Determination of the Photochemical Efficiency of *o*-Quinodimethane Ring Closure in Room-Temperature Solutions by Using Time-Delayed, Two-Color Photolysis Technique

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Photochemical efficiency of *o*-quinodimethane (**3**) ring closure at room temperature was determined by using a *time-delayed, two-color* photolysis technique. *o*-Quinodimethane (**3**) was generated by the photolysis of 1,2-bis[(phenylseleno)methyl]benzene (**1**) by a KrF (248 nm) laser pulse and thus-generated **3** was photolyzed by a subsequent XeCl (308 nm)/XeF (351 nm) laser pulse with varying delay time of 0 to 3 s. The time profile of **3** was monitored by the chemical analyses of benzocyclobutene (**5**) (a photochemical product of **3**), which was formed by a one-photon process, and the spiro dimer of **3** (**4**) (a thermal product of **3**) in the *two-color* photolysis experiments. The time profile of **3** followed a second-order decay kinetics. The photochemical efficiency was obtained by the analysis of the delay-time dependence of the product yields; those of the consumption of **3** and the conversion **3** → **5** by a single pulse of the excimer laser were 81% and 5.7% for the XeCl laser, and 73% and 2.3% for the XeF laser. This difference was attributed to the different excited states involved in the photolysis. In contrast to the photolysis of **3** in argon or rigid organic matrixes, it was revealed that photochemical conversion **3** → **5** was *not* the main path in the solutions, and intermolecular reactions predominated.

Introduction

o-Quinodimethane [**3**; 5,6-bis(methylene)cyclohexa-1,3-diene][1] is a thermally unstable short-lived intermediate, and it has been extensively studied from both synthetic[2,3] and physical standpoints.[4] It is believed that the thermal reactions of **3** at room temperature or below are well established and their main products are oligomers, polymers, and the [4 + 2] spiro dimer [**4**; 3′,4′-dihydro-6-methylenespiro(2,4-cyclohexadiene-1,2′(1′*H*)-naphthalene)].[5] On the other hand, the photochemical reaction of **3** has been only conducted in argon[4f,h] or rigid organic[4a,b] matrixes at low temperatures, and its photoproduct is reported to be benzocyclobutene [**5**; bicyclo[4.2.0]octa-1,3,5-triene]. From these matrix isolation studies, it is also believed that photochemistry of **3** is well defined. However, it is not surprising that the photoproduct of **3** obtained by these matrix isolated experiments was a unimolecular photoproduct, **5**, because the diffusion of the molecules is restricted in such an environment so that intermolecular reactions are prevented. To clarify whether conversion **3** → **5** is also the major photochemical path in *general* reaction environments, i.e., the environments in which the diffusion of **3** is not restricted, determination of the photochemical efficiency of conversion **3** → **5** in solutions is necessary. However, the photochemical reaction of **3** in solutions has not been reported so far because of the occurrence of a fast thermal reaction of **3** even at −150 °C,[6] and suitable experimental techniques have not been developed for such studies. We report here the determination of the photochemical efficiencies of conversion **3** → **5** in room-temperature solutions by using a *time-delayed, two-color* pulse laser photolysis technique.[7]

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[5] For example, Errede, L. A. *J. Am. Chem. Soc.* **1961**, *83*, 949−954.

[6] Spectroscopic studies on the photolysis of **3** have been reported at −196 °C in organic matrixes[4a,b] and at 10−15 K in argon matrixes.[4f,h] Irradiation (>254 nm) of **3** in the organic and argon matrixes gave benzocyclobutene (**5**), which was detected by UV absorption spectrometry. Compound **5** was isolated after the photolysis of **3** in the organic matrixes but without its chemical yield.[4a,b] On melting of the matrix at ca. −150 °C before the photolysis, **3** was easily converted to spiro dimer **4** by a thermal [4 + 2] cycloaddition reaction.[4a,b]

[7] For example, (a) Netto-Ferreira, J. C.; Wintgens, V.; Scaiano, J. C. *Tetrahedron Lett.* **1989**, *30*, 6851−6854. (b) Bendig, J.; Mitzner, R. *Ber. Bunsen-Ges. Phys. Chem.* **1994**, *98*, 1004−1008. (c) Ouchi, A.; Koga, Y. *Tetrahedron Lett.* **1995**, *36*, 8999−9002. (d) Jiménez, M. C.; Miranda, M. A.; Scaiano, J. C.; Tormos, R. *Chem. Commun.* **1997**, 1487−1488.

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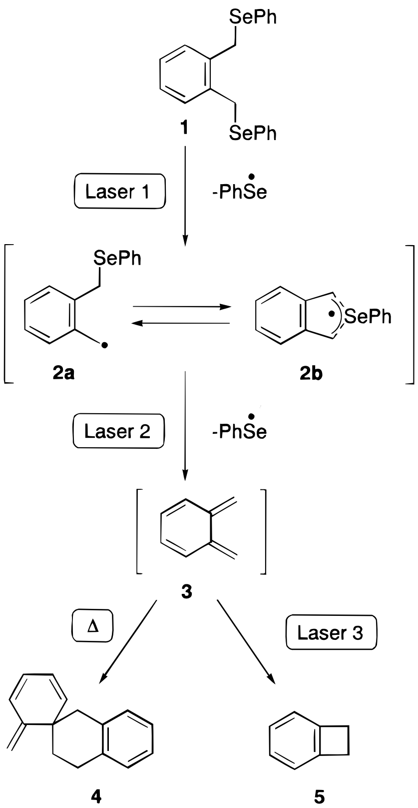
Scheme 1



The strategy used in our experiments for the photolysis of **3** in room-temperature solutions was the fast generation of **3** and its photolysis before the occurrence of its thermal reaction. We have generated the short-lived intermediate **3** by the first laser pulse and, by the second laser pulse, we have targeted **3** at a particular time in the course of the reaction. The fast generation of **3** was accomplished by KrF excimer laser photolysis of 1,2-bis[(phenylseleno)methyl]benzene (**1**) through a two-photon process,[8] and successive photolyses of **3** were conducted by a XeCl or a XeF excimer laser (cf. Scheme 1). In our time-delayed, two-color laser photolysis experiments at room temperature,[9] we have traced the formation of a photochemical product, benzocyclobutene **5**, and a thermal product, spiro dimer **4**. The photochemical efficiency of the formation of **5** was determined by the analysis of the delay-time dependence of the product yields.

