7376 *J. Org. Chem.* **1997,** *62,* 7376−7383

A Facile Synthesis of Tetra- and Dihydronaphthalene Derivatives by Excimer Laser Photolysis of 1,2-Bis(substituted-methyl)benzenes in the Presence of Olefins and Acetylene[†]

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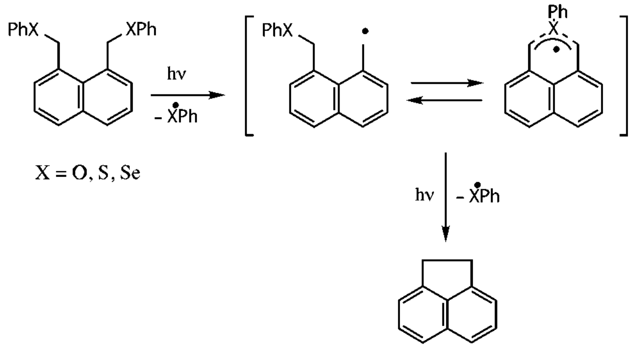
Received May 29, 1997[⊗]

o-Quinodimethane (**3A**) was generated effectively by excimer laser photolyses of 1,2-bis(phenoxymethyl)benzene (**1-O**), 1,2-bis[(phenylthio)methyl]benzene (**1-S**), and 1,2-bis[(phenylseleno)methyl]benzene (**1-Se**) in acetonitrile solutions *via* a two-photon process, which was followed by cycloaddition of **3A** with several dienophiles—maleic anhydride (**4a**), dimethyl maleate (**4b**), dimethyl fumarate (**4c**), fumaronitrile (**4d**), and dimethyl acetylenedicarboxylate (**4e**)—to give corresponding cycloadducts **5**. Three kinds of excimer lasers, namely, KrF (248 nm), XeCl (308 nm), and XeF (351 nm) excimer lasers were used for the reaction. The KrF excimer laser was found to be most effective for obtaining high consumption of **1-(O, S, Se)** and yield of **5**; the maximum yield of the cycloadduct obtained was 48%.

Introduction

Recent studies on the application of lasers to organic photochemistry have revealed the occurrence of many reactions which only proceed by the use of lasers.[1] The difference between such laser reactions and conventional photolyses is that the former can provide more precise control over the reactions of intermediates[2−5] and/or excited states[6,7] which are involved in the photochemical processes. However, in spite of the findings of the laser specific reactions only a few can be employed as useful synthetic purposes.

Scheme 1



In the course of our research on the laser photochemistry, we have found an efficient double homolytic C−X (X = O, S, Se) bond cleavage by the use of excimer lasers, which proceeds through a two-photon process;[8] the reaction is the laser photolysis of 1,8-bis(substituted-methyl)naphthalenes (substituent: OPh, SPh, SePh), which generates acenaphthene in 72% yield by a stepwise two-photon process with use of KrF excimer laser (248 nm) and SePh radical leaving groups (Scheme 1).

This efficient reaction can be applied to the generation of *o*-quinodimethane [**3A**; 5,6-bis(methylene)cyclohexa-1,3-diene] by the laser photolysis of 1,2-bis(phenoxymethyl)benzene (**1-O**), 1,2-[bis(phenylthio)methyl]benzene (**1-S**), and 1,2-[bis(phenylseleno)methyl]benzene (**1-Se**) through a two-photon process (Scheme 2). *o*-Quinodimethane (**3A**) has attracted much attention of both theoretical and synthetic chemists and it is known as a versatile building block for organic synthesis.[9] The major synthetic utilization is cycloaddition reactions between

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[†] Dedicated to Professor Waldemar Adam on the occasion of his 60th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1997.

(1) Reviews: (a) Kleinermanns, K.; Wolfrum, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 38−58. (b) Wilson, R. M.; Schnapp, K. A.; Hannemann, K.; Ho, D. M.; Memarian, H. R.; Azadnia, A.; Pinhas, A. R.; Figley, T. M. *Spectrochim. Acta, Part A* **1990**, *46*, 551−558. (c) Wilson, R. M.; Adam, W.; Schulte Oestrich, R. *Spectrum* **1991**, *4*, 8−17. (d) Wilson, R. M.; Schnapp, K. A. *Chem. Rev.* **1993**, *93*, 223−249. (e) Johnston, L. J. *Chem. Rev.* **1993**, *93*, 251−266.

(2) Laser-jet photolysis: *e.g.* (a) Wilson, R. M.; Romanova, T. N.; Azadnia, A.; Bauer, J. A. K.; Johnson, R. P. *Tetrahedron Lett.* **1994**, *35*, 5401−5404. (b) Adam, W.; Kita, F. *J. Am. Chem. Soc.* **1994**, *116*, 3680−3683. (c) Adam, W.; Kita, F.; Schulte Oestrich, R. *J. Photochem. Photobiol. A* **1994**, *80*, 187−197. (d) Adam, W.; Patterson, J. *J. Org. Chem.* **1995**, *60*, 7769−7773. (e) Wilson, R. M.; Patterson, W. S.; Austen, S. C.; Ho, D. M.; Bauer, J. A. K. *J. Am. Chem. Soc.* **1995**, *117*, 7820−7821. (f) Adam, W.; Walther, B. *Tetrahedron* **1996**, *52*, 10399−10404. (g) Schnapp, K. A.; Motz, P. L.; Stoeckel, S. M.; Wilson, R. M.; Bauer, J. A. K.; Bohne, C. *Tetrahedron Lett.* **1996**, *37*, 2317−2320.

(3) Laser drop photolysis: (a) Banks, J. T.; Scaiano, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 6409−6413. (b) Scaiano, J. C.; Banks, J. T. *J. Braz. Chem. Soc.* **1995**, *6*, 199−210. (c) Banks, J. T.; Scaiano, J. C. *J. Phys. Chem.* **1995**, *99*, 3527−3531. (d) Banks, J. T.; Scaiano, J. C. *J. Photochem. Photobiol. A.* **1996**, *96*, 31−33.

(4) Two-color, two-pulse photolysis: (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.; Yabe, A. *Chem. Lett.* **1995**, 945−946. (d) Ouchi, A.; Koga, Y. *Tetrahedron Lett.* **1995**, *36*, 8999−9002.

