond of DHQ to form 4-methoxy or 4-hydroxy derivatives of the corresponding tetrahydroquinolines (THQ) (Scheme 1). In the case of secondary DHQ (R = H), the successive formation of two intermediate species with the lifetimes from unities to tens of milliseconds, depending on the nature of substituents in the aromatic ring, was observed by the flash photolysis method.[3—5] The kinetic studies performed in a wide interval of alkali and acid concentrations indicate that cyclic *o*-quinomethaneimine is the first intermediate species, which is protonated by the solvent to form an intermediate cation. In the case of tertiary DHQ (R = Me), only one intermediate product (cation) was observed 10 ns after the exciting pulse in acidic, neutral, and alkaline solutions.[3] Most likely, in this case a zwitterion is the precursor of the cation.

The absorption spectra and rate constants for decay of the cations formed from 2,2,4,6-tetramethyl- (**1**) and 1,2,2,4,6-pentamethyl-1,2-dihydroquinoline (**2**) in acidic and neutral solutions of MeOH are similar: k_2 at ~20 °C are equal to 600 and 790 s^{-1} for DHQ **1** and **2**, respectively. However, the behavior of these compounds in alkaline media differs sharply.[3] In the case of DHQ **1** in alkaline solutions, no cation is formed, and the lifetime of its precursor, *o*-quinomethaneimine, increases by almost two orders of magnitude, *viz*., to 250 ms at $[KOH] > 10^{-3}$ mol L^{-1}. The yield of the adduct remains ~100%, and the quantum yield of the reaction decreases slightly. In the case of compound **2**, the addition of an alkali shortens the lifetime of the cation. The rate constant for quenching of the latter by an alkali ($k_{2'}$) is equal to $7 \cdot 10^6$ L mol^{-1} s^{-1}. As for compound **1**, the quantum yield of the reaction remains virtually unchanged up to $[KOH] = 5 \cdot 10^{-4}$ mol L^{-1} at a ~100% yield of the adduct.

The obtained experimental results were interpreted[3] from the viewpoint of the existence of two resonance structures of the cation that formed, *viz*., carbocationic and *o*-quinomethaneiminium structures. An increase in the lifetime of the first intermediate species in the case of compound **1** was explained by the reverse reaction of the cation in the *o*-quinomethaneiminium form with KOH (k_{-1}) (Scheme 2). The k_{-1} value calculated from the kinetic data was $2.5 \cdot 10^7$ L mol^{-1} s^{-1}.[3] In the case of compound **2**, this reaction should afford the same intermediate product as that in the case of compound **1**. However, no *o*-quinomethaneimine formation was detected by pulse photolysis of compound **2** in the presence of alkali, and no adduct derived from compound **1** was found in the reaction products. Thus, it is evident that this reaction does not occur. Quenching of the cation generated from compound **2** by alkali can be attributed to its reaction in the carbocationic form with KOH to form the hydroxy adduct (see Scheme 2).

Thus, if the assumption about the different mechanisms of the reaction of the intermediate cations generated from DHQ **1** and **2** with alkali is valid, the formation of the hydroxy adduct along with methoxy adduct should be expected upon photolysis of compound **2** in methanolic alkali. Unfortunately, the reaction products, especially hydroxy adducts, decompose in the light in an alkaline

