

# Photochemistry of Pyracycloquinone Studied by Laser Flash Photolysis with UV/VIS and IR Detection

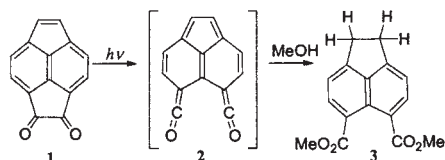
Shigero Oishi,\* Tomoko Urabe, and Rika Kotake

Department of Chemistry, School of Science, Kitasato University, Kitasato, Sagami-hara 228-8555

(Received May 1, 2002; CL-020378)

Direct evidence for the existence of an intermediate bisketene ( $\Phi = 0.14$ ,  $\epsilon_{575} = 2300 \text{ M}^{-1} \text{ cm}^{-1}$ ), generated from pyracycloquinone, was obtained by laser flash photolysis with UV/VIS and IR detection. The bisketene was found to react with DMSO to give acenaphthylene-5,6-dicarboxylic anhydride and dimethyl sulfide, quantitatively.

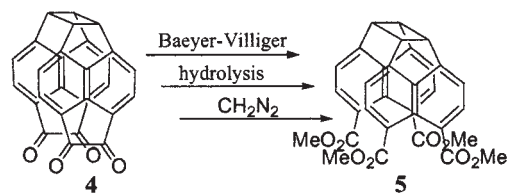
It has been reported that the photolysis of pyracycloquinone (**1**) in the presence of methanol gave dimethyl acenaphthene-5,6-dicarboxylate (**3**).<sup>1</sup> Though bisketene (**2**) was estimated to be a plausible intermediate, there was no direct evidence on this. We describe here the dynamic behavior of **2** observed by means of laser flash photolysis with UV/VIS and IR detection, and also the photo-dimerization of **1**, which has been reported not to take place.



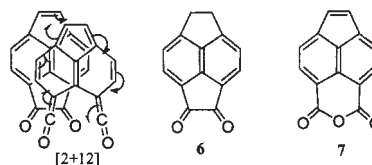
Chloroform<sup>2</sup> solutions of **1** (0.41 mM) were deaerated by bubbling argon for 20 min and then subjected to pulsed laser photolysis at 355 nm.<sup>3</sup> Figure 1A shows transient spectra, in which the absorption maximum appears at around 575 nm. The absorption decayed obeying the first-order kinetics and its lifetime was determined as 19  $\mu\text{s}$  at 20 °C. The lifetime and intensities of the absorption were not influenced by oxygen, indicating that the transient was not in an excited triplet state nor was formed via the triplet. Figure 1B shows the transient IR spectra<sup>3</sup> obtained for 1,2-dichloroethane solutions of **1** (5.0 mM). Two bands at 2130 and 2070  $\text{cm}^{-1}$  can be assigned to characteristic symmetric and anti-symmetric stretching vibration of **2**, respectively.<sup>4</sup> These peaks decayed obeying the first-order kinetics and their lifetimes were the same as that obtained from the experiments in UV/VIS region stated above. This means that

the peak at 575 nm also is due to the bisketene, **2**. Using quantum yields for the generation of **2**, which will be described later, a molar extinction coefficient of **2** was determined as 2300  $\text{M}^{-1} \text{ cm}^{-1}$  at 575 nm, by a comparative method with benzophenone triplet.<sup>5</sup>

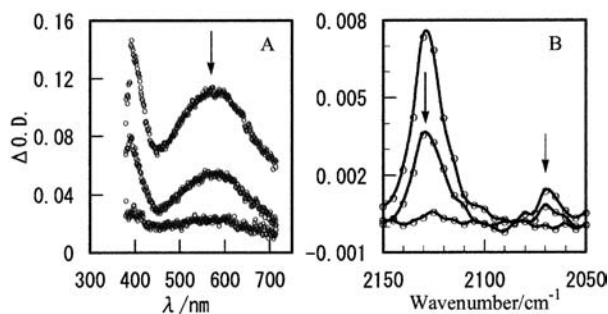
Since the decay at 2130  $\text{cm}^{-1}$  was observed to synchronize with the recovery of bleaching at 1740  $\text{cm}^{-1}$  due to a peak of **1**, it could be deduced that **2** turned back to **1** in the conditions of strict exclusion of nucleophiles. However, the fact that **1** was recovered not completely, suggests that a small part of excited species undergoes the other reaction. In order to analyze products of photoreaction in the absence of nucleophile, 150 mg of **1** dissolved in 40 ml of chloroform (18 mM) was irradiated under vacuum for 10 h with a 150 W high-pressure mercury lamp and optical filter ( $\lambda > 340 \text{ nm}$ ). A powder (90 mg) sparingly soluble in usual solvents precipitated, the amount of which corresponded to that of **1** converted, and was identified as the *syn*-dimer (**4**) of **1** by the following derivation to the tetramethyl ester (**5**).<sup>6,7</sup> Interestingly, in the literature,<sup>1b</sup> it was clearly stated that the dimerization did not take place.