(5) Laser photolysis: *e.g.* (a) Alkenings, B.; Bettermann, H.; Dasting, I.; Schroers, H.-J. *Vib. Spectrosc.* **1993**, *5*, 43−49. (b) Pérez-Prieto, J.; Miranda, M. A.; Font-Sanchis, E.; Kónya, K.; Scaiano, J. C. *Tetrahedron Lett.* **1996**, *37*, 4923−4926. (c) Pérez-Prieto, J.; Miranda, M. A.; García, H.; Scaiano, J. C. *J. Org. Chem.* **1996**, *61*, 3773−3777. (d) Ouchi, A.; Koga, Y.; Adam, W. *J. Am. Chem. Soc.* **1997**, *119*, 592−599.

(6) Reactions from higher excited states: *e.g.* (a) Pola, J.; Taylor, R. *Tetrahedron Lett.* **1994**, *35*, 2799−2800. (b) Ichinose, N.; Kawanishi, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2017−2018. (c) North, S. W.; Blanck, D. A.; Gezelter, J. D.; Longfellow, C. A.; Lee, Y. T. *J. Chem. Phys.* **1995**, *102*, 4447−4460. (d) Kawamata, K.; Kikuchi, K.; Okada, K.; Oda, M. *J. Phys. Chem.* **1995**, *99*, 3548−3553.

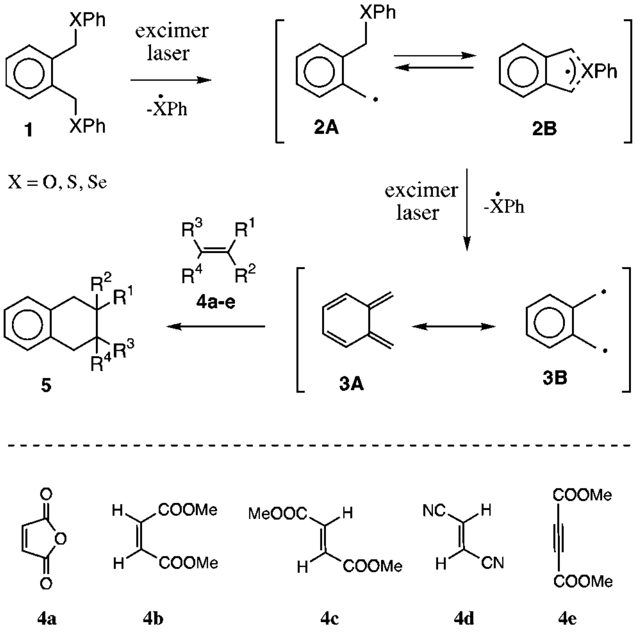
(7) Reactions by nonresonant two-photon excitation: (a) Kira, M.; Miyazawa, T.; Koshihara, S.; Segawa, Y.; Sakurai, H. *Chem. Lett.* **1995**, 3−4. (b) Miyazawa, T.; Koshihara, S.; Segawa, Y.; Kira, M. *Ibid.* **1995**, 217−218.

(8) (a) Ouchi, A.; Adam, W. *J. Chem. Soc., Chem. Commun.* **1993**, 628−629. (b) Ouchi, A.; Yabe, A.; Adam, W. *Tetrahedron Lett.* **1994**, *35*, 6309−6312. (c) Reference 4d.

(9) Reviews: (a) McCullough, J. J. *Acc. Chem. Res.* **1980**, *13*, 270−276. (b) Charlton, J. L.; Alauddin, M. M. *Tetrahedron* **1987**, *43*, 2873−2889. (c) Scaiano, J. C.; Wintgens, V.; Netto-Ferreira, J. C. *Pure Appl. Chem.* **1990**, *62*, 1557−1564. (d) Martin, N.; Seoane, C.; Hanack, M. *Org. Prep. Proced. Int.* **1991**, *23*, 237−272.

S0022-3263(97)00953-5 CCC: $14.00

Scheme 2



3A and dienophiles, and many synthetic applications have been attempted,[10,11] especially in the field of steroids synthesis.[10] Several methods have been developed for the efficient generation of *o*-quinodimethane (**3A**), which can be used for preparative purposes;[12] however, most of these methods require long synthetic steps for the preparation of its precursors and/or time-consuming synthetic procedures. Our method shown in Scheme 2 provides a fast and simple preparation of *o*-quinodimethane (**3A**) from easily accessible precursors **1**; compound **1** (X = O, S, Se) can be prepared by a one-step procedure in an excellent yield (89–99%) from commercially available 1,2-bis(bromomethyl)benzene, and **3A** is generated efficiently from **1-(O, S, Se)** within a pulse of an excimer laser. *o*-Quinodimethane (**3A**) is then trapped with various dienophiles **4** to give the corresponding cycloadducts **5** (Scheme 2).

In this paper we report a full detail on the generation of *o*-quinodimethane (**3A**) by using KrF (248 nm),[13] XeCl (308 nm), and XeF (351 nm) excimer lasers and the trapping of **3A** with several dienophiles under various photolysis conditions.

Results

Absorption spectra of 1,2-bis(phenoxymethyl)benzene (**1-O**), 1,2-[bis(phenylthio)methyl]benzene (**1-S**), and 1,2-bis[(phenylseleno)methyl]benzene (**1-Se**) in acetonitrile are shown in Figure 1. The molar absorptivities of each substrate at 248, 308, and 351 nm are summarized in Table 1. The dienophiles used in the reaction were maleic anhydride (**4a**), dimethyl maleate (**4b**), dimethyl fumarate (**4c**), fumaronitrile (**4d**), and dimethyl acetylenedicarboxylate (**4e**). The molar absorptivities of the dienophiles **4a**–**e**, corresponding cycloadducts **5a**–**e**, and the coupling products of the radical leaving groups, *i.e.*, diphenyl disulfide (**6-S**) and diphenyl diselenide (**6-Se**), are also summarized in Table 1.