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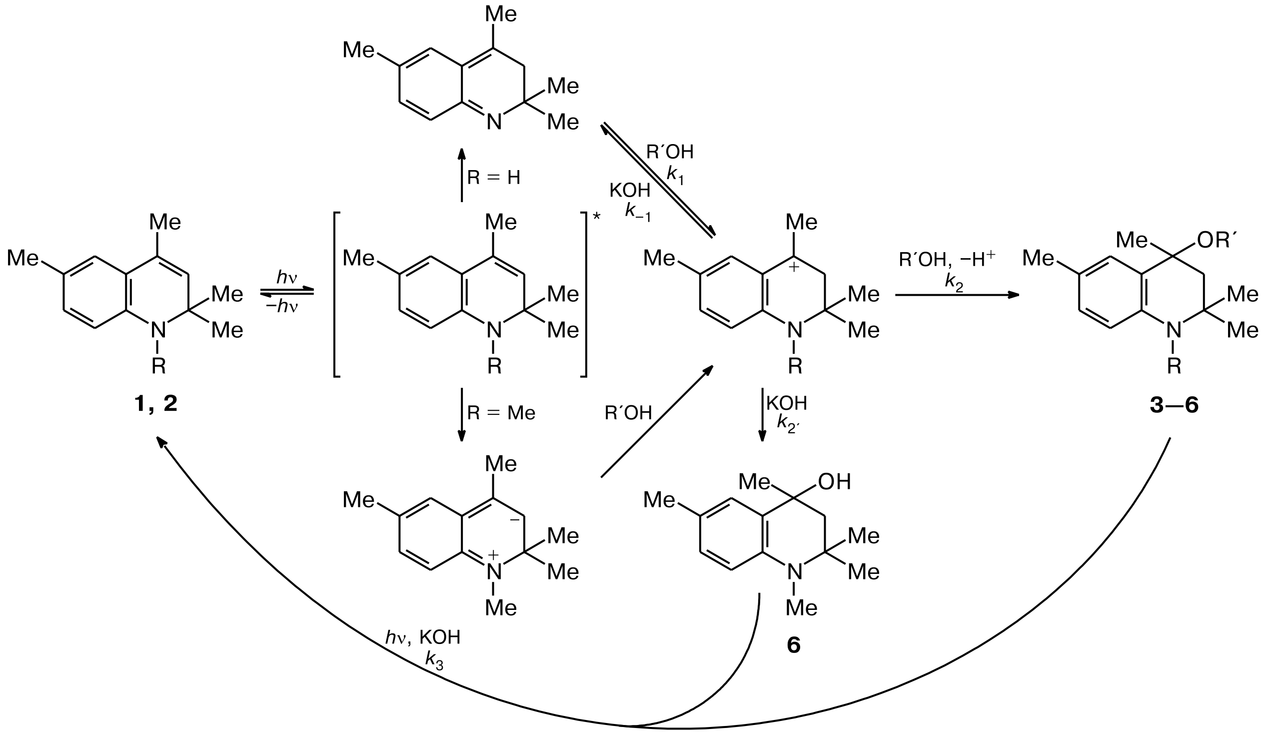
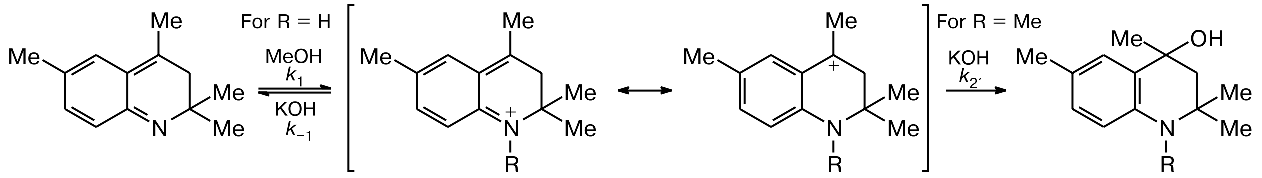
Scheme 1



R = H (**1**), Me (**2**)
R = H, R′ = Me (**3**)
R = H, R′ = H (**4**)
R = Me, R′ = Me (**5**)
R = Me, R′ = H (**6**)

Scheme 2



solution to form the starting DHQ.[3] Therefore, no formation of hydroxy adducts was earlier detected upon the photolysis of compounds **1** and **2** in MeOH with addition of alkali. In this work, we attempted to solve this problem by changing the photolysis conditions.

Results and Discussion

To solve the stated problem, it was necessary, first, to obtain the hydroxy adduct of compound **2** in the individual form and, second, to choose a method for the analysis of a mixture of products, which would allow determination of both the hydroxy and the methoxy adducts. It was shown in preliminary experiments that the hydroxy adduct of compound **2** was unstable and, being generated upon preparative steady-state photolysis in H_2O—Pr^iOH (3 : 1, vol/vol) mixtures, decomposed almost completely during isolation.[1,2] In this work we succeeded to obtain the hydroxy adduct by a standard method described earlier[2] having modified its isolation procedure (see Experimental).

The comparison of the ^1H NMR spectra of 4-methoxy-(**5**)[2] and 4-hydroxy-1,2,2,4,6-pentamethyl-1,2,3,4-tetrahydroquinoline (**6**) obtained in this work revealed the following distinctions. First, the difference between the chemical shifts (Δδ) of the axial and equatorial protons in position 3 for compounds **5** and **6** is 0.46 and 0.02 ppm, respectively, and the positions of the center of gravity of the chemical shifts of the doublet signals for the protons almost coincide (δ 1.92 and 1.91). Second, the signal of the proton in position 5 of the aromatic ring in the spectrum of compound **6** exhibits a downfield shift compared to the signal for this proton in the spectrum of compound **5** (δ 7.07 and 7.18 for compounds **5** and **6**, respectively). Similar distinctions have previously been observed in the ^{1}H NMR spectra of the methoxy (**3**) and hydroxy adducts (**4**) of compound **1** (Δδ 0.56 and 0.16 for the axial and equatorial protons in position 3 and δ 6.96 and 7.09 for the proton in position 5, respectively).[2] In addition, the spectra of the hydroxy adducts contain signals for the proton of the OH group (δ 4.50—4.70). Thus, the ^{1}H NMR spectra allow the identification of compound **6** in a mixture with compound **5** and of compound **4** in a mixture with **3** from signals for the protons in position 3, aromatic protons in position 5, and a signal for the proton of the OH group. The quantitative ratio of products in a mixture can also be determined using ^{1}H NMR spectra.

