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Effect of Irradiation Timing and Wavelength in the Time-Delayed, Two-Color Photolysis of 1,2-Bis[(phenylseleno)methyl]benzene: Transient Targeting of *o*-Quinodimethane in Room-Temperature Solutions

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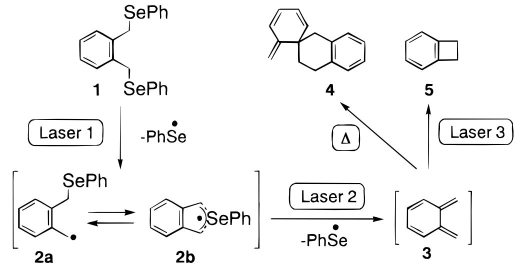
The utilization of lasers in organic photochemistry has enabled many reactions that could not be conducted by the use of conventional light,[1] and some special techniques have been developed and used for the photolysis, such as laser jet[2] and laser drop[3] photolysis techniques. A main theme in organic laser chemistry is the photolysis of photochemically generated short-lived intermediates. Multicolor laser photolysis has been used in order to achieve maximum efficiency in the photolyses by matching the wavelength to both the starting materials and the intermediates. When pulsed lasers are used in such multicolor photolysis,[4] it enables us to have precise control not only of the wavelengths but also of the timing of the irradiation. It means that we can target a specific intermediate at a particular time in the course of the reaction. This method, time-delayed, multicolor photolysis, provides an additional means for the study of the time profile of intermediates by product analyses, and this is especially useful in the cases where spectroscopic techniques are not applicable due to absorption overlapping of the reaction intermediates.

We report here the photolysis of *o*-quinodimethane[5] [**3**, 5,6-bis(methylene)cyclohexa-1,3-diene], a thermally unstable short-lived intermediate, in room-temperature solutions by using *one-color* and *time-delayed*, *two-color*[4a,b] excimer laser photolysis techniques. *o*-Quinodimethane **3** has been extensively studied from both synthetic[6] and physical standpoints.[7] The thermal reactions of **3** at room temperature or below have been well established, and **3** is reported to form mainly oligomers, polymers, and spiro dimer **4**.[8] To the best of our knowledge, the photochemical reaction of **3** in room-temperature solutions has not been reported so far.[9] This is probably due to its high thermal reactivity, by which thermal products are formed before its photochemical reaction can proceed. In our laser photolysis experiments at room temperature, we have observed the formation of benzocyclobutene **5** (photochemical product of **3**) together with *o*-quinodimethane spiro dimer **4** (thermal product of **3**) in both photolyses. The time profile of **3** was obtained by delay-time dependence of **4** and **5** in the *time-delayed, two-color* laser photolyses.

Scheme 1



The strategy used in our experiments for the photolysis of **3** was the fast generation of **3** and its photolysis before the occurrence of its thermal reaction. The fast generation of **3** was accomplished by the KrF excimer laser photolysis of 1,2-bis[(phenylseleno)methyl]benzene **1** in 10^{-4} M acetonitrile solution under a nitrogen gas atmosphere,[10] and successive photolyses of **3** were also conducted by lasers (Scheme 1). The *time-delayed, two-color* photolysis was conducted by one pair of laser pulses; the pair of laser pulses consisted of one pulse of the KrF excimer laser [248 nm, 1.25×10^{21} photons$\cdot$m$^{-2}\cdot$pulse^{-1}] and one subsequent pulse of a XeCl [308 nm, 1.88×10^{21} photons$\cdot$m$^{-2}\cdot$pulse^{-1}] or a XeF [351 nm, 1.88×10^{21} photons$\cdot$m$^{-2}\cdot$pulse^{-1}] excimer laser, which was flashed after various delay times ranging from 0 ns to 3 s. In comparison, the *one-color* photolyses were performed by using a pulse of the KrF, XeCl, and XeF excimer lasers with the same laser fluences as those in the two-color photolysis. The yields of **4** and **5** and the consumption of **1** were determined by HPLC analysis in comparison with the authentic samples.

