

# Wavelength-Dependent Reactivity of a Quinolinone: Toward a Photochromic Three-State System

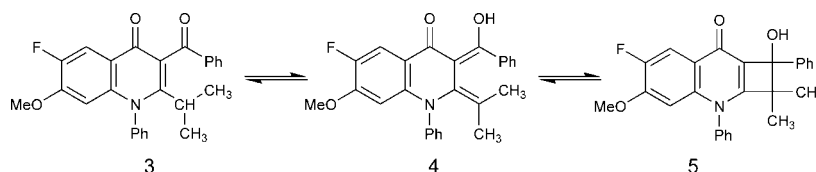
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## ABSTRACT



The photochemical reactivity of the quinolinone **3** was investigated using NMR by monitoring its reactions under appropriate irradiation wavelengths. Besides the irreversible formation of degradation products which were structurally identified, the reversible formation of the enol **4** and cyclobutenol **5** was also observed. The enol and cyclobutenol can be switched or reversed back to the quinolinone **3**, resulting in a photochromic three-state system in which the relative ratio of the three components largely depends on the irradiation wavelength used.

The photochemistry of *ortho*-alkylphenyl ketones has been thoroughly explored, and the reaction mechanism is now well-established.<sup>1</sup>  $\gamma$ -Hydrogen abstraction produces a bi-radical triplet *o*-xylylenol.<sup>2</sup> It decays to isomeric ground-state *o*-xylylenols with both *Z* and *E* configurations of the OH group with regards to the *ortho*-alkyl group.<sup>3,4</sup> The *Z*-enol is very short-lived, reverting to starting ketone by a rapid 1,5-sigmatropic H-shift, while the *E*-isomer is long-lived enough to undergo a thermal cyclization into cyclobutenol derivatives.<sup>5,6</sup> Besides the reversibility of the enol

into the ketone, the control by light and/or heat of its reversible cyclization into a four-membered ring represents a challenge as it enables us to envisage a photochromic fully switchable three-species system.<sup>7</sup> Quinolinone **1** (Figure 1) has been recently investigated. The expected enols were observed, but the formation of undesirable cyclization and oxidation side products gave rise to a rapid loss of photochromic properties.<sup>8</sup>

On the other hand, irradiation of the derivative **2** did not lead to any enol but generated two stable diastereomeric cyclized structures. These photoisomers returned to the initial state under visible light irradiation, thus resulting in a two-

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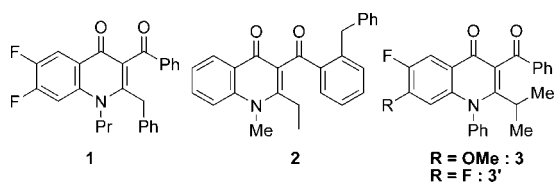
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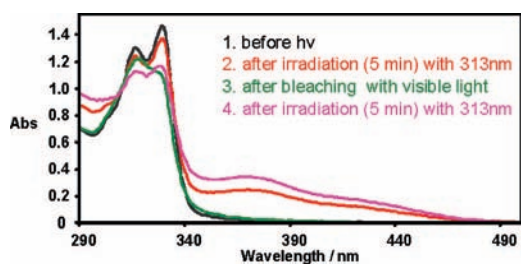
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**Figure 1.** Structures of quinolinones.

state fully photoswitchable photochromic system.<sup>9,10</sup> These results paved the way for the design of multistate photo-switchable molecules within the quinolinone series.

Quinolinone **3** was therefore synthesized and investigated by UV–visible spectroscopy (Figure 2). An increase of the



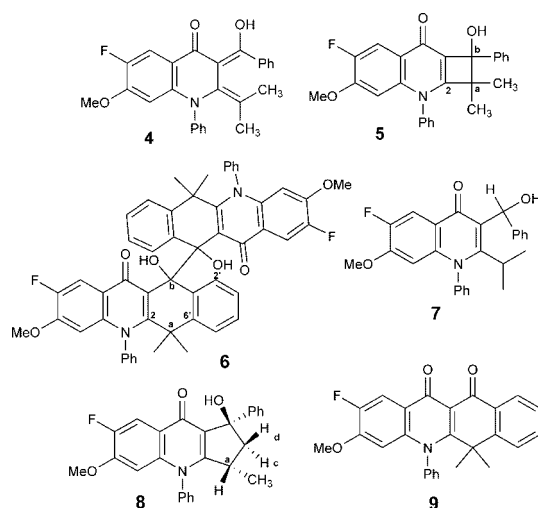
**Figure 2.** Absorption spectra of **3** in acetonitrile before irradiation (black), after irradiation with 313 nm light (red), after irradiation with visible light (green), and after reirradiation with 313 nm light (pink).