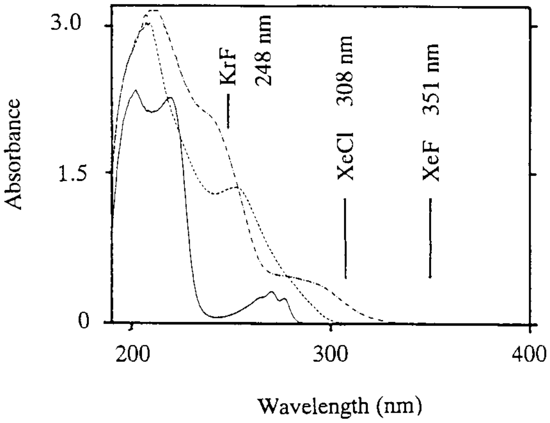


Figure 1. Absorption spectra of 1,2-bis(phenoxymethyl)benzene (**1-O**)[—], 1,2-[bis(phenylthio)methyl]benzene (**1-S**)[----], and 1,2-bis[(phenylseleno)methyl]benzene (**1-Se**)[-•-•-]. Concentration 10^{-4} M in acetonitrile, optical path 10 mm. The wavelength of the excimer laser emissions are marked in the figure.

Table 1. Molar Absorptivities of 1, 4, 5, and 6 at 248, 308, and 351 nm[a]

compound	molar absorptivity (ϵ) ($M^{-1}\cdot cm^{-1}$) 248 nm	308 nm	351 nm
1-O	670	30	0
1-S	13600	40	0
1-Se	16800	1800	20
4a	160	10	0
4b	470	0	0
4c	400	6	0
4d	0	0	0
4e	230	6	0
5a	140	0	0
5b	160	0	0
5c	160	0	0
5d	110	0	0
5e	1630	70	0
6-S	7800	1020	120
6-Se	14500	790	840

[a] Measured by a UV-vis spectrophotometer in acetonitrile solutions.

Transmittance of the reactant solutions (10^{-4} M **1**, 10^{-3} M **4**) was measured by an UV-vis spectrophotometer and by excimer laser irradiations (Table 2). The transmittance of the lasers were calculated from the energies of the transmitted light between sample solutions and acetonitrile. As seen in Table 2, >90% of photons were absorbed at 248 nm in the spectroscopic measurements and >80% of photons were absorbed in the KrF laser irradiation with 10-mm optical path except for the solution of **1-O** and **4a**; however, >70% of the photons were transmitted in the cases of the KrF laser irradiation with 1-mm optical path. On the other hand, the spectroscopic measurements at 308 nm showed that only <4% of the photons were absorbed for the solution of **1-(O, S)** and **4a**, and 33% of absorption for **1-Se** and **4a**; in the case of the laser irradiations, practically no absorption

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(10) Reviews: (a) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10–23. (b) Oppolzer, W. *Synthesis* **1978**, 793–802. (c) Funk, R. L.; Vollhardt, K. P. C. *Chem. Soc. Rev.* **1980**, *9*, 41–61. (d) Kametani, T.; Nemoto, H. *Tetrahedron* **1981**, *37*, 3–16.

(11) *e.g.* (a) Charlton, J. L.; Bogucki, D.; Guo, P. *Can. J. Chem.* **1995**, *73*, 1463–1467. (b) Bogucki, D. E.; Charlton, J. L. *J. Org. Chem.* **1995**, *60*, 588–593. (c) Nemoto, H.; Satoh, A.; Fukumoto, K.; Kabuto, C. *J. Org. Chem.* **1995**, *60*, 594–600.

(12) (a) Kambe, N.; Tsukamoto, T.; Miyoshi, N.; Murai, S.; Sonoda, N. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3013–3018. (b) Sano, H.; Ohtsuka, H.; Migita, T. *J. Am. Chem. Soc.* **1988**, *110*, 2014–2015. (c) Hoey, M. D.; Dittmer, D. C. *J. Org. Chem.* **1991**, *56*, 1947–1948. (d) Fujihara, H.; Yabe, M.; Furukawa, N. *J. Org. Chem.* **1993**, *58*, 5291–5292. (e) Sato, H.; Isono, N.; Okamura, K.; Date, T.; Mori, M. *Tetrahedron Lett.* **1994**, *35*, 2035–2038; and see references cited therein.

(13) Preliminary results with a KrF excimer laser: Ouchi, A.; Koga, Y. *Chem. Commun.* **1996**, 2075–2076.

Table 2. Transmittance of the Reactant Mixture Solutions at 248 and 308 nm[a]

precursor (10^{-4} M)	dienophile (10^{-3} M)	transmittance (%)				
		248 nm			308 nm	
		spectrophotometer	KrF excimer laser[b]		spectrophotometer	XeCl excimer laser[b]
		op:[c] 10 mm	op:[c] 10 mm	op:[c] 1 mm	op:[c] 10 mm	op:[c] 1 mm
1-O	**4a**	63	52	91	97	99
1-S	**4a**	5	8	78	96	99
1-Se	**4a**	2	7	71	67	96
1-Se	**4b**	1	4	71	–	–
1-Se	**4c**	1	6	72	–	–
1-Se	**4d**	8	16	87	–	–
1-Se	**4e**	2	6	71	–	–

[a] Measured in acetonitrile solutions. [b] Laser fluence: 1.25 × 10^{21} photons·m^{-2}·$pulse^{-1}$. [c] op: optical path.