In the case of *one-color* photolyses, the yields of **4** and **5** and the consumption of **1** by a pulse of the excimer laser, were 7.0%, 6.3%, and 91% with the KrF laser and 2.2%, 0%, and 44% with the XeCl laser.[11,12b] No reaction proceeded with the XeF laser, which was due to the lack of the absorption of **1** at 351 nm. Despite the larger number of photons, lower consumption of **1** in the XeCl laser photolysis than that of the KrF laser can be explained by the difference in molar absorptivity of **1** (16 800 M$^{-1}\cdot$cm^{-1} at 248 nm and 1800 M$^{-1}\cdot$cm^{-1} at 308 nm) and also by the participation of different excited states[13b] at each laser wavelength. The formation of **5**[14] is rationalized by further photolysis of **3** within the same laser pulse (Scheme 1, laser 1 = laser 2 =

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(8) *E.g.*: Errede, L. A. *J. Am. Chem. Soc.* **1961**, *83*, 949−954.

(9) Spectroscopic studies on the photolysis of **3** have been reported at −196 °C in organic matrixes[7a,b] and at 10−15 K in argon matrixes.[7f,h]

(10) Thus generated **3** was trapped with maleic anhydride in a the yield of 43%.[13.]

(11) TLC analyses of the laser reaction products showed the existence of a significant amount of compounds at the origin, which were expected to be oligomers and polymers.[8.]

(12) The results were obtained from the average of (a) two and (b) three independent runs.

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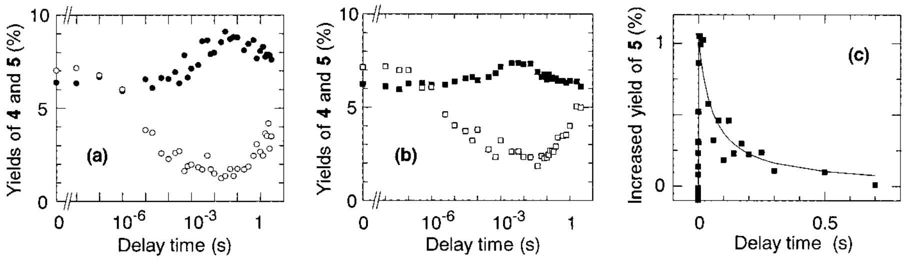

Figure 1. Yields of spiro dimer **4** and benzocyclobutene **5** as a function of the delay time of (a) KrF and XeCl lasers and (b) KrF and XeF lasers and (c) *increased yield* of **5** as a function of the delay time of the KrF and XeF lasers with second-order kinetic fitting:[12a] **4**, open symbols; **5**, closed symbols. Combinations of lasers: KrF–XeCl (○, ●); KrF–XeF (□, ■). Concentration: 10^{-4} M **1** in acetonitrile. Optical path: 1 mm. Laser fluence: 1.25×10^{21} (KrF) and 1.88×10^{21} (XeCl and XeF) photons·m^{-2}·pulse^{-1}.

laser 3). This result is in accord with the formation of **5** by conventional light photolysis of **3** in low-temperature matrixes.[7a,b,f,h]

Figure 1a,b shows the yields of spiro dimer **4** and benzocyclobutene **5** as a function of the delay time of the two laser pulses in the *time-delayed, two-color* photolyses. The consumption of **1** in the *two-color* photolyses, 91–94%, was independent of the delay times and almost the same as that in the *one-color* photolysis by KrF laser, 91%. As seen in Figure 1a,b, the additional formation of **5** strongly depended on the delay time. At short delay times, the yields of **4** and **5** were almost the same as those of the *one-color* photolysis with the KrF excimer laser. However, a maximum on the yield of **5** and a minimum on the yield of **4** were observed at the delay time of *ca.* 20 ms.

The increase of the yield of **5** in the *two-color* photolyses is explained by the photolysis of **3** by the XeCl/XeF laser pulse, *i.e.*, the photolysis of two-photon intermediate **3** to form **5** (Scheme 1: laser 1 = laser 2 = KrF laser, laser 3 = XeCl/XeF laser). However, another possibility is the photolysis of one-photon intermediate **2a**/**b** through a two-photon process (Scheme 1: laser 1 = KrF laser, laser 2 = laser 3 = XeCl/XeF laser) because the presence of intermediate **2a**/**b** was also observed by flash photolysis experiments.[15] To clarify the mechanism of the additional formation of **5**, an experiment on the XeCl laser fluence dependence was conducted in the *time-delayed, two-color* photolysis. Figure 2 shows the *increased yield* of **5** as a function of the XeCl laser fluence at a fixed delay time of 2 ms. The *increased yield* is defined as the difference in the yield of **5** between the *time-delayed, two-color* photolysis and the *one-color* KrF laser photolysis. As seen in Figure 2, the *increased yield* of **5** was proportional to the first power of the XeCl laser fluence. This result indicates that the formation of **5** by the XeCl laser irradiation proceeded through a one-photon process; *i.e.*, **3** → **5** but not **2a**/**b** → **3** → **5**.