colorability has been observed after the following cycle: irradiation at 313 nm, bleaching with visible light, then reirradiation at 313 nm. To explore this unexpected result, structural and kinetic analyses of the photochemistry of **3** in degassed apolar toluene and degassed polar acetonitrile have been carried out using NMR spectroscopy.<sup>11</sup>

Wide-band UV irradiation of **3** in toluene led to the formation of the enol **4**, the dimer **6**, and the alcohol **7**, while in acetonitrile, two new photoproducts were additionally detected: the cyclobutenol **5** and the cyclopentenol **8**. All these compounds were structurally identified and characterized by NMR spectroscopy (Figure 3).

The isomer of the enol **4** was proved to be *Z* (with regards to C=O) as the high deshielding of OH ( $\delta = 17$  ppm) indicated the H-bonding between OH and C=O.

The four-membered ring in the cyclobutenol **5** was proved from <sup>1</sup>H–<sup>13</sup>C NMR long-range correlations (HMBC). The two methyl groups became diastereotopic thus resulting in two separated lines at 0.54 and 1.25 ppm, coupled through three bonds with C2 at 163 ppm and with Cb at 83 ppm. Dimer **6**



**Figure 3.** Structure of the various photoproducts of **3**.

was unequivocally identified using long-range correlations from the quaternary C6' at 145.4 ppm to the dimethyl protons at 1.53 and 1.73 ppm and the aromatic H2' at 6.94 ppm, evidencing the Ca–C6' cyclization. The dimeric entity was proved from a parallel experiment, carried out using a mixture of **3** and its difluoro derivative (**3'**), leading, under the same conditions of irradiation, to three dimers: two were symmetrical (**3-3** and **3'-3'**), and the third one was mixed (**3-3'**). The dimer **6** evolved thermally but very slowly to a new structure **9**. The reaction was accelerated upon aeration of the sample. However, although **6** and **9** are considered as side products, it must be noted that it was possible to photochemically regenerate the dimeric structure from compound **9** in toluene, which is a hydrogen-donor solvent. Indeed, the reaction was not observed in benzene, except when benzhydrol was added.

In the photoreduced alcohol derivative **7**, a scalar coupling between the methyl protons at 0.84 and 1.17 ppm and a septuplet at 2.52 ppm indicated the presence of the isopropyl group. In the COSY map, a cross peak exhibited a correlation between Hb at 6.25 ppm and OH at 6.80 ppm, thus underlining the reduction of the carbonyl function.

Finally, the rearranged five-membered ring **8** was characterized via the scalar couplings from the proton Ha with the single methyl group and with the diastereotopic Hc and Hd. The formation of **8** indicates the involvement of a 1,5 biradical as the result of hydrogen abstraction on the  $\delta$  carbon in its alkyl side chain.<sup>12,13</sup>

For the kinetic analyses, a sample was irradiated, and <sup>1</sup>H NMR spectra were recorded periodically. By measuring the peak intensities of each photoproduct, the time evolution of their concentrations can be plotted.

Among all the previously assigned structures, the dimer **6**, the alcohol **7**, and the cyclopentenol **8** are irreversible degradation products. As displayed in Figure 4, the monitor-

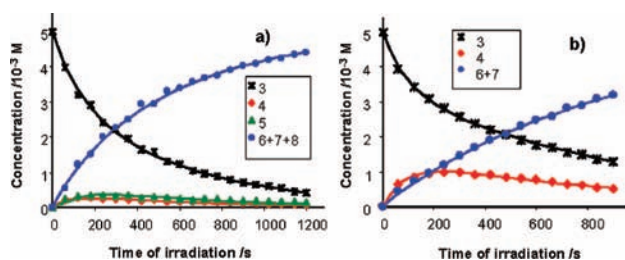
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**Figure 4.** Time evolution of concentrations of **3**, **4**, **5**, and merged **6 + 7 + 8** during wide-band UV irradiation (a) in acetonitrile and (b) in toluene. Solid lines have been plotted as a visual aid.

ing of the photochemical reaction shows that photodegradation is the main reaction process when the system is irradiated with wide-band UV light. To reduce this, irradiation has been carried out using monochromatic UV light at 313 and 365 nm.