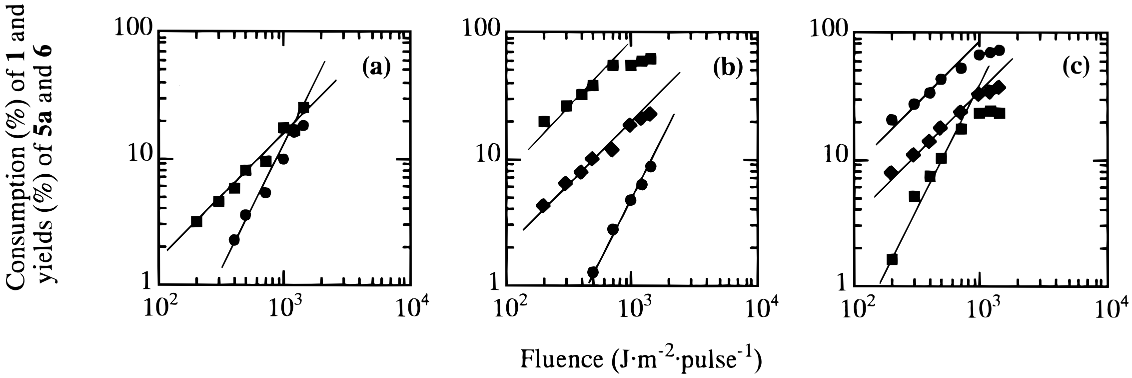

Figure 2. The dependence of the KrF excimer laser fluence on the consumption of **1-O** (a), **1-S** (b), **1-S**e (c) and the yields of **5a** and **6-(S, Se)**. Substrates: **1-(O, S, Se)** (■), **5a** (●), **6 -(S, Se)** (◆); concentration in acetonitrile: 10^{-4} M **1-(O, S, Se)** and 10^{-3} M **4a**; optical path 10 mm; number of KrF laser shots 1 shot. The results are the average of two independent runs; the experimental errors are given as Supporting Information.

was observed for the solutions of **1-(O, S)** and **4a**, and only 4% for **1-Se** and **4a**. The solutions of **1-(O, S, Se)** and **4a** showed practically no absorption at 351 nm, both for the spectroscopic and the XeF laser irradiation measurements.

Fluence dependence on the reactions between **1-(O, S, Se)** and maleic anhydride (**4a**) is shown in Figure 2 for the fluence range of 0.2 × 10^3 to 1.4 × 10^3 J·m^{-2}·$pulse^{-1}$ (0.25 × 10^{21} to 1.75 × 10^{21} photons·m^{-2}·$pulse^{-1}$). As seen in Figure 2a–c, the slopes of the consumption of **1-(O, S, Se)** and the yield of **6-(S, Se)** *vs* laser fluence for a double-logarithmic plot were unity, whereas that of the yield of **5a** was two. This result indicates one-photon processes for the consumption of **1** and the formation of **6**, and a two-photon process for the formation of **5**. However, the saturation of the consumption of **1-(S, Se)** (Figure 2b and c), and the yields of **5a** and **6-Se** in the reaction with **1-Se** (Figure 2c) was observed at high laser fluence. In the cases of the photolyses with 1-mm optical path, the saturation of the consumption of **1-(S, Se)** and the yields of **5a** and **6-(S, Se)** were observed even from lower fluence.[14]

Photolysis Condition. In order to study the effect of reaction conditions, four types of photolysis conditions were applied to the reactions of **1-(S, Se)** and **4a**. Firstly, standard photolysis was conducted with low fluence (LF, 1.25 × 10^{21} photons·m^{-2}·$pulse^{-1}$) KrF excimer laser irradiation on a solution of 10^{-4} M **1-(S, Se)** and low concentration (LC; 10^{-3} M) **4a** with 10-mm optical path [type i mode] [Figures 3a (**1-S**) and 3d (**1-Se**)]. Secondly, the effect on the concentration of dienophile was investigated by conducting the photolysis with high concentration (HC; 10^{-2} M) **4a** [type ii mode] [Figures 3b (**1-S**) and 3e (**1-Se**)]; other reaction conditions—the concentration of **1-(S, Se)**, optical path, and the fluence of the KrF laser—were the same as those of the standard condition. Thirdly, the effect of the laser fluence was examined by the reaction with high fluence (HF; 3.12 × 10^{22} photons·m^{-2}·$pulse^{-1}$) laser photolysis [type iii mode] [Figures 3c (**1-S**) and 3f (**1-Se**)]; other conditions were the same as those of the standard condition. Finally, the effect of optical path was studied by changing the optical path from 10 mm to 1 mm [type iv mode] [Figures 4a (**1-O**), 4b (**1-S**), and 4c (**1-Se**)].

In the standard photolysis condition [type i mode], the consumption rate of **1** is almost the same between **1-S** (Figure 3a) and **1-Se** (Figure 3d). Under this photolysis condition, the photons are mostly absorbed by **1-(S, Se)** because the molar absorptivity of **1-(S, Se)** is two orders of magnitude larger than that of **4a** (*cf.* Table 1). However, the formation rate of **5a** was faster for **1-Se** than for **1-S**, and the yield of **5a** was higher in the case of **1-Se**. The similar trend was observed on the reactivity of **1-S** and **1-Se** in the other photolysis conditions, *i.e.* in type ii–iv modes.

The increase of the dienophile concentration [type ii mode] resulted in the decrease of the consumption rate of **1-(S, Se)** and of the formation rate of **5a** and **6-(S, Se)** compared with those of the standard condition [Figure 3a *vs* 3b (**1-S**); Figure 3d *vs* 3e (**1-Se**)]. The decrease can be rationalized by the innegligible absorption of photons by **4a** which became comparable to that of **1-(S, Se)** (*cf.* Table 1) since the concentration of **4a** is 100-fold more than that of **1-(S, Se)**; thus, the number of photons absorbed by **1-(S, Se)** is diminished and the decrease in

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(14) Original data are given as Supporting Information.