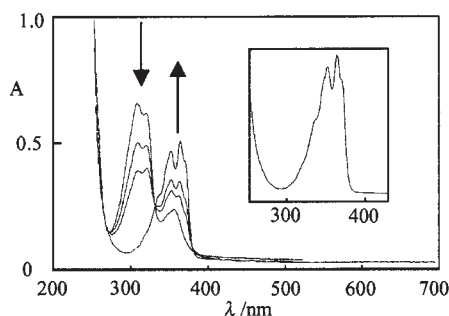
From analogy with the case of acenaphthylene,<sup>8</sup> an excimer is inferred to be responsible for the stereoselective dimerization. The possibility of [2 + 12] electrocyclic reaction of **1** with **2** was excluded by the fact that varying the concentration of **1** did not influence the lifetime of **2**.



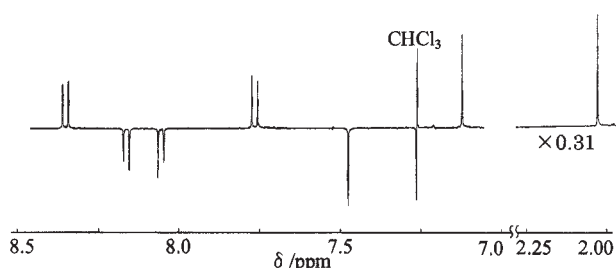
We attempted to follow spectral changes for the dimerization by improving the solubility of **4** using DMSO, but could not achieve this. Instead, we found a novel reaction of **2** with DMSO.<sup>9</sup> Figure 2 shows the time-course of UV spectra when 1,2-dichloroethane solutions of **1** (0.027 mM) and DMSO (1.0 M) were irradiated at 366 nm under Ar atmosphere. A band at 308 nm decreased in accord with the increase of two peaks at 352 and 364 nm, corresponding to acenaphthylene-5,6-dicarboxylic anhydride (**7**) as shown in the inset. A further confirmation was carried out using <sup>1</sup>H NMR; CDCl<sub>3</sub> solutions of **1** (22 mM) and DMSO (1.0 M) were sealed in NMR sample tubes under vacuum and irradiated for 3 min ( $\lambda > 340 \text{ nm}$ ). Differential spectra



**Figure 1.** (A) Transient UV/VIS spectra at 1, 10, and 38  $\mu\text{s}$  after the laser pulse. (B) Transient IR spectra at 1, 9.8, and 38  $\mu\text{s}$  after the laser pulse.

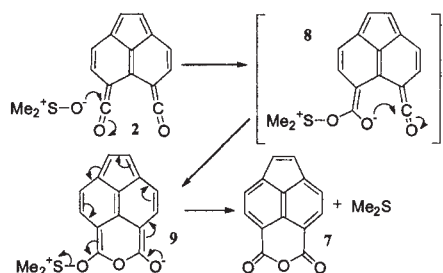


**Figure 2.** The spectral change for the irradiation (366 nm) of **1** in 1,2-dichloroethane containing DMSO at 0, 1, 2, and 24 min. The inset shows a spectrum for **7** in the same solvent.

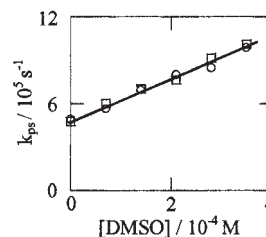


**Figure 3.** The differential  $^1\text{H}$  NMR spectrum for the irradiation **1** in  $\text{CDCl}_3$  containing DMSO. Negative peaks correspond to **1** consumed. Positive peaks, due to the products, at 8.35 (2H, d,  $J = 7.2$ ), 7.77 (2H, d,  $J = 7.2$ ), 7.12 (2H, s), and 2.03 (6H, s), coincide with those for 4(7)-, 3(8)-, 1(2)-H of **7**, and  $\text{CH}_3$  of dimethyl sulfide.