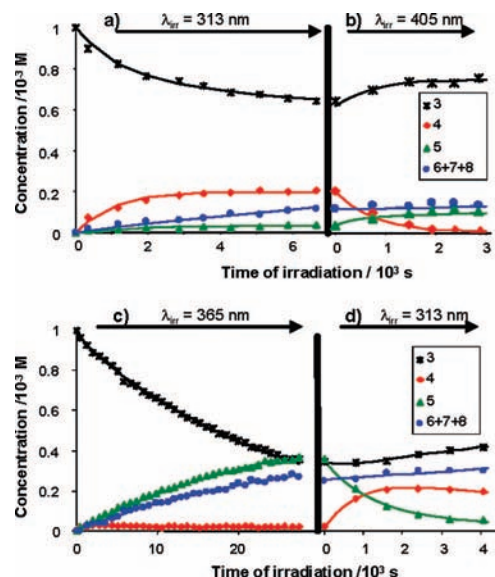
In toluene, irradiation with 313 nm light results in the accumulation of the enol **4** up to 50%, while the concentration in side products does not go over 12% (see Supporting Information). The cyclobutenol **5** is not detected, nor with 365 nm light, even at low temperature. This indicates that whatever the irradiation conditions (wide UV band, 313 or 365 nm) the cyclobutenol is not observed in a toluene solution.

In acetonitrile, irradiation at 313 nm also favors a notable formation of the enol **4**, while the cyclobutenol **5** remains the minor product. Results displayed in Figure 5a and Figure 5d show a similar product distribution whatever the initial conditions, irradiating at 313 nm, either pure quinolinone **3** or the mixture obtained after 365 nm irradiation. In contrast, irradiation at 365 nm of pure quinolinone **3** leads mainly to the cyclobutenol **5**, while the enol **4** becomes the minor product (Figure 5c). On the other hand, photobleaching with 405 nm of the mixture obtained after 313 nm irradiation is shown in Figure 5b. Enol **4** is transformed into the expected quinolinone **3** but also into the cyclobutenol **5**.

All these kinetic curves recorded from  $^1\text{H}$  NMR data under continuous monochromatic irradiation have been submitted to kinetic analysis and numerical fitting to estimate the apparent rate constants of the various photoisomerization and photodegradation processes. Results are collated in Table 1.

The apparent photochemical rate constants displayed in Table 1 are proportional to the quantum yield of the photochemical process and to the molar extinction coefficient of the photosensitive compound ( $h_{ij}/\Phi_{ij}\epsilon_i$ ). Hence, the ratio of the parameters  $h_{4-3}$  and  $h_{4-5}$  (enol **4** back to quinolinone **3** vs enol **4** to cyclobutenol **5**) can be directly related to the ratio of quantum yields of the formation of **3** and **5** from **4**. In our conditions, this ratio, which does not depend on the irradiation wavelength, lies around 2 indicating that from enol **4** the back-reaction to quinolinone **3** is twice as efficient as the cyclization to cyclobutenol **5**.

It is likely that upon irradiation of quinolinone **3** with 313 and 365 nm light intramolecular  $\gamma$ -hydrogen abstraction occurs, leading to a 1,4 biradical whose rearrangement gives



**Figure 5.** Time evolution of concentrations of enol **4**, cyclobutenol **5**, and side products (**6 + 7 + 8**) upon irradiation of the quinolinone **3** in acetonitrile at (a) 313 nm and (c) 365 nm. Part b (405 after 313 nm) and part d (313 after 365 nm) show the effect of a change in the irradiation wavelength on the kinetics. Data points are the experimental results. Solid lines are the numerical simulations of the kinetic model using the list of photochemical processes and parameters in Table 1.

**Table 1.** Apparent Photochemical Rate Constants for Processes Occurring under Irradiation of **3** in Acetonitrile at Various Wavelengths

processes	Figure 2a $\lambda = 313$ nm	Figure 2d $\lambda = 313$ nm	Figure 2b $\lambda = 405$ nm	Figure 2c $\lambda = 365$ nm
3→4: $h_{3-4}$	2.06E-04	0.76E-04		0.80E-04
4→3: $h_{4-3}$	5.05E-04	1.27E-04	7.29E-04	13.8E-04
4→5: $h_{4-5}$	2.57E-04	0.65E-04	3.64E-04	6.40E-04
5→4: $h_{5-4}$	15.9E-04	7.20E-04		
3→deg:				
$h_{3-deg}$	0.25E-04	0.37E-04	0.06E-04	0.17E-04
$h_{4-5}/h_{4-3}$	1.96	1.95	2.00	2.16