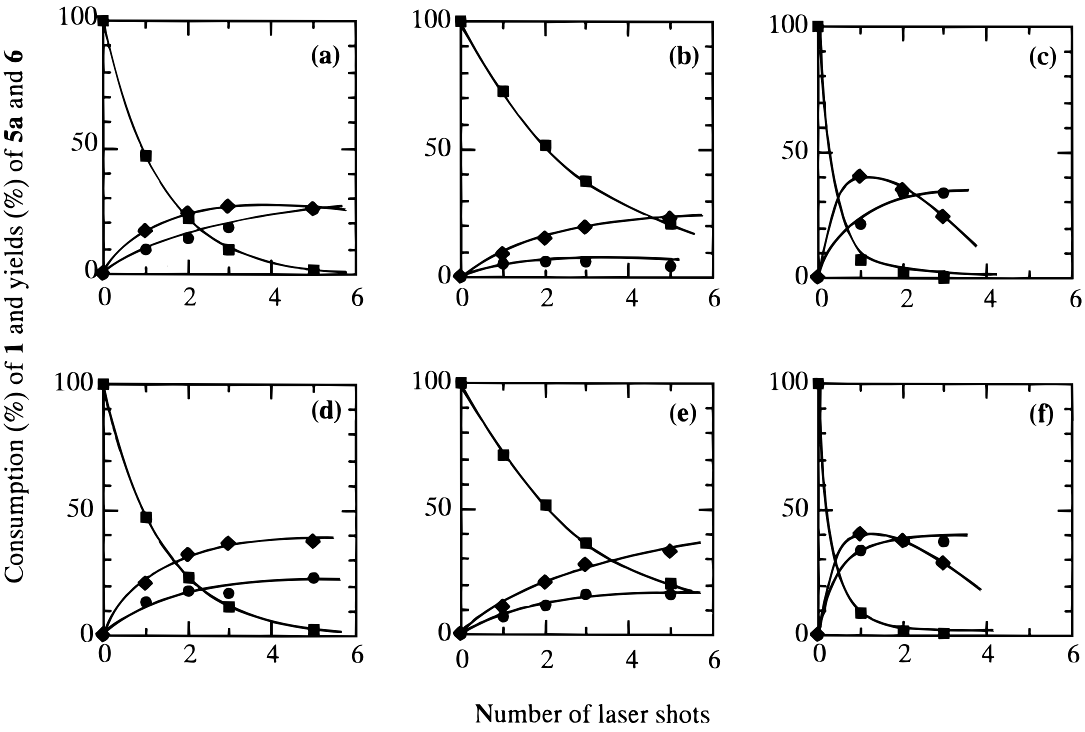

Figure 3. The consumption of substrate **1-(S, Se)** and the yields of cycloadduct **5a** and **6-(S, Se)** as a function of the number of KrF excimer laser shots. Substrate, laser fluence, and concentration of **4a**: (a)**1-S**, LF, LC; (b) **1-S**, LF, HC; (c) **1-S**, HF, LC; (d) **1-Se**, LF, LC; (e) **1-Se**, LF, HC; (f) **1-Se**, HF, LC. Substrates **1-(S, Se)** (■), **5a** (●), **6-(S, Se)** (◆); concentration in acetonitrile: 10^{-4} M **1-(S, Se),** and 10^{-3} M (LC) or 10^{-2} M (HC) **4a**; laser fluence 1.25×10^{21} (LF) or 3.12×10^{22} (HF) photons·m^{-2}·pulse^{-1}; optical path 10 mm. The results are the average of two independent runs; the experimental errors are given as Supporting Information.

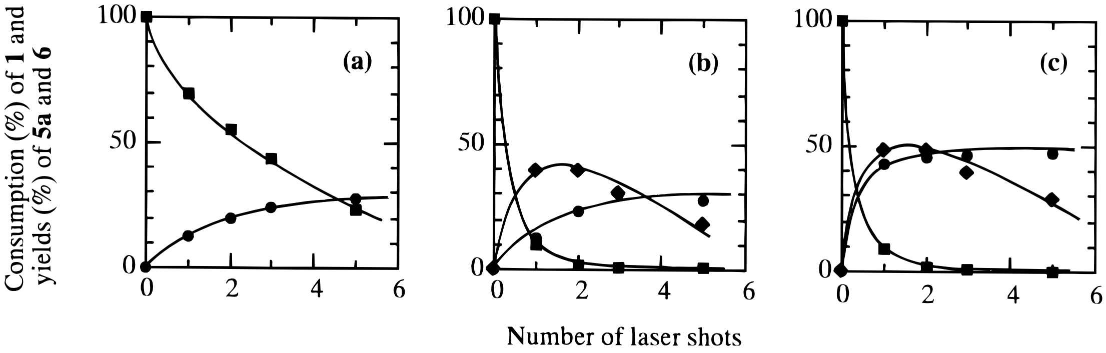

Figure 4. The consumption of (a) **1-O**, (b) **1-S**, (c) **1-Se** and the yields of **5a** and **6-(S, Se)** as a function of the number of KrF excimer laser shots. Substrates **1-(O, S, Se)** (■), **5a** (●), **6-(S, Se)** (◆); concentration 10^{-4} M **1-(O, S, Se)** and 10^{-3} M **4a**; laser fluence 1.25×10^{21} photons·m^{-2}·pulse^{-1}; optical path 1 mm. The results are the average of two independent runs; the experimental errors are given as Supporting Information.

the consumption rate of **1-(S, Se)**, and the formation rate of **5a** and **6-(S, Se)** is expected.

By changing the laser fluence from 1.25×10^{21} to 3.12×10^{22} photons·m^{-2}·pulse^{-1} [type iii mode] the large increase in the consumption rate of **1-(S, Se)** and the formation rate of **5a** and **6-(S, Se)** was observed [Figure 3a *vs* 3c (**1-S**); Figure 3d *vs* 3f (**1-Se**)]. As seen in Figures 3c and 3f, the yield of **6-(S, Se)** decreased with the increase of laser pulses, which indicates the decomposition of **6-(S, Se)** by the laser. On the contrary, the saturation of the yield of **5a** indicates that **5a** is not decomposed by the subsequent laser pulses. During the laser irradiation, ablation of liquid was observed from the surface of the solution; however, the weight loss after one laser shot was 0.4% for the solution of **1-S** and **4a** and 0.5% for that of **1-Se** and **4a**, which shows that the weight loss of the solution by the ablation was negligible.

Additional photolysis condition, high fluence (HF) and high **4a** concentration (HC), was applied on the solution of **1-(S, Se)** and **4a**. The decrease in the consumption rate of **1-(S, Se)** and the yields of **5a** and **6-(S, Se)** was observed; the yield of **5a** was lower than those in type i−iii modes.[14]

The application of shorter optical path (1 mm)[type iv mode] showed the increase in both the consumption of **1-(S, Se)**, and the yields of **5a** and **6-(S, Se)** compared with those in the standard condition [Figure 3a *vs* 4b (**1-S**); Figure 3d *vs* 4c (**1-Se**)]. In the case of **1-Se**, the best yield of **5a** was obtained by this photolysis condition among type i−iv modes. In the case of **1-S**, however, the best yield of **5a** was obtained in type iii mode. The decrease in the yield of **6-(S, Se)** was observed by the subsequent laser pulses, similar to that in type iii mode, which indicates the decomposition of **6-(S, Se)** by the