The evolution of the absorption spectra of compound **2** during photolysis in MeOH is presented in Fig. 1. Since the spectra of the initial compound and the adduct overlap, the latter also absorbs light during formation. The adducts were established to be photostable in neutral and acidic media, and light absorption did not result in noticeable degradation of these compounds. However, the products, especially hydroxy adducts, rapidly transformed into the initial DHQ upon light absorption in an alkaline solution.[3] Evidently, faster decomposition of the hydroxy adduct will lead to the accumulation of the relatively stable methoxy adduct in the system, and this process will prevent solution of the problem. The presented short-wave transmission boundaries of the Pyrex glass and FS1 filter (Fig. 1) show that the long-wave absorption band of the product falls into the transmission region of the Pyrex glass, whereas the transmission region of the FS1 filter covers only a part of the red wing of this band. Therefore, with the FS1 filter the light absorption by the product decreases and, hence, its decomposition should also decrease to favor the accumulation of the hydroxy adduct if present in the reaction products.

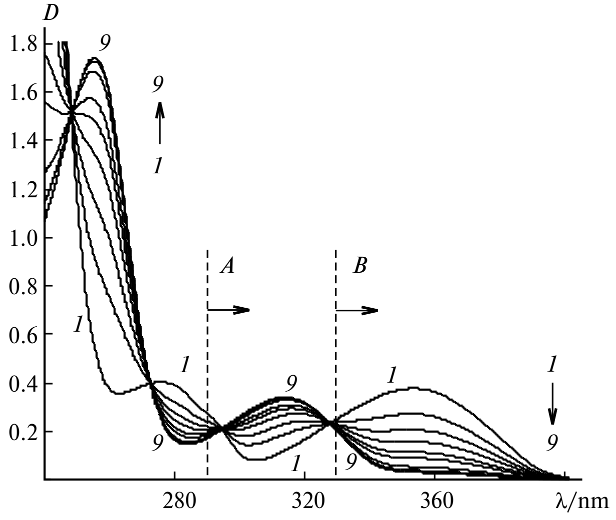


Fig. 1. Evolution of the absorption spectrum of 1,2,2,4,6-pentamethyl-1,2-dihydroquinoline (**2**) (*1*) ($2 \cdot 10^{-4}$ mol L^{-1}) during photolysis in MeOH at 20 °C. The spectra were recorded after 2 (*2*), 4 (*3*), 6 (*4*), 8 (*5*), 10 (*6*), 15 (*7*), 20 (*8*), and 30 (*9*) min (curve *9* corresponds to adduct **5**). Short-wave transmission boundaries of the Pyrex glass (*A*) and FS1 filter (*B*) are shown by dotted lines.

Nevertheless, if the photolysis of compounds **1** and **2** in MeOH in the presence of KOH with a concentration of $2 \cdot 10^{-3}$ mol L^{-1} is carried out using the FS1 filter to the complete consumption of the starting compounds, methoxy adducts **3** and **5**, respectively, are the main reaction products, and no hydroxy adducts are formed. When choosing the concentration of alkali in the reaction mixture, one has to take into account two opposite factors. On the one hand, the greater the amount of an alkali added the higher the concentration of the hydroxy adduct formed. On the other hand, an increase in the alkali concentration increases sharply the photoinduced solvolysis of this product. The absence of hydroxy adducts in the products of complete hydrolysis does not mean that they are not formed during the reaction. As mentioned above, the hydroxy adduct is less stable under these conditions, which facilitates the accumulation of the more stable methoxy adduct. Therefore, we analyzed products that formed at the 50% photolysis depth. In the case of compound **1**, the starting DHQ and methoxy adduct **3** were detected in the reaction mixture. In the case of photolysis of compound **2**, the reaction mixture contained the starting DHQ, methoxy adduct **5**, and hydroxy adduct **6**, whose amount comprised ~15% of adduct **5**. Note that it is difficult to detect product **6** in the case of an incomplete conversion of **2** due to the overlap of signals for the methyl protons in position 4 of the starting compound (δ 1.89) and the protons in position 3 of the hydroxy adducts (δ 1.90 and 1.92). Therefore, product **6** was identified and the quantitative ratio of products **5** and **6** was determined from the ratio of signals for the aromatic proton in position 5.