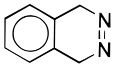
The photochemical efficiencies of the consumption of **3** and conversion **3** → **5** by a pulse of the excimer lasers were 81% and 5.7%, respectively, for the XeCl laser, and 73% and 2.3% for the XeF laser. This indicates that photochemical conversion **3** → **5** was *not* the main path in solution, which is in contrast to the results in the restricted rigid matrixes.

To the best of our knowledge, this is the first report on the determination of photochemical efficiency of short-lived intermediates by product analysis. This technique complements conventional spectroscopic methods in the study of short-lived intermediates especially in the cases where many intermediates which have absorptions in the same spectroscopic regions are generated by the photolysis. Such spectral overlap of the intermediates often occurs when molecules are designed to give high photochemical efficiency.

Results

Precursors of *o*-Quinodimethane 3. A necessary requirement for the precursor of **3** in our time-delayed, two-color photolysis experiments is high efficiency of the formation of **3** by a single laser pulse. If the efficiency is low, several time-delayed, two-color photolysis cycles are necessary to obtain detectable amounts of the products, **4** and **5**. However, the occurrence of secondary reactions of **4** (vide infra) is expected to cause complication in the analysis of the reaction. Therefore, the selection of a suitable precursor for **3** is essential in our experiments.

The precursor used in the rigid organic matrix experiments was 1,4-dihydrophthalazine (**6**);[4a,b] however, **6** is reported to be unstable at room temperature so that **6** was excluded as a possible precursor in our experiment. Other compounds that have been used as precursors of **3**[1] are 2-indanone (**7**), 3-isochromanone (**8**), sultine [**9**; 1,4-dihydro-2,3-benzoxathiin 3-oxide], and 1,3-dihydroisothionaphthene 2,2-dioxide (**10**).



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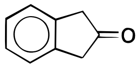

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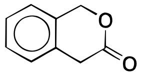

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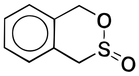

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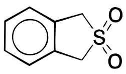

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Compounds **7**−**10** had very small or no absorption above 300 nm, but considerable absorption was observed below 270 nm so that a KrF (248 nm) excimer laser was used for the generation of **3**. The molar absorption coefficient of **7**−**10** at 248 nm are 840 $M^{-1}\cdot cm^{-1}$ for **7**, 210 $M^{-1}\cdot cm^{-1}$ for **8**, 175 $M^{-1}\cdot cm^{-1}$ for **9**, and 160 $M^{-1}\cdot cm^{-1}$ for **10**. The photolyses were conducted by a single pulse of a KrF (1.25×10^{21} photons·m^{-2}·$pulse^{-1}$) excimer laser on 10^{-4} M acetonitrile solutions; the consumption was found to be 9.5% for **7**, 3.8% for **8**, 6.7% for **9**, and 2.2% for **10**.[10a] An attempt to trap **3** by maleic anhydride (**11**) through a cycloaddition reaction was also conducted for **7**−**10**; 10^{-4} M acetonitrile solutions of **7**−**10** were photolyzed by a single pulse of the KrF excimer laser (1.25×10^{21} photons·m^{-2}·$pulse^{-1}$) in the presence of 10^{-3} M **11**. The yield[11] of the cycloadduct and the consumption of the precursor were 4.7 and 9.4%, respectively, for **7**, 1.4 and 3.3% for **8**, 3.5 and 7.2% for **9**, and 0.7 and 1.9% for **10**.[10a] This indicates that the photochemical efficiency of **7**−**10** is not sufficient to use these compounds as precursors of **3** in our time-delayed, two-color experiments.

We have recently developed an efficient precursor of **3**, 1,2-bis[(phenylseleno)methyl]benzene (**1**).[8] The consumption of **1** and the yield[11] of the cycloadduct of **3** and **11** by a single pulse of the KrF excimer laser under the same condition as before were 91% and 43%, respectively. Although the formation of **3** from **1** proceeds by a two-photon process, which was confirmed by experiments on laser fluence dependence,[8] the photochemical efficiency

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(8) (a) Ouchi, A.; Koga, Y. *Chem. Commun.* **1996**, 2075−2076. (b) Ouchi, A.; Koga, Y. *J. Org. Chem.* **1997**, *62*, 7376−7383.

(9) Ouchi, A.; Koga, Y. *J. Org. Chem.* **1998**, *63*, 6780−6781.

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

(11) The yield is based on the starting material.

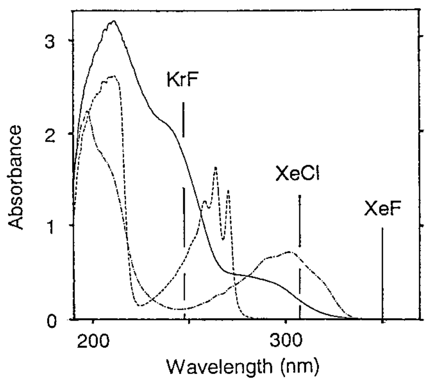

Figure 1. Absorption spectra of 1,2-bis[(phenylseleno)methyl]benzene **1** (—), spiro dimer **4** (—•—•—), and benzocyclobutene **5** (- - -). Concentration: 10^{-4} M (**1**, **4**) and 10^{-3} M (**5**) in acetonitrile, optical path: 10 mm. The wavelengths of the laser emissions are indicated in the figure.

for the formation of **3** is sufficiently high. Therefore, **1** was selected as the precursor of **3** in our experiments. It is important to note that spectroscopic methods could not be used for tracing **3** because many other species—such as, monoradical **2a**/**b**, phenylseleno radical, diphenyl diselenide—which have absorptions in the same spectroscopic regions were generated at the same time by the photolyses. Although **1** was designed to give high photochemical efficiency for the generation of **3**, spectral overlap of such species made it impossible to determine the time profile of **3** by optical spectrometry.