Table 3. Consumption of Precursor 1 and Yield of Cycloadducts 5[a]

precursor **1**	dienophile **4**	reaction temp (°C)[b]	number of laser pulses	yield of **5** (%)	consumption of **1** (%)
1-O	**4a**	rt	1	13 ± 0.3	30 ± 1.9
		rt	5[c]	28 ± 1.4	77 ± 2.9
1-S	**4a**	rt	1	13 ± 0.6	90 ± 0.2
		rt	3[c]	30 ± 2.3	99 ± 0.1
1-Se	**4a**	rt	1	43 ± 2.2	91 ± 0.7
		rt	5[c]	48 ± 0.6	∼100 ± 0.3
		60	1	44 ± 1.9	96 ± 1.5
		60	3[d]	60 ± 7.7	∼100 ± 0.2
1-Se	**4b**	rt	1[c]	4.7 ± 0.3	89 ± 1.7
		60	1[d]	4.9 ± 0.7	92 ± 1.6
1-Se	**4c**	rt	1	16 ± 1.9	88 ± 1.6
		rt	5[c]	20 ± 2.7	∼100 ± 0.1
		60	1	17 ± 0.9	93 ± 1.5
		60	3[d]	20 ± 1.0	99 ± 0.2
1-Se	**4d**	rt	1[c]	39 ± 4.2	93 ± 0.4
		60	1	40 ± 0.3	95 ± 1.2
		60	2[d]	44 ± 1.7	99 ± 0.6
1-Se	**4e**	rt	1	2.3 ± 0.3	94 ± 0.8
		rt	5[c]	4.0 ± 0.1	∼100 ± 0.2
		60	1	1.3 ± 0.6	95 ± 0.2
		60	3[d]	3.9 ± 0.6	99 ± 0.2

[a] KrF excimer laser fluence: 1.25 × 10^{21} photons·m^{-2}·pulse^{-1}; optical path: 1 mm; concentration: 10^{-4} M **1** and 10^{-3} M **4** in acetonitrile; the results are the average of two independent runs. [b] rt: room temperature. [c] Highest yield of **5** at room temperature obtained among 1-, 2-, 3-, and 5-laser-pulse photolyses. [d] Highest yield of **5** at 60 °C obtained among 1-, 2-, and 3-laser-pulse photolyses.

laser. No decomposition of **5a** occurred by the subsequent laser irradiations, which is consistent with the result of type iii mode.

The reaction of **1-O** and **4a** was also conducted in type iv mode (Figure 4a). As seen in Figures 4a–c, the consumption of **1-O** was much slower than those of **1-(S, Se)**; the consumption rate was **1-Se** ≈ **1-S** ≫ **1-O**. However, in spite of the slow consumption rate, the yield of **5a** was comparable to that in the case of **1-S**; the yield of **5a** was **1-Se** ≫ **1-S** ≈ **1-O**.

The same trend was observed in the reaction of **1-(S, Se)** and **4d** in type i and iii modes,[14] and of **1-Se** and **4b** in type i mode.[14] The consumption rate of the starting material **1-(S, Se)** and the formation rate of **6-(S, Se)** in these reactions were identical with those of **1-(S, Se)** and **4a**.

Wavelength dependence on the reactions of **1-(O, S, Se)** and **4a** in type iv mode was studied by using KrF, XeCl, and XeF excimer lasers. The results on the KrF excimer laser photolyses are already shown in Figures 4a–c. No reaction took place for **1-O** with the use of XeCl laser, [14] which is explained by the lack of absorption at 308 nm (*cf.* Table 1). Slight consumption of **1-S** (9.4% at the fifth laser shots) and the formation of **6-S** (1.5% at the fifth laser shots) were observed for **1-S** but practically no **5a** was formed.[14] As seen in Figure 5, the reaction proceeded in the case of **1-Se** but with slower consumption rate of **1-Se** and lower yield of **5a** compared with those in the KrF laser photolyses [Figure 4c (KrF laser) *vs* 5 (XeCl laser)]. The yield of **6-Se** reached to the same level as that of KrF laser; however, in contrast to the case of KrF laser photolysis, **6-Se** showed no decrease with additional laser pulses. This is explained by the lower molar absorptivity of **6-Se** at 308 nm compared with that at 248 nm (*cf.* Table 1).

With use of XeF excimer laser, no reaction took place for **1-S** due to the absence of absorption at 351 nm (*cf.* Table 1). In the case of **1-Se**, only a slight consumption of the starting material (3.6% at the fifth laser shots) was observed, and the yields of **5a** (0.7% at the fifth laser shots) and **6-Se** (1.0% at the fifth laser shots) were practically negligible;[14] this is also explained by a very weak absorption at 351 nm.

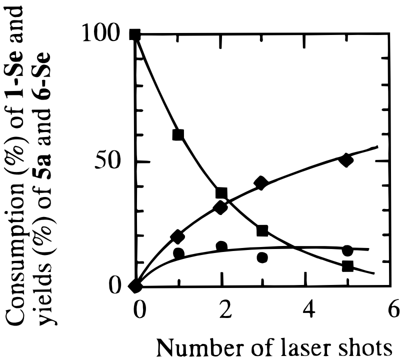

Figure 5. The consumption of **1-Se** and the yields of **5a** and **6-Se** as a function of the number of XeCl excimer laser shots. Substrates **1-Se** (■), **5a** (●), **6-Se** (◆); concentration 10^{-4} M **1-Se** and 10^{-3} M **4a**; laser fluence 1.25 × 10^{21} photons·m^{-2}·pulse^{-1}; optical path 1 mm. The results are the average of two independent runs; the experimental errors are given as Supporting Information.

Cycloaddition with Various Dienophiles. The reaction of **1-Se** and the other dienophiles **4b**–**e** was conducted in type iv mode,[14] whose results are summarized in Table 3. The consumption rate of **1-Se** and the formation rate of **6-Se** in these photolyses were almost the same as those of **1-Se** and **4a**. As seen in Table 3, the consumption of **1-Se** was not dependent on the type of dienophiles used; this is consistent with the fact that the most of the photons were absorbed by **1-Se** under this reaction condition, which is due to the large difference in the molar absorptivities between **1-Se** and **4** (*cf.* Table 1). In the case of the reaction of **1-Se** and **4c**, obtained cycloadduct was only **5c**, and no stereoisomer **5b** was observed.[15] In the reaction of **1-Se** and **4e** a small amount of dehydrogenated product, 2,3-bis(methoxycarbonyl)naphthalene (**7**) was detected in addition to the expected cycloadduct **5e**.