Figure 1c shows the *increased yield* of **5** as a function of the delay time of the KrF and XeF lasers. This time profile corresponds to the decay curve of **3** in conventional flash photolysis experiments[15] because the *increased yield* of **5** reflects the concentration of **3** at each delay time. As seen in Figure 1c, **3** decreased with second-order kinetics. This is consistent with the results of spectroscopic experiments conducted with different precursors;[5c,7d,g] the decay is explained by the thermal dimerization.

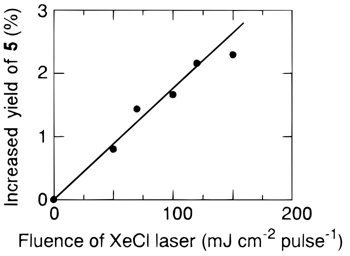

Figure 2. Laser fluence dependence on the *increased yield* of benzocyclobutene **5** as a function of the XeCl excimer laser fluence.[12a] **5**: ●. Concentration: 10^{-4} M **1** in acetonitrile. Optical path: 1 mm. Delay time: 2 ms. KrF laser fluence: 1.25×10^{21} photons·m^{-2}·pulse^{-1} (100 mJ·cm^{-2}·pulse^{-1}).

The existence of the maximum for the yield of **5** in Figure 1a,b means that the highest concentration of **3** was reached at *ca.* 20 ms delay time. This result indicates the existence of a slow process for the generation of **3**. On the other hand, the formation of a considerable amount of **5** by the *one-color* photolysis of the KrF laser implies the existence of another very fast process, which enables **3** to absorb the third photon within the same laser pulse (<30 ns). The origin of the two processes is not clear at present because the rise of a transient species has been generally ignored in conventional flash photolysis studies.

The wavelength dependence in photochemical conversion **3** → **5** is best shown as the difference in the *increased yield* of **5** at the maximum of Figure 1a,b. The *increased yield* of **5** was 2.8-fold higher for the XeCl laser (308 nm) than the XeF laser (351 nm). This result cannot be explained by the difference in molar absorptivity of **3** at each wavelength because the reported molar absorptivity is 2.5-[16] to 3.8-fold[7b] larger at 351 nm than at 308 nm. This tendency is opposite to that of the *increased yield* of **5**. The reported λ_{max} of the first absorption band of **3** is 370, and 308 nm is located just at the minimum of its shorter wavelength side.[5c,7b,16] Therefore, the involvement of higher excited state, S_2, is expected in the photochemical conversion **3** → **5**. Indeed, participation of the S_2 state for the conversion **3** → **5** has been postulated;[8b,c] however, it is believed that the $S_0 \rightarrow S_2$ transition should be buried under the more intense $S_0 \rightarrow S_1$ band. We think that our result on the wavelength dependence on the *increased yield* of **5** is consistent with this prediction on the involvement of the $S_0 \rightarrow S_2$ transition for the conversion **3** → **5**, which is still not explicitly observed by spectroscopic means.

Supporting Information Available: Experimental details and preparation of compounds **1**, **4**, and **5** (4 pages).

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(14) It is important to note that **5** is not formed by the thermal reaction of **3** below room temperature. *Cf.* Cava; M. P.; Deana, A. A. *J. Am. Chem. Soc.* **1959**, *81*, 4266–4268.

(15) Transient absorption was observed at 320 nm by the photolysis of **1** by using a pulse of a 266 nm laser, and the absorption is in good accord with that of the ortho-substituted benzyl radical:[16] unpublished result. However, the decay of **3** was difficult to observe because of the overlapping of several species such as phenyl seleno radicals, diphenyl diselenide, intermediate **2a**/**b**, and other unidentified species.

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