Absorption Spectra. Figure 1 shows the absorption spectra of 1,2-bis[(phenylseleno)methyl]benzene (**1**), benzocyclobutene (**5**), and spiro dimer **4**. The molar absorption coefficient (ϵ) of **1** at the three laser wavelengths was 16800 (at 248 nm), 1800 (at 308 nm), and 20 (at 351 nm) $M^{-1}\cdot cm^{-1}$. Similarly, ϵ of **5** was 640 (at 248 nm) and 0 (at 308 and 351 nm) $M^{-1}\cdot cm^{-1}$, and that of **4** was 1100 (at 248 nm), 6100 (at 308 nm), and 6 (at 351 nm) $M^{-1}\cdot cm^{-1}$. *o*-Quinodimethane (**3**) has been reported[4a−c,12] to have strong absorption at $<$240 nm, an absorption minimum at ca. 300 nm, a maximum at 373 nm ($\epsilon >$ 3000), and the absorption edge at ca. 430 nm. The ratio of the ϵ of **3** at the three laser emissions was reported to be 3.8:1:3.8 (248 nm: 308 nm: 351 nm)[4b] and 1:2.5 (308 nm: 351 nm).[12]

The Yield of *o*-Quinodimethane 3 by a Pulse of the KrF Excimer Laser. Direct measurement of the yield of **3** generated by a pulse of the KrF excimer laser was not possible by means of conventional chemical analysis because of its short lifetime. Spectroscopic techniques were also not applicable because other species which had absorption in the same wavelength region as **3** were generated at the same time. We have therefore used a trapping technique to obtain the yield of **3**.

We have reported trapping of **3** by maleic anhydride (**11**), a cycloaddition reaction, in the *one-color* KrF laser (1.25×10^{21} $\text{photons}\cdot\text{m}^{-2}\cdot\text{pulse}^{-1}$) photolysis of **1**. The yield[11] of the cycloadduct with one pulse of the KrF laser was 41%.[8] However, to obtain the yield of **3**, it is necessary to know the trapping efficiency of **3** by **11**. To determine the trapping efficiency, we used a standard procedure for the generation of **3**, i.e., the reaction of [*o*-[(trimethylsilyl)methyl]benzyl]trimethylammonium iodide (**12**) and tetrabutylammonium fluoride (**13**).[13] Trahanovsky et al.[4g] have shown that **3** was quantitatively formed from **12** by using more than 25 equiv of **13**. Therefore, we have conducted a trapping experiment of **3** by **11** through generation of **3** from 10^{-4} M **12** and 100 equiv of **13** in acetonitrile in the presence of 10^{-3} M **11**. The concentrations of **12** and **11** were set equal to those of **1** and **11** in the one-color KrF laser photolysis. However, decomposition of the anhydride moiety occurred under the experimental conditions so that the determination of the trapping efficiency of **3** by **11** was unsuccessful.

We have therefore used fumaronitrile (**14**) as an alternative trapping agent. Under the same experimental condition as in the reaction of **3** and **11**, the cycloadduct of **3** and **14** was obtained in 82%.[14] The yield of the cycloadduct was almost the same (81%) when 200 equiv of **13** were used. It is reported that 39%[11] of the cycloadduct of **3** and **14** is formed by a pulse of the KrF excimer laser photolysis of 10^{-4} M **1** in the presence of 10^{-3} M **14** in acetonitrile.[8] From the yield of the cycloadduct of **3** and **14** in the one-color KrF excimer laser photolysis (39%) and the trapping efficiency of **3** by **14** (82%), we conclude that the yield of **3** from **1** by the photolysis of a pulse of the KrF laser was 48%.

One-Color Excimer Laser Photolyses. Photolysis of 10^{-4} M **1** in acetonitrile was conducted by a KrF (248 nm, 1.25×10^{21} $\text{photon}\cdot\text{m}^{-2}\cdot\text{pulse}^{-1}$), XeCl (308 nm, 1.88×10^{21} $\text{photon}\cdot\text{m}^{-2}\cdot\text{pulse}^{-1}$), and XeF (351 nm, 1.88×10^{21} $\text{photon}\cdot\text{m}^{-2}\cdot\text{pulse}^{-1}$) excimer lasers. The yields[11] of **4** and **5** and the consumption of **1** by a pulse of the excimer laser were 7.0%, 6.3%, and 91%, respectively, for the KrF laser, and 2.2%, $\sim$ 0% (below the detection level), and 44% for the XeCl laser.[10a] Some unidentified peaks were observed in HPLC analyses, and TLC analyses also showed the existence of a significant amount of unidentified compounds at the origin. These compounds are expected to be oligomers and polymers.[5] On the contrary, no reaction proceeded with the XeF laser, which was due to the absence of the absorption of **1** at 351 nm.

Time-Delayed, Two-Color Photolyses. Figures 2a,b show the yields[11] 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 horizontal axes in Figures 2a,b are shown in a logarithmic scale in order to indicate clearly the fast changes at short delay times.[15] The 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 and one subsequent pulse of the XeCl or XeF excimer laser which was fired after various delay times. 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 KrF laser photolysis (91%). This indicates that the consumption of **1** proceeded mainly by the KrF laser. On the contrary, the yields of **4** and **5** were strongly dependent on the delay time of the second XeCl or XeF laser pulse. At short delay times, the yields of **4** and **5** were almost the same as those of the one-color KrF laser photolysis. However, a maximum on the yield of **5** and a

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[12] Fujiwara, M.; Mishima, K.; Tamai, K.; Tanimoto, Y.; Mizuno, K.; Ishii, Y. *J. Phys. Chem. A* **1997**, *101*, 4912−4915.

[13] (a) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 863−865. (b) *Ibid.* **1982**, *104*, 7609−7622.

[14] The yields of the cycloadduct of **3** and **14** were 81.6 ± 0.8% (100 equivof **13**) and 81.4 ± 1.4% (200 equiv of **13**).

[15] The figures with horizontal axes in linear scale are shown in Supporting Information.