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(15) The stereoisomer **5b** obtained from **4c** in Table 1 of ref 13 was found to be a different compound.

Table 4. Plausible Absorptions of 1-O, 1-S, and 1-Se for the First and the Second Photons

	absorption chromophores[a]					
	first photon			second photon		
substrate	248 nm	308 nm	351 nm	248 nm	308 nm	351 nm
1-O	**PhO** ($\pi-\pi^*$: ${}^1L_b$) **Bn** ($\pi-\pi^*$: ${}^1L_b$)	none	none	**PhO** ($\pi-\pi^*$: ${}^1L_b$) **Bz** ($\pi-\pi^*$)	–	–
1-S	**PhS** ($\pi-\pi^*$: ${}^1L_b$) **Bn** ($\pi-\pi^*$: ${}^1L_b$) **S** (n, π^*)	**PhS** ($\pi-\pi^*$: ${}^1L_b$)	none	**PhS** ($\pi-\pi^*$: ${}^1L_b$) **Bz** ($\pi-\pi^*$) **2B** ($\pi-\pi^*$) **S** (n, π^*)	**PhS** ($\pi-\pi^*$: ${}^1L_b$) **Bz** ($\pi-\pi^*$) **2B** ($\pi-\pi^*$)	–
1-Se	**PhSe** ($\pi-\pi^*$: ${}^1L_b$) **Bn** ($\pi-\pi^*$: ${}^1L_b$) **Se** (n, π^*)	**PhSe** ($\pi-\pi^*$: ${}^1L_b$)	**PhSe** ($\pi-\pi^*$: ${}^1L_b$)	**PhSe** ($\pi-\pi^*$: ${}^1L_b$) **Bz** ($\pi-\pi^*$) **2B** ($\pi-\pi^*$) **Se** (n, π^*)	**PhSe** ($\pi-\pi^*$: ${}^1L_b$) **Bz** ($\pi-\pi^*$) **2B** ($\pi-\pi^*$)	**PhSe** ($\pi-\pi^*$: ${}^1L_b$) **Bz** ($\pi-\pi^*$) **2B** ($\pi-\pi^*$)

[a] **PhO**: phenoxy group; **PhS**: phenylthio group; **PhSe**: phenylseleno group; **Bn**: *o*-dialkylbenzene; **S**: sulfur atom; **Se**: selenium atom; **Bz**: substituted benzyl radical of **2A**; **2B**: bridged-form monoradical.

The reactions were also conducted at 60 °C in order to investigate the temperature effect on the yield of cycloadducts **5a**–**e** by facilitating the thermal reaction of *o*-quinodimethane (**3A**) and dienophiles **4a**–**e**;[14] the results are also shown in Table 3. As seen in the table, only dienophiles **4a** and **4d** showed slight increase in the yield of **5a** and **5d**, but no change was seen in the reactions with other dienophiles. The consumption of **1-Se** was the same between the reactions at room temperature and at 60 °C.

Discussion

Absorption of Photons. The fluence dependence experiments on the formation of **5a** from **1-(O, S, Se)** and **4a** (Figures 2a–c) showed that **5a** was formed by a two-photon process. The absorption of the first photon by **1-(O, S, Se)** is much dependent on the kind of heteroatom involved in the molecule. Each substrate, **1-(O, S, Se)**, is comprised of three chromophores, *i.e.*, two PhX (X = O, S, Se) leaving groups and one *o*-dialkylbenzene ring. The kind of excitations which correspond to the absorption of the chromophores at the three laser wavelength is summarized in Table 4.

In the cases of KrF (248 nm) laser irradiations (*cf.* Table 4), two PhX (X = O, S, Se) groups and one *o*-dialkylbenzene (**Bn**) are responsible for the absorption of photons. The absorptions of PhX and **Bn** chromophores are both attributed to the secondary absorption band (${}^1L_b$) of the benzene ring.[16] In the case of **1-(S, Se)**, additional absorption corresponding to n → π^* excitation of S and Se atoms[17] is also present in the photolysis. During the photolysis, the photons are mainly absorbed by PhX rather than **Bn** because in the case of **1-O**, the molar absorptivity of the *two* PhO groups is estimated to be *ca.* 12-fold larger than that of **Bn**;[18] in the case of **1-S** the molar absorptivity of the *two* PhS groups is estimated to be at least 85-fold larger than that of **Bn**,[19] and a similar trend is expected for **1-Se** in analogy with the cases of **1-O** and **1-S**.

In the cases of XeCl (308 nm) laser photolyses (*cf.* Table 4), **1-O** has no absorption at this wavelength. However, **1-(S, 1-Se)** have an absorption which is attributed to the $\pi-\pi^*$ (${}^1L_b$) excitation of the two PhX (X = S, Se) groups, but no absorption is expected from **Bn** group. Therefore, the photolyses of **1-(S, 1-Se)** at this wavelength proceed solely by the excitation of the PhX leaving groups. In the cases of XeF (351 nm) laser photolyses (*cf.* Table 4), only **1-Se** has absorption at the laser wavelength which is due to the PhSe groups, but no absorption was observed for **1-(O, S)**.

The probable species for the absorption of the second photon is monoradical **2**.[20] Transient spectrum of the photolysis of **1-(O, S, Se)** contained the same absorption as that of parent benzyl radical—a strong absorption in the region of 300–330 nm and terminating at ca. 370 nm due to the $D_n(2A_2) \rightarrow D_0(1B_2)$ excitation,[21] which is not much affected by alkyl substitutions. This is an evidence for the involvement of the substituted benzyl radical **2A**. Semiempirical MO calculations of the monoradical **2**, however, predicted the existence of two possible forms, a benzyl-type open-form **2A** and a bridged-form **2B**. The calculations showed the heats of formation of 80.9 and 72.1 kcal·mol^{-1} for **2A-S** and **2B-S**, and 59.2 and 36.8 kcal·mol^{-1} for **2A-Se** and **2B-Se**. In the case of **2-O**, the heat of formation for **2A-O** was calculated to be 44.6 kcal·mol^{-1};[22] however, the calculation starting from the bridged-form **2B-O** did not gave stable structure but led to the open-form **2A-O**. The result indicates that monoradicals **2-S** and **2-Se** favor the bridged-forms **2B-S** and **2B-Se**, whereas the **2-O** can only take the open-form **2A-O**.

