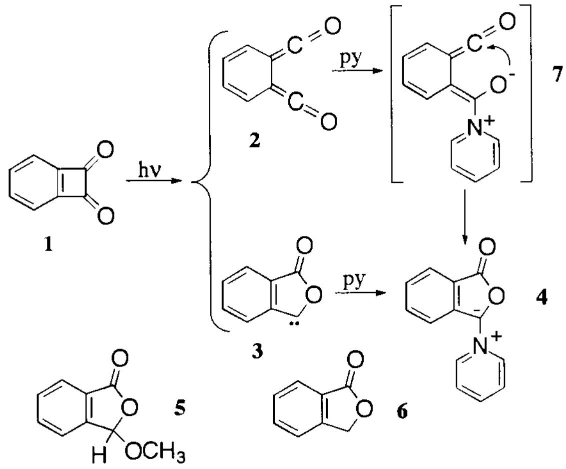
Photochemistry of Benzocyclobutene-1,2-dione Studied by Laser Flash Photolysis with UV/VIS and IR Detection

Shigero Oishi and Jun Ozaki
Department of Chemistry, School of Science, Kitasato University, Kitasato, Sagamihara 228-8555

(Received July 21, 1998; CL-980550)

Kinetic behavior of bisketene generated by the photolysis of benzocyclobutene-1,2-dione in solution was investigated by TRIR and it was found that the formation of pyridine ylide could be explained by the reaction of pyridine with the bisketene, not oxacarbene.

The photochemistry of benzocyclobutene-1,2-dione (**1**) has been investigated by many groups and a variety of intermediates have been proposed depending on the experimental conditions; bisketene (**2**), oxacarbene (**3**), benzocyclopropenone, and benzyne. Among them, we have been interested in oxacarbene **3**, which has been suggested to give pyridine ylide (**4**) or the reaction product with methanol (**5**).[1-5] Attempts to observe **3** by means of time-resolved infrared spectroscopy revealed that bisketene **2** was the precursor of the pyridine ylide **4**.



1,2-Dichloroethane solutions of **1** (10 mM) were deaerated by bubbling argon for 20 min and then subjected to pulsed laser photolysis at 266 nm (the fourth harmonic of a Q-switched Nd:YAG laser; Quanta-Ray DCR-11) with monitoring infrared region (2200-1700 cm^{-1}) in a time base of 1 µs/div.[6] Two peaks due to the formation of bisketene **2** (2125 and 2070 cm^{-1}) and bleaching of **1** at 1782 cm^{-1} could be observed consistently with the literature.[2] Though the carbonyl stretching region (around 1750 cm^{-1}) of a lactone (**6**), similar to oxacarbene **3** in structure, was examined carefully, no absorption could be detected. But we noticed that pyridine accelerated the decay of the absorption due to bisketene **2**. Figure 1A shows pseudo-first-order rate constants (k_{ps}) for the decay of bisketene **2** at 2070 and 2125 cm^{-1} plotted against pyridine concentration. The second-order rate constant for the reaction of bisketene **2** with pyridine (k_{py}) was determined as 2.2×10^{8} mol^{-1}·l·s^{-1} by using the following equation,

$$k_{ps} = k_{bk} + k_{py}[\text{pyridine}]$$

where the reciprocal of k_{bk} represented the lifetime of bisketene **2** in the absence of pyridine (50 µs). Since the absorption corresponding to monoketene (**7**) did not appear, pyridine ylide **4** would be formed in a concerted manner with the attack of pyridine.[7,8]

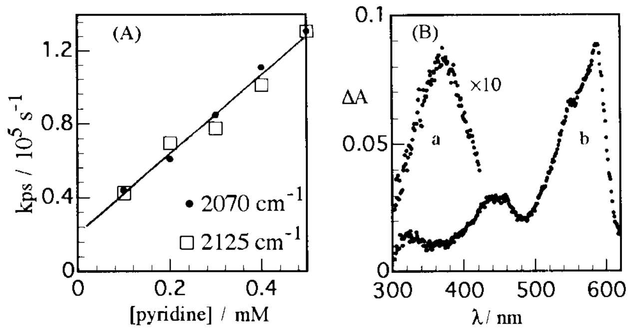


Figure 1. (A) Pseudo-first order rate constants (at 20 °C) for the decay of bisketene **2** plotted against pyridine concentration. (B) Transient UV/VIS spectra at 5 µs after the laser pulse for 1,2-dichloroethane solutions of (a) **1** (1mM) solely and (b) **1** (0.3 mM) in the presence of pyridine (1.28mM). These spectra were normalized in such a way that **1** absorbed 2.5 mJ of laser pulse in both cases.

The rate constant for the formation of **4** obtained from the growth at 590 nm (Figure 1B) also obeyed the pseudo-first-order kinetics[5] and the second-order rate constant for the reaction of pyridine with bisketene **2** was found to be 2.4×10^{8} mol^{-1}·l·s^{-1}, which was consistent with the value determined from the decay of bisketene at IR region.

Though the bisketene **2** has an absorption at 380 nm as shown in Figure 1B, this absorption is small and may overlap with absorption due to other species. Actually, the decay at 380 nm could not be analyzed as a first-order reaction.

The experiments using benzophenone as a triplet sensitizer at 355 nm gave essentially the same results as above. In conclusion, these results indicate that the main precursor for **4** should be bisketene **2**. A further investigation using other nucleophiles is in progress.

References

1 Cf., e. g., T. T. Tidwell, "Ketenes," Wiley-Interscience, New York(1995).
2 A. D Allen, J. D. Colomvakos, F. Diederich, I. Engle, X. Hao, R. Liu, J. Lusztyk, J. Ma, M. A. McAllister, Y. Rubin, K. Sung, T. T. Tidwell, and B. D. Wagner, *J. Am. Chem. Soc.*, **119**, 12125(1997).
3 R. Warmuth, *Angew. Chem., Int. Ed. Engl.*, **36**, 1347(1997).
4 W. Adam and W. S. Patterson, *J. Org. Chem.*, **60**, 7769(1995).
5 D. R. Boate, L. J. Johnston, P. C. Kwong, E. Lee-Ruff, and J. C. Scaiano, *J. Am. Chem. Soc.*, **112**, 8858(1990).
6 S. Oishi, Y. Watanabe, and Y. Kuriyama, *Chem. Lett.*, **1994**, 2187.
7 B. D. Wagner, B. R. Arnold, G. S. Brown, and J. Lusztyk, *J. Am. Chem. Soc.*, **120**, 1827(1998).
8 N. Camara de Lucas, J. C. Netto-Ferreira, J. Andraos, J. Lusztyk, B. D. Wagner, and J. C. Scaiano, *Tetrahedron Lett.*, **38**, 5147(1997).