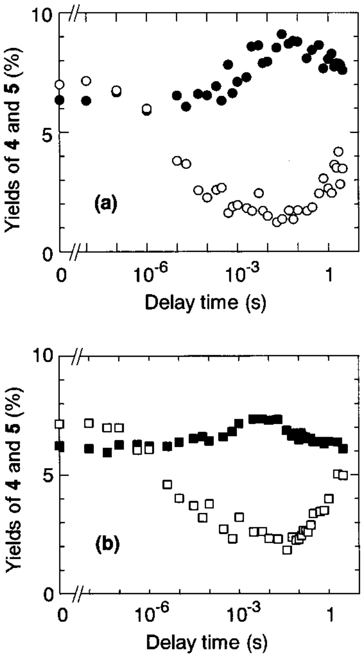

Figure 2. Yields[11] of spiro dimer **4** and benzocyclobutene **5** as a function of the delay time between the (a) KrF and XeCl lasers, and (b) KrF and XeF lasers.[10b] **4**: open symbols; **5**: closed symbols. Combinations of lasers: KrF–XeCl (○, ●); KrF–XeF (□, ■). Concentration: 10^{-4} M **1** 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}.

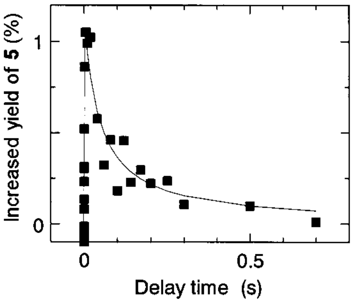

Figure 3. Increased yield[11] of benzocyclobutene **5** as a function of the delay time between the KrF and XeF lasers with second-order kinetic fitting.[10b] Concentration: 10^{-4} M **1** in acetonitrile. Optical path: 1 mm. Laser fluence: 1.25×10^{21} (KrF) and 1.88×10^{21} (XeF) photons·m^{-2}·pulse^{-1}.

minimum on the yield of **4** were observed at the delay time of ca. 20 ms. Also in the two-color experiments, TLC analyses showed the existence of a significant amount of compounds at the origin,[5] most likely oligomers and polymers. Some unidentified byproducts were also detected by HPLC analyses in the two-color photolyses.

Figure 3 shows the *increased yield* of **5** as a function of the delay time of the KrF and XeF lasers. The increased yield is defined as the difference in the yield[11] of **5** between the time-delayed, two-color photolysis and the one-color KrF laser photolysis. The horizontal axis in Figure 3 is shown in linear scale so that this time profile corresponds to the decay curve of **3** in conventional flash photolysis experiments[16] because the increased yield of **5** reflects the concentration of **3** at each delay time. As seen in Figure 3, **3** decreased with second-order kinetics. This is in accord with the previous flash photolysis studies and is explained by the thermal dimerization of **3**.[1c,4d,g]

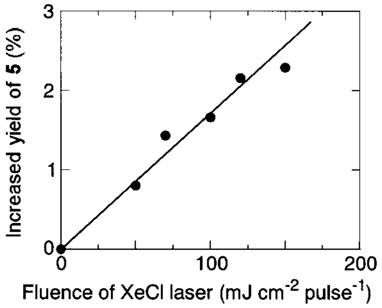

Figure 4. Increased yield[11] of benzocyclobutene **5** as a function of the XeCl excimer laser fluence.[10b] Concentration: 10^{-4} M **1** in acetonitrile. Optical path: 1 mm. Delay time: 2 ms. KrF laser fluence: 1.25×10^{21} photons·m^{-2}·pulse^{-1} (100 mJ·cm^{-2}·pulse^{-1}).

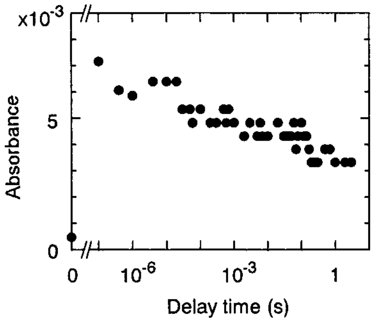

Figure 5. Absorption of the XeF laser as a function of the delay time. Concentration: 10^{-4} M **1** in acetonitrile. Optical path: 1 mm. Laser fluence: 1.25×10^{21} (KrF) and 1.88×10^{21} (XeF) photons·m^{-2}·pulse^{-1}.

Fluence Dependence on the Yield of Benzocyclobutene 5 in the Time-Delayed, Two-Color Photolysis. To know the number of photons necessary for the additional formation of **5**, an experiment on the XeCl laser fluence dependence was conducted in the time-delayed, two-color photolysis. Figure 4 shows the increased yield of **5** as a function of the XeCl laser fluence at the fixed delay time of 2 ms. As seen in the figure, 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 was a one-photon process.

Absorption of the Second Laser Pulse in the Time-Delayed, Two-Color Photolysis. The delay time dependence on the absorption of the second laser (XeF laser) was measured at 351 nm. The XeF laser was used as the second laser to eliminate the absorption of the starting material **1** and the products **4** and **5**. Figure 5 shows the absorbance at 351 nm as a function of the delay time in the two-color photolysis. The horizontal axis in the figure is shown in logarithmic scale in order to show clearly the fast change at short delay times. As seen in the figure, the time profile of the absorption at delay times $>10^{-2}$ s was consistent with that of the yield of **5** (cf., Figure 2a,b); both the absorption and the yield of **5** decreased in this time domain. The leveling off of the absorbance at 3.2×10^{-3} is due to the absorption of

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[16] Transient absorption was observed at 360–370 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 previous reports:[4a–c,12] unpublished result. However, the decay of **3** was difficult to observe because of the overlapping of several species such as phenylseleno radicals, diphenyl diselenide, intermediate **2a**/**b**, and other unidentified species.

diphenyl diselenide. However, the time profiles of the absorption (Figure 5) and the yield of **5** (Figure 2a,b) were quite different at shorter delay times. In the case of the absorption, a rapid increase occurred between 0 and 10^{-7} s and showed a gradual decrease between 10^{-7} and 10^{-2} s, whereas a gradual increase in the yield of **5** was observed between 10^{-7} and 10^{-2} s. These results indicate the existence of a transient species that has a shorter lifetime than **3**; the transient species absorbed 351-nm light but was not photochemically converted to **3**.