Thus, the results of analysis of the photolysis products in an alkaline medium confirm the assumption[3] that the intermediate cation generated from compound **2** reacts with the alkali to form the hydroxy adduct, while compound **1** does not form such an adduct. From the kinetic data[3] it follows that this can be the case if the rate constant for the reaction of the cation generated from DHQ **1** with KOH yielding the hydroxy adduct is more than two orders of magnitude lower than the rate constant $k_{2'}$ for compound **2**. As mentioned above, the rate constants for the addition of MeOH are similar for these two compounds. Since the addition reactions of the hydroxyl anion, on the one hand, and alcohol or water molecule, on the other hand, differ basically (the former is a single-step process, and the second reaction occurs in two steps, namely, as the addition of R´OH followed by proton elimination), the application of the regularities in changes in the rate constants for different compounds found in one of the reactions to another reaction is not quite correct. In addition, it has recently[6] been mentioned that in the case of *p*-quinomethaneimines the substituent at the N atom plays a determining role in the reactivity of the corresponding cations. For example, the rate constants for the hydroxy adduct formation for unsubstituted *p*-quinomethaneimine and its *N*-AcO-substituted derivative differ by more than five orders of magnitude.

Experimental

2,2,4,6-Tetramethyl-1,2-dihydroquinoline (**1**) with m.p. 42 °C (Reakhim) was sublimed *in vacuo* before use. 1,2,2,4,6-Pentamethyl-1,2-dihydroquinoline (**2**) (b.p. 150—152 °C, 12 Torr) was synthesized using a previously published procedure[7] from compound **1** and MeI. ^{1}H NMR (DMSO-d$_6$), δ: 1.21 (s, 6 H); 1.89 (d, 3 H, J = 1.1 Hz); 2.16 (s, 3 H); 2.68 (s, 3 H); 5.33 (d, 1 H, J = 1.1 Hz); 6.40 (d, 1 H, J_m = 8.25 Hz); 6.81 (d, 1 H, J_o = 2.2 Hz); 6.85 (dd, 1 H, J_m = 8.25 Hz, J_o = 2.2 Hz).

Twice distilled water, MeOH (Merck, for spectroscopy), Pr^{i}OH (Reakhim, special-purity grade), and KOH (Chemapol, analytical grade) were used.

Absorption spectra in the UV and visible regions were measured on a Shimadzu UV-1601 PC spectrophotometer in quartz cells with optical path lengths of 0.2 and 1 cm.

Steady-state photolysis of compounds **1** and **2** (10 mg of a substance in 20 mL of MeOH, $[\mathrm{DHQ}] \approx 2.5 \cdot 10^{-3}$ mol L^{-1}) was carried out by the light from a DRSh-1000 mercury lamp, exciting the long-wave absorption band ($\lambda_{\max}$(MeOH) = 343 and 359 nm for compounds **1** and **2**, respectively) at ~20 °C in a glass (Pyrex) flask with magnetic stirring by the full light of a mercury lamp (in this case, the light filter was a glass with transmission at $\lambda > 290$ nm) or in a quartz flask with the FS1 light filter with transmission in the region from 330 to 450 nm. The reaction was monitored spectrophotometrically in quartz cells with optical path lengths of 0.2 cm with periodical sampling. The solvent was distilled off *in vacuo*, the residue was dissolved in DMSO-d$_6$, and the products were analyzed by ^{1}H NMR spectroscopy on a Bruker WM-250 spectrometer during the reaction and after its completion. The products formed from DHQ **1** and **2** upon photolysis in MeOH in the absence and in the presence of KOH ($2.0 \cdot 10^{-3}$ mol L^{-1}) were compared.

4-Hydroxy-1,2,2,4,6-pentamethyl-1,2,3,4-tetrahydroquinoline (6). Compound **2** (10 mg, ~$5 \cdot 10^{-2}$ mmol) was dissolved in an H$_2$O—Pr^{i}OH (3 : 1, v/v) mixture (20 mL), and the solution was photolyzed by the full light of a mercury lamp in a Pyrex flask until the starting compound consumed completely (2 h). Then Pr^{i}OH was distilled off from the reaction mixture *in vacuo* at ~20 °C. The product was extracted from water with heptane, and heptane was distilled off *in vacuo* at ~20 °C. The residue (a light yellow oil) was dissolved in DMSO-d$_6$. The ^{1}H NMR spectrum of the resulting solution showed the presence of virtually one product **6**. ^{1}H NMR, δ: 1.13 (s, 3 H); 1.23 (s, 3 H); 1.39 (s, 3 H); 1.90 (d, 1 H, J = 13.7 Hz); 1.92 (d, 1 H, J = 13.7 Hz); 2.18 (s, 3 H); 2.67 (s, 3 H); 4.72 (s, 1 H); 6.47 (d, 1 H, J_m = 8.3 Hz); 6.86 (dd, 1 H, J_m = 8.3 Hz, J_o = 2.1 Hz); 7.18 (d, 1 H, J_m = 2.1 Hz).

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