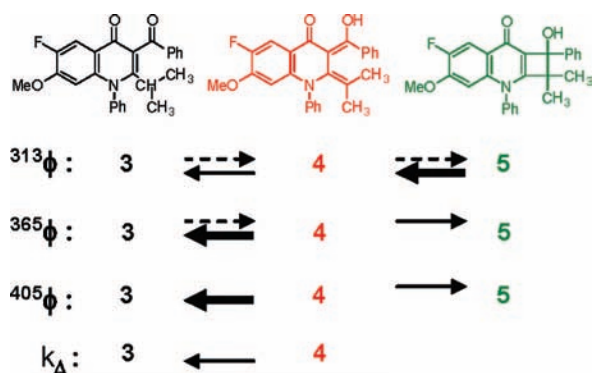
rise to the enol **4**. The latter undergoes a cyclization to cyclobutenol **5**. This reaction is here photochemical as already observed by Griesbeck et al.<sup>14</sup> and absolutely not thermal as usually reported in the literature for *o*-alkylphenyl ketones.<sup>5b,6</sup> The only observed thermal reaction is the back-reversion of enol **4** toward the quinolinone **3** in acetonitrile ( $^{295}k_{\Delta} = 2 \cdot 10^{-4} \text{ s}^{-1}$ ).

After 313 nm irradiation, the ratio of enol **4**/cyclobutenol **5** is higher than 1 but lower than 1 after 365 or 405 nm irradiation. This effect can be correlated with UV spectra displayed in Figure 2. The red spectrum obtained after irradiation with 313 nm light exhibits a remarkable absorbance at 365 and 405 nm, thus characterizing the enol absorption bands. It is then expected that the enol **4** would

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be easily photobleached under 365 or 405 nm irradiation as shown in Figure 3b and 3c. This is corroborated by the green UV spectrum recorded after visible irradiation, displaying the absorption bands of the cyclobutenol. Finally, reirradiation with 313 nm light transforms the cyclobutenol into enol, but more efficiently than the transformation of the initial quinolinone, and hence in complete agreement with the rate constants calculated and reported in Table 1. The ratio of about 9 between the parameters  $h_{5-4}$  and  $h_{3-4}$  (enol from cyclobutenol vs enol from quinolinone) further supports the greater efficiency of the process from cyclobutenol **4** compared with that from the initial quinolinone **3**.

Therefore, we propose the reaction pathways shown in Figure 6 to suggest the various processes connecting the



**Figure 6.** Summary of the various isomerization processes. The size of the arrows is a visual indication of the relative importance of the apparent rate constants. Their relative ratio can be slightly affected by a change in the initial concentrations of **3**, **4**, and **5**.

three-state system. Irradiation in acetonitrile of quinolinone **3** with 313 nm light generates a small amount of cyclobutenol **5**, the enol **4** playing the role of a photoreversible intermediate. The main process is the transformation of the cyclobutenol **5** into enol **4**. The situation is somewhat different under 365 nm irradiation where the main process is the back-isomerization of the enol **4** into the quinolinone **3**. Under these conditions, the photoreactivity of the cyclobutenol **5**

is negligible and it accumulates. As quinolinone **3** does not absorb 405 nm irradiation light and is therefore not reactive under these conditions, irradiation of enol **4** leads to a mixture of **3** and **5**. Thermal relaxation also enables the reversion of the enol **4** to the initial quinolinone **3**.

In toluene, this three-state system is rendered into a simpler photochemical reversion between **3** and **4**, i.e., to a two-state system.

In conclusion, the photochemistry of quinolinone **3** in two solvents, toluene and acetonitrile, has been investigated. Upon wide-band UV irradiation, the major part of the reactivity corresponds to degradation processes with the formation of photo-oxidized, photorearranged, and photoreduced products. Under monochromatic irradiation, the photodegradation has been drastically reduced. The relative distribution of the photoreversible compounds **3**, **4**, and **5** depends on the irradiation wavelength. After 313 nm irradiation, the system reaches a situation where quinolinone **3** > enol **4** > cyclobutenol **5**. After 365 nm irradiation, the situation is clearly different with quinolinone **3**  $\approx$  cyclobutenol **5**  $\gg$  enol **4**. Different again is the situation observed after 405 nm irradiation: quinolinone **3** > cyclobutenol **5** > enol **4**. The present results underline a potential three-state photochromic system. It enables us to envisage some structural modifications to improve the resistance to degradation as well as to transform it into a fully photoswitchable three-state system.

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**Supporting Information Available:** Details of irradiation techniques and NMR experiments, with characterization of all cited compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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