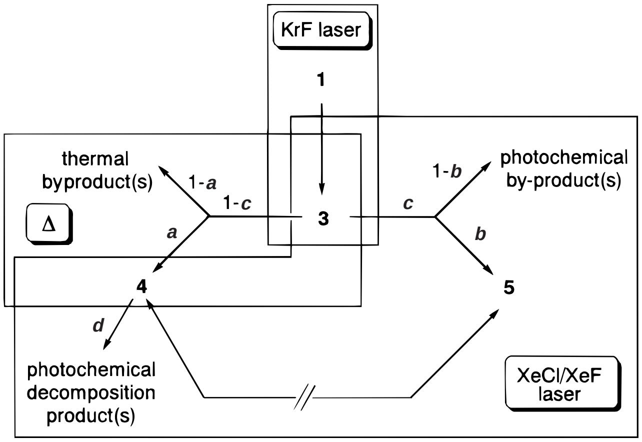
Photochemical Stability of Benzocyclobutene 5 and the Spiro Dimer 4. Photolyses of **4** and **5** were conducted in 10^{-4} M acetonitrile solutions with one pulse of the KrF, XeCl, or XeF excimer laser.[17] The reaction conditions were the same as those in the one-color laser photolyses of **1**. In the case of **4**, no decomposition was observed with a pulse of the KrF and XeF lasers and 10% decomposition with the XeCl laser. When **4** was irradiated in the presence of 1 equiv of diphenyl diselenide, the decomposition slightly increased to 14% with the XeCl laser and 5% with the XeF laser. However, in all cases, **5** was *not* observed after the laser irradiations. This indicates that the reverse reaction **4** → **3** was not involved in the photolysis. In the case of **5**, no decomposition was observed in all the three laser irradiations.[17]

Discussion

Reaction Mechanism on the Formation of Spiro Dimer 4 and Benzocyclobutene 5. In the case of one-color photolyses, the consumption of **1** in the XeCl laser photolysis was lower than that with the KrF laser despite the larger number of photons in the former pulse. This result can be explained by the difference in the molar extinction coefficient of **1** (16800 $M^{-1}\cdot cm^{-1}$ at 248 nm and 1800 $M^{-1}\cdot cm^{-1}$ at 308 nm) and also by the participation of different excited states at each laser wavelength.[8b] The generation of **3** by the laser photolysis is evidenced by the trapping of **3** by various dienophiles, and it is also proved that **3** is formed by a two-photon process.[8] The formation of **5**[18] is rationalized by further photolysis of **3** within the same laser pulse (Scheme 1: Laser 1 = Laser 2 = Laser 3). This is consistent with the formation of **5** by conventional light photolysis of **3** in low-temperature matrixes.[4a,b,f,h]

The increase of the yield of **5** in the time-delayed, two-color photolyses (cf., Figure 2) is explained by the photolysis of **3** by the second 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.[16] The experiment on the XeCl laser fluence dependence in the two-color photolysis showed that the increased yield of **5** was proportional to the first power of the XeCl laser fluence (cf., Figure 4). This result indicates that the formation of **5** by the XeCl laser irradiation proceeded through a one-photon process so that the photochemical process was **3** → **5** and not **2a**/**b** → **3** → **5**.

Scheme 2



In the case of the two-color photolyses, the existence of the maximum for the yield of **5** in Figure 2a,b means that 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 KrF laser photolysis implies the existence of another very fast process for the generation of **3** which enables **3** to absorb third photon within the same laser pulse (<30 ns). The origin of the two processes is not clear at present due to the lack of information in this time domain.

Reaction Paths of *o*-Quinodimethane 3. Scheme 2 shows the reaction paths of **3** in the time-delayed, two-color photolysis. First, **3** is generated by a pulse of the KrF laser. When the photolysis of **3** is conducted by a pulse of the XeCl/XeF laser, a part of **3** ($100c$ %, $0 \le c \le 1$) undergoes photochemical processes and the rest [$100(1 - c)$ %] reacts by thermal processes. In the photochemical processes, a part of **3** forms **5** ($100b$ %, $0 \le b \le 1$), and the rest [$100(1 - b)$ %] leads to the formation of other photochemical byproducts. On the other hand, in the thermal processes, the formation of **4** ($100a$ %, $0 \le a \le 1$) and other byproducts [$100(1 - a)$ %] are expected.

From the control experiments, partial decomposition of **4** was observed by the second XeCl/XeF laser irradiation especially in the presence of diphenyl diselenide. Therefore, we assume that $100d$ % ($0 \le d \le 1$) of **4** formed by the thermal process are decomposed by the second laser pulse. It was also proved by the control experiments that **5** was not generated by the XeCl/XeF laser photolyses of **4**.

Time Profile of *o*-Quinodimethane 3. The time profiles of **3**−**5** in the one-color KrF laser and the time-delayed, two-color photolyses are shown schematically in Schemes 3a and 3b, respectively. The rise time of **3** is neglected in these figures because the rise time is much shorter than the decay time (cf., Figures 2a,b and 3) so that the time profile of each species can be approximated as shown in Schemes 3a,b. As shown in Scheme 3a, when **1** is irradiated by a pulse of the KrF laser (at $t = 0$), **3** is generated by a two-photon process with the concentration of $[QM]_0$, and at the same time **5** is formed with the concentration of $[CB]_s$ by a three-photon process via **3**. The concentration of **5** did not change in the course of the reaction, because **5** was stable in room-temperature

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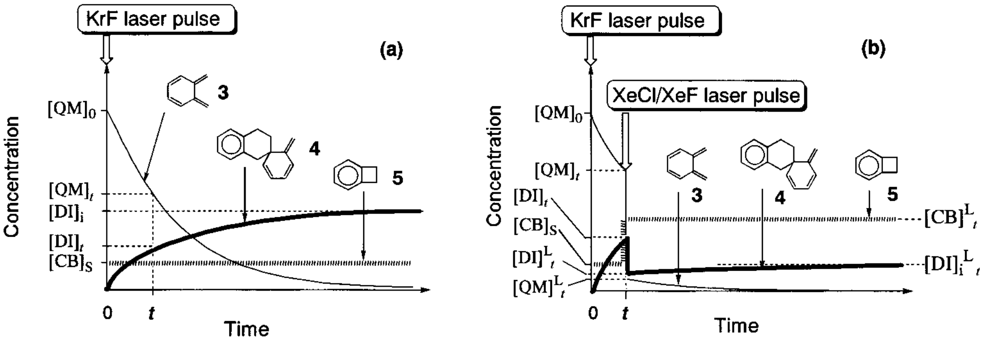
[17] The conversions[10a] of **4** and **5** were 0.6 (+0.6, −0.8) % and 1.4 (+1.1, −1.0) % for the KrF laser, 9.9 (+1.4, −1.0) % and 0 (+0.6, −1.0) % for the XeCl laser, 0 (+1.6, −0.9) % and 0 (+0.7, −1.1) % for the XeF laser.