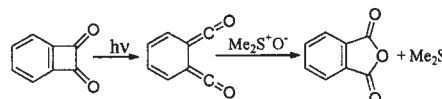
(Figure 3) tell obviously that **1** gives rise to **7** and dimethyl sulfide, quantitatively; DMSO played as an oxidant. In the LFP observation at UV/VIS and IR, the pseudo-first order rate constants for the decay of **2** increased linearly with increasing the concentration of DMSO; the rate constant for the reaction of **2** with DMSO was determined as  $1.46 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (Figure 4). This value means that **2** will react completely with DMSO, if its concentration is 1.0 M. So, using 1,2-dichloroethane solutions containing 1.0 M of DMSO, quantum yields for the decrease of **1** and for the increase of **7**, on the irradiation at 366 nm, were measured as 0.145 and 0.141, respectively. This indicates that quantum yields for the formation of **2** also amount to 0.14. These findings are most rationally explained by the following scheme, where the oxygen of DMSO initiates the reaction by a



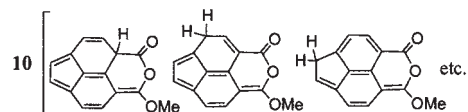
nucleophilic attack to the carbonyl carbon. Since the absorption corresponding to monoketene (**8**) did not appear in the LFP at an IR region, **9** would be formed in a concerted manner with the attack of the oxygen of DMSO. This type of reaction was found to occur also for benzocyclobutene-1,2-dione to give phthalic anhydride.



**Figure 4.** Pseudo-first order rate constants (20 °C) for the decay of **2** plotted against DMSO concentrations. Marks of  $\circ$  and  $\square$  represent the experiments in VIS (575 nm) and IR (2130  $\text{cm}^{-1}$ ) regions, respectively.



Dependence of the lifetime of **2** on the concentration of methanol was examined at 2130  $\text{cm}^{-1}$  and 575 nm, and revealed that the rate of the reaction of **2** with methanol depended on the square of methanol concentration; the rate constant was obtained as  $4.2 \times 10^6$  and  $5.3 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$ , respectively.<sup>10</sup> In order to trace the photoreaction, the experiments corresponding to Figure 3, using methanol instead of DMSO, were conducted. Many peaks appeared but no signal agreed to those of authentic **3**. However, after the treatment of silica-gel column, **3** could be obtained consistently with the literature.<sup>1</sup> Therefore, **3** could not be regarded as the first product from **2**. Considering the



reaction with DMSO, we tentatively suppose that structures (**10**) represent the first reaction products.

#### References and Notes

- a) J. A. Castellano, F. M. Beringer, and R. E. K. Winter, *J. Org. Chem.*, **37**, 3151 (1972). b) B. M. Trost, *J. Am. Chem. Soc.*, **91**, 918 (1969).
- Chloroform was washed with water to remove ethanol and dried over anhydrous magnesium sulfate. This chloroform and all other solvents in this letter were distilled from calcium hydride before use.
- S. Oishi, M. Watanabe, and T. Muraishi, *Chem. Lett.*, **1993**, 713; S. Oishi and J. Ozaki, *Chem. Lett.*, **1998**, 1071.
- The DFT calculations (B88-PW91) on CAChe. Oxford Molecular Ltd.
- R. Bensasson and E. J. Land, *Trans. Faraday Soc.*, **67**, 1904 (1971).
- Spectral data for **4**: MS-EI,  $m/z$ : 412( $\text{M}^+$ ).  $^1\text{H}$  NMR(DMSO- $d_6$ )  $\delta$  5.25 (4H, s), 7.54 (4H, d,  $J = 7.6$  Hz), 7.73 (4H, d,  $J = 7.2$  Hz). The signals for aromatic protons appeared at a higher magnetic field compared with those of diketopylacene (**6**) ( $\delta$  7.66 and 7.98), because naphthalene moieties affected each other by the ring current effect in *syn* geometry.
- Spectral data for **5**: MS-EI,  $m/z$ : 536( $\text{M}^+$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.76 (12H, s), 4.86 (4H, s), 7.15 (4H, d,  $J = 7.2$  Hz), 7.75 (4H, d,  $J = 7.2$  Hz).  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ )  $\delta$  46.4, 51.7, 120.4, 125.7, 125.9, 131.9, 142.1, 148.6, 168.8. Also in **5**, the signals for aromatic protons shifted to a higher magnetic field compared with those of **3** ( $\delta$  7.36 and 7.99), indicating that **5** had *syn* geometry.
- a) D. O. Cowan and R. L. E. Drisko, *J. Am. Chem. Soc.*, **92**, 6286 (1970). b) D. O. Cowan and J. C. Kozlar, *J. Am. Chem. Soc.*, **97**, 249 (1975).
- Vinylsulfoxide was known to react with dichloroketene to begin the additive Pummerer rearrangement. G. H. Posner, E. Asirvatham, and S. F. Ali, *J. Chem. Soc., Chem. Commun.*, **1985**, 542.
- This may be consistent with the observation that ketenes reacted predominantly with the dimer of water. Cf., e.g., T. T. Tidwell, "Ketenes," Wiley-Interscience, New York (1995), pp 571–585.