[18] 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.

Scheme 3



solutions. However, thus-generated **3** undergoes dimerization by a thermal [4 + 2] cycloaddition to give spirodimer **4**. When the concentrations of **3** and **4** at time *t* are $[\mathrm{QM}]_t$ and $[\mathrm{DI}]_t$, respectively, we obtain

$$[\mathrm{DI}]_t = (a/2)([\mathrm{QM}]_0 - [\mathrm{QM}]_t) \qquad (a\text{: const.; } 0 \le a \le 1) \quad (1)$$

At $t = \infty$, when the concentration of **4** is $[\mathrm{DI}]_i$, eq 1 becomes

$$[\mathrm{DI}]_i = (a/2)[\mathrm{QM}]_0 \qquad (1')$$

because, $[\mathrm{QM}]_\infty = 0$.

Scheme 3b is the time profile of **3**–**5** in the time-delayed, two-color photolysis. When the second laser is irradiated at the delay time of *t*, the concentrations of **3** and **5** immediately change from $[\mathrm{QM}]_t \rightarrow [\mathrm{QM}]^{\mathrm{L}}{}_t$ and $[\mathrm{CB}]_s \rightarrow [\mathrm{CB}]^{\mathrm{L}}{}_t$, respectively, due to the photochemical reaction **3** → **5**. Thus, we obtain

$$[\mathrm{CB}]^{\mathrm{L}}{}_t - [\mathrm{CB}]_s = b([\mathrm{QM}]_t - [\mathrm{QM}]^{\mathrm{L}}{}_t) \qquad (b\text{: const.; } 0 \le b \le 1) \quad (2)$$

$$[\mathrm{QM}]^{\mathrm{L}}{}_t = (1 - c)[\mathrm{QM}]_t \quad (c\text{: const.; } 0 \le c \le 1) \quad (3)$$

Equations 2 and 3 are reduced to

$$[\mathrm{QM}]_t = (1/bc)([\mathrm{CB}]^{\mathrm{L}}{}_t - [\mathrm{CB}]_s) \qquad (4)$$

Equation 4 indicates that the value $([\mathrm{CB}]^{\mathrm{L}}{}_t - [\mathrm{CB}]_s)$ is proportional to the concentration of **3** at the delay time *t*, $[\mathrm{QM}]_t$.

Figure 3 shows the increased yield of **5** as a function of the delay time. In practice, $t = 0$ corresponds to the delay time where the concentration of **3** becomes its maximum, i.e., at ca. 20 ms in Figure 3. The increased yield of **5** is proportional to the value $([\mathrm{CB}]^{\mathrm{L}}{}_t - [\mathrm{CB}]_s)$ so that the decay curve in Figure 3 corresponds to the decay curve of **3** obtained by spectroscopic methods. The curve in Figure 3 shows second-order decay, which is consistent with the results of spectroscopic studies of **3** conducted with different precursors.[1c,4d,g]

Efficiency of the Thermal Formation of Spiro Dimer 4. We have revealed that 48%[11] of **3** was formed from 10^{-4} M **1** by a pulse of the KrF laser. Therefore, $[\mathrm{QM}]_0 = 4.8 \times 10^{-5}$ M. The value $[\mathrm{DI}]_i$ is related to the yield of **4** obtained by the one-color KrF excimer laser photolysis, which was $[\mathrm{DI}]_i = 3.5 \times 10^{-6}$ M (7.0% yield of **4** from 10^{-4} M **1**; two molecules of **3** are necessary for the formation of **4**). From eq 1′ and the values $[\mathrm{QM}]_0$ and $[\mathrm{DI}]_i$ given above, we obtain

$$a = 2[\mathrm{DI}]_i/[\mathrm{QM}]_0 = 0.15$$

This indicates that the efficiency of the thermal process **3** + **3** → **4** was 15%.

o-Quinodimethane (**3**) showed second-order decay, both by our experiment and by flash photolysis studies, and this was explained by the thermal dimerization which led to **4**.[1c,4d,g] However, as shown above, the efficiency of the thermal reaction **3** + **3** → **4** was only 15% so that other bimolecular processes, which probably lead to the higher molecular weight compounds, must be involved in the thermal processes.

Photochemical Decomposition of Spiro Dimer 4 in the Reaction Mixture. The control experiments revealed that the photochemical decomposition of **4** was accelerated by the presence of diphenyl diselenide. This was rationalized by the reaction of **4** and photochemically generated phenylseleno radicals. In the reaction mixture, the presence of radical species other than phenylseleno radicals was anticipated so that the extent of the decomposition of **4** in the reaction mixture was expected to be larger.

When the second laser is fired in the two-color photolysis, the concentration of **4** changes from $[\mathrm{DI}]_t \rightarrow [\mathrm{DI}]^{\mathrm{L}}{}_t$ due to decomposition, so that

$$[\mathrm{DI}]^{\mathrm{L}}{}_t = (1 - \mathrm{d})[\mathrm{DI}]_t \quad (d\text{: const.; } 0 \le d \le 1) \quad (5)$$

The final concentration of **4**, $[\mathrm{DI}]_i{}^{\mathrm{L}}{}_t$, is

$$[\mathrm{DI}]_i{}^{\mathrm{L}}{}_t = [\mathrm{DI}]^{\mathrm{L}}{}_t + (a/2)[\mathrm{QM}]^{\mathrm{L}}{}_t \qquad (6)$$

From eqs 1, 1′, 3, 5, and 6, we have

$$[\mathrm{QM}]_t = \{2/a(c - d)\}\{(1 - d)[\mathrm{DI}]_i - [\mathrm{DI}]_i{}^{\mathrm{L}}{}_t\} \quad (7)$$

At $t = \infty$, $[\mathrm{QM}]_t$ becomes zero so that the value *d* derived from eq 7 is

$$d = 1 - ([\mathrm{DI}]_i{}^{\mathrm{L}}{}_\infty/[\mathrm{DI}]_i) \qquad (8)$$

because the case $c \approx d$ only leads to a trivial solution. The concentration $[\mathrm{DI}]_i{}^{\mathrm{L}}{}_\infty$ is related to the yield of **4** at longer delay time where the yield becomes constant (cf. Figure 2),[19] which was 1.8×10^{-6} M (3.5% yield of **4** from 10^{-4} M **1**; two molecules of **3** are necessary for the

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[19] The leveling off of the yield of **4** is clearly observed when the delay time is shown in a linear scale. Cf. Supporting Information.

formation of **4**) for the XeCl laser and 2.5×10^{-6} M (5.0% yield of **4** from 10^{-4} M **1**) for the XeF laser.

By substituting $[DI]_i{}^L{}_\infty$ and $[DI]_i$ values to eq 8, we obtain

$$d_{XeCl} = 0.50 \quad \text{and} \quad d_{XeF} = 0.29$$

These values d_{XeCl} and d_{XeF} indicate that a larger portion of **4** was decomposed by the XeCl laser than by the XeF laser. This tendency is in accord with the control experiments, but the extent of the decomposition was 4- to 6-fold larger than those of the control experiments conducted in the presence of diphenyl diselenide.

Efficiency of the Photochemical Formation of Benzocyclobutene 5 from *o*-Quinodimethane 3. The ratio of photochemical and thermal processes by the irradiation of the second laser pulse is indicated by the values *c* and $1 - c$, respectively. From eqs 1′ and 7 at $t = 0$, the value *c* is

$$c = 1 - ([DI]_i{}^L{}_0/[DI]_i) \qquad (9)$$

Concentration $[DI]_i{}^L{}_0$ is related to the yield of **4** at the delay time of 0 (in practice, as indicated before, at the delay time of ca. 20 ms). When the second laser was the XeCl laser, the yield of **4** at $t = 0$ was 1.3% so that $[DI]_i{}^L{}_0 = 6.5 \times 10^{-7}$ M. Similarly, when the second laser was the XeF laser, $[DI]_i{}^L{}_0 = 9.5 \times 10^{-7}$ M. By substituting the values $[DI]_i{}^L{}_0$ and $[DI]_i$ ($= 3.5 \times 10^{-6}$ M) into eq 9, we obtain

$$c_{XeCl} = 0.81 \quad \text{and} \quad c_{XeF} = 0.73$$

These values of c_{XeCl} and c_{XeF} indicate that the proportion of the photochemical process of **3** by a pulse of the XeCl laser was 81% and that of the XeF laser was 73%. The rest of **3** reacted by thermal processes. Although the molar absorptivity of **3** was 2.5-[12] to 3.8-fold[4b] larger at 351 nm than at 308 nm, the efficiency of the consumption of **3** was ca. 1.1-fold larger when the XeCl laser was used instead of the XeF laser. The tendency on the molar absorptivity is opposite to that of the *c* values, and the result is best explained by the participation of different excited states.[20]

The efficiency of the photochemical conversion **3** → **5** in the photochemical processes is related to the value *b*. The value *b* obtained from eqs 4 and 7 is

$$b = \{a(c - d)/2c\}([CB]^L{}_t - [CB]_s)/\{(1 - d)[DI]_i - [DI]_i{}^L{}_t\} \qquad (10)$$

In principle, the value of *b* can be obtained from any delay time *t*; however, the most reliable values for $[CB]^L{}_t$ and $[DI]_i{}^L{}_t$ are obtained at $t = 0$ where $[CB]^L{}_t$ gives its maximum and $[DI]_i{}^L{}_t$ gives its minimum because relative experimental errors should be smallest. When the second laser was the XeCl laser, the yield of **5** was 9.1% (from 10^{-4} M **1**) so that $[CB]^L{}_0 = 9.1 \times 10^{-6}$ M. Similarly, when the second laser was the XeF laser, $[CB]^L{}_0 = 7.4 \times 10^{-6}$ M. The yield of **5** in the one-color KrF laser photolysis was 6.3% (from 10^{-4} M **1**) so that $[CB]_s = 6.3 \times 10^{-6}$ M. By substitution of these concentrations and the values *a*, *c*, and *d* into eq 10, we obtain

$$b_{XeCl} = 0.071 \quad \text{and} \quad b_{XeF} = 0.031$$

The values b_{XeCl} and b_{XeF} indicate that the efficiency of the photochemical conversion **3** → **5** by a pulse of the XeCl laser was 7.1% and that by the XeF laser was 3.1%.

The net photochemical efficiency for the photochemical conversion **3** → **5** is presented by the product *bc* so that

$$bc_{XeCl} = 0.057 \quad \text{and} \quad bc_{XeF} = 0.023$$

Therefore the net photochemical efficiency is 2.5-fold higher for the XeCl laser than the XeF laser. These results cannot be explained by the difference of the molar absorptivity of **3** at each wavelength because the reported molar absorptivity is 2.5-[12] to 3.8-fold[4b] larger at 351 nm than at 308 nm and this tendency is opposite to that of the values bc_{XeCl} and bc_{XeF}. The reported λ_{max} of the first absorption band of **3** is 370 nm, and the laser wavelength of 308 nm is located just at the minimum of its shorter wavelength side.[1c,4b,12] Therefore, the involvement of higher excited state is expected in the photochemical conversion **3** → **5**. Indeed, participation of the S_2 state for the conversion **3** → **5** has been postulated;[4b,c] however, $S_0 \rightarrow S_2$ transition is still not explicitly observed by spectroscopic means, and it is believed that the transition should be buried under more intense $S_0 \rightarrow S_1$ band. We think that our result on the wavelength dependence of the photochemical efficiency of the formation of **5** is consistent with this prediction on the involvement of the $S_0 \rightarrow S_2$ transition for the conversion **3** → **5**.

The values b_{XeCl} and b_{XeF} clearly indicate that photochemical conversion **3** → **5** is *not* the main path in the solution. Intermolecular reactions are likely to be the main photochemical pathways in such environments, and we are now investigating the intermolecular photochemical products in the reaction.

Conclusion

Photochemical efficiencies of *o*-quinodimethane (**3**) at room temperature were determined by using the time-delayed, two-color excimer laser photolyses technique. The time profile of **3** was monitored by chemical analysis of benzocyclobutene (**5**) (a photochemical product of **3**) and the spiro dimer **4** (a thermal product of **3**) in the two-color photolysis experiments. The time profile of **3** followed second-order decay kinetics. Photochemical efficiencies were obtained by analysis of the delay-time dependence of the product yields; those of the consumption of **3** and the conversion **3** → **5** by a single pulse of an excimer laser were 81% and 5.7% for the XeCl laser, and 73% and 2.3% for the XeF laser. The difference between the two lasers was attributed to different excited states involved. In contrast to the photolysis of **3** in argon or rigid organic matrixes, it was revealed that photochemical conversion **3** → **5** was not the main path in the solutions and intermolecular reactions seemed to be the main paths.

Experimental Section

1,2-Bis[(phenylseleno)methyl]benzene (**1**) and the cycloadduct of **3** and **11**, and that of **3** and **14**, were prepared according to the reported procedures.[21] Detailed descriptions on the

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[20] Cf. Excitation spectrum of **3** in ref 4a,b.

[21] Reference 8b, Supporting Information.

preparation of compounds **4**, **5**, **9**, **10**, and **12** are given as Supporting Information. Tetrabutylammonium fluoride hydrate (**13**) and 2-indanone were purchased from Aldrich Chemical Co. Inc., fumaronitrile (**14**) from Wako Chemicals, 3-isochromanone (**8**) from Tokyo Kasei Kogyo Co., Ltd., and spectroscopic grade acetonitrile from Cica-Merck/Kanto Chemicals.

Time-Delayed, Two-Color Laser Photolyses. The reactions were conducted on 0.05 mL of 10^{-4} M **1** acetonitrile solutions under a nitrogen atmosphere at room temperature by using a synthetic quartz cuvette of 10-mm width and 1-mm optical path. The first laser pulse was generated by a Lambda Physik EMG 201 MSC [KrF, 1.25×10^{21} photons·m^{-2}·pulse^{-1} (100 mJ·cm^{-2}·pulse^{-1}), pulse width (fwhm): 30 ns] and the second pulse by a Lambda Physik EMG 102 MSC [XeCl, 1.88×10^{21} photons·m^{-2}·pulse^{-1} (121 mJ·cm^{-2}·pulse^{-1}), pulse width (fwhm): 14 ns] or by a Lambda Physik COMPex 102 [XeF, 1.88×10^{21} photons·m^{-2}· pulse^{-1} (106 mJ·cm^{-2}·pulse^{-1}), pulse width (fwhm): 19 ns] excimer lasers. The pulse energy was measured by means of a Gentec ED-500 joulemeter and a Tektronic T912 10 MHz storage oscilloscope. The delay time was defined as the time between two peaks of the KrF and XeCl or XeF laser pulses and varied from 0 ns to 3 s. The delay times between the two laser pulses were controlled by a Stanford Research Systems DG535 four-channel digital delay/pulse generator. The delay times of the two laser pulses were measured with a Hamamatsu Photonics R1193U-55 biplanar phototube and a Iwatsu Electric TS-8123 storage scope.

Fluence Dependence of the Time-Delayed, Two-Color Laser Photolysis. The photolyses were conducted by using the KrF [1.25×10^{21} photons·m^{-2}·pulse^{-1} (100 mJ·cm^{-2}·pulse^{-1})] and XeCl [varied between 0.78 and 2.33×10^{21} photons·m^{-2}·pulse^{-1} (50−150 mJ·cm^{-2} ·pulse^{-1})] lasers at the delay time of 2 ms.

Transmittance of the Second Laser Pulse in the Time-Delayed, Two-Color Photolysis. The photolyses were conducted by using the KrF (1.25×10^{21} photon·m^{-2}·pulse^{-1}) and XeF (1.88×10^{21} photon·m^{-2}·pulse^{-1}) lasers. The experimental setup and the solutions were the same as those in the time-delayed, two-color laser photolyses. The energies of the transmitted XeF laser was measured with the biplanar phototube and the storage scope, and the absorbance was calculated based on the transmitted energy of the solvent acetonitrile.

One-Color Excimer Laser Photolyses of 1 and Decomposition of 4, 5, and 7−10. The photolyses of **1**, **4**, **5**, and **7**−**10** were conducted using the same experimental setup and procedure as those of the time-delayed, two-color laser photolyses but with a single excimer laser. The fluence of the lasers were the same as that in the two-color experiments.

Trapping of *o*-Quinodimethane 3 by Fumaronitrile 14. The reactions were conducted by following the reported procedure[4g] with a 10^{-4} M [*o*-[(trimethylsilyl)methyl]benzyl]-trimethylammonium iodide (**12**) acetonitrile solution and 100 or 200 equiv of tetrabutylammonium fluoride (**13**) (1.0 M in acetonitrile) in the presence of 10^{-3} M **14**.

Analyses of the Products. The yields of **4**, **5**, cycloadduct of **3** and **14**, and consumption of **1** were determined by HPLC analysis (detection wavelengths of UV detectors: 254 and 300 nm) on a Merck Supersphere 60 RP-8e column (244 mm × 4 mm i.d.), and their retention times were compared with authentic samples.

Acknowledgment. We thank the Agency of Industrial Science and Technology (MITI Japan) for financial support.

Supporting Information Available: Preparation of compounds **4**, **5**, **9**, **10**, and **12**, and Figure 2 with the delay time in linear scale (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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