The probable excitations which are responsible for the second photon absorption is also summarized in Table 4. The difference of the absorbing species between the first and the second photon is the participation of the intermediate radical **2A** and/or **2B** instead of the *o*-dialkylbenzene (**Bn**) group. The absorption of the bridged-form **2B** is expected to show a significant red shift[20,23] compared with that of the open-form **2A**, which is due to a highly extended conjugation of the π-electron system.

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(16) Jaffé, H. H.; Orchin, M. *Theory and Application of Ultraviolet Spectroscopy*; John Wiley & Sons: New York, 1962; Chapter 12, section 12.2.

(17) Reference 16; Chapter 17, section 17.2.

(18) The molar absorptivity and λ_{max} of the ${}^1L_b$ absorption band are reported to be 204 M^{-1}·cm^{-1} and 254 nm for benzene, 225 M^{-1}·cm^{-1} and 261 nm for toluene, and 1480 M^{-1}·cm^{-1} and 269 nm for anisole: ref 16; Table 12.4.

(19) The molar absorptivity and λ_{max} of thioanisole is reported to be 9550 M^{-1}·cm^{-1} and 254 nm: ref 16; Table 17.1.

(20) Preliminary experiments on the flash photolysis of **1-S** and **1-Se** showed λ_{max} at *ca.* 320 nm, corresponding to open-form monoradical **2A**, and broad absorption in the range 430–500 nm, corresponding to bridged-form monoradical **2B** and PhX radical.

(21) *e.g.* Tokumura, K.; Udagawa, M.; Ozaki, T.; Itoh, M. *Chem. Phys. Lett.* **1987**, *141*, 558–563.

(22) Calculated by using PM3 method (RHF, CI) in the MOPAC version 6.0: *cf.* Stewart, J. J. P. *QCPE Bull.* **1989**, *9*, 10.

(23) The bridged-form of the monoradical generated from 1,8-bis(substituted-methyl)naphthalene (substituent: SPh, SePh) showed broad absorption at 400–520 nm, whereas the absorption of the open-form monoradical was observed at 330–380 nm: Ouchi, A.; Koga, Y.; Alam, M. M.; Ito, O. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1705–1709.

This conjugation is possible because, according to the MO calculations, the bond order of the two C(benzylic)−X and one C(phenyl)−X bonds were calculated to be *ca.* 0.7 so that a π electron is expected to exist on the two benzylic carbons; this is confirmed by the spin density obtained by the MO calculation. Therefore, the feature of the monoradical **2B** might be better considered as a single chromophore rather than two independent ones. Higher stability of the bridged-form **2B** to the open-form **2A** can be also explained by such conjugation.

In the case of KrF laser photolysis (*cf.* Table 4), the second photon absorption of **1-O** occurs at the remaining PhO group and the benzyl radical (**Bz**) of open-form **2A-O**, whereas the absorption of **1-(S, Se)** is attributed to the $\pi-\pi^*$ excitation of PhX (X = S, Se) group and **Bz** of open-form **2A-(S, Se)**, and bridged-form monoradical **2B-(S, Se)**, and to the n → π^* excitation of S and Se atoms.

Contribution of the open-form monoradical absorption becomes more important in the cases of XeCl laser photolyses. In the case of **1-(S, Se)**, the absorption occurs at the PhX (X = S, Se) group and **Bz** of **2A-(S, Se)**, and **2B-(S, Se)**, all through the $\pi-\pi^*$ excitations. The same excitation is responsible in the case of XeF laser photolyses of **1-Se**. However, **2A** and **2B** cannot be generated in the cases of XeCl laser photolysis of **1-O** and XeF laser photolysis of **1-(O, S)** because of the lack of the first photon absorption.

The competition of the first photon absorption between substrate **1** and dienophile **4** can be assessed from the molar absorptivities (*cf.* Table 1). In the standard photolysis condition [type i mode], 10^{-4} M **1** and 10^{-3} M **4** were employed so that the most of the photons are absorbed by **1** in the case of **1-(S, Se)**; in the case of **1-O**, however, the absorption of photons between **1** and **4** becomes comparable and is much dependent on the type of **4** used. For the second photon, the competition of the photon absorption between **2A**/**B** and **4** is somewhat difficult to estimate because the molar absorptivity of **2A** and **2B** at each laser wavelength have not been measured so far.

Effect of Heteroatoms. The rate of the consumption of **1-(O, S, Se)** in the type iv KrF laser photolysis with **4a** (Figures 4a−c) was found to be in the order **1-Se** $\approx$ **1-S** $\gg$ **1-O**. The order is in good accord with the order of the molar absorptivities, **1-Se** > **1-S** $\gg$ **1-O** (*cf.* Table 1). The molar absorptivity of **1-S** and **1-Se** had almost the same value but that of **1-O** was two orders of magnitude smaller than the others. In contrast to the consumption of **1-(O, S, Se)** the yield of **5a** was in the order **1-Se** $\gg$ **1-S** $\approx$ **1-O**. A prominent difference between the tendency of the consumption of **1-(O, S, Se)** and the yield of **5a** is that a big difference was observed between **1-S** and **1-O** in the consumption, whereas large difference was observed between **1-Se** and **1-S** in the yield.

This contrast in the tendency becomes more clear when the reaction was conducted in type i mode (*cf.* Figure 2a−c); the order of the yield of **5a** became **1-Se** > **1-O** > **1-S**. This unexpected order in the yield of **5a** seems to reflect the facility of the second bond cleavage. A naive comparison of C−X (X = O, S, Se) bond dissociation energies gives the expected order **1-Se** > **1-S** > **1-O**.[24] However, the semiempirical MO calculation, as shown before, revealed that the monoradical favors bridged-form **2B-(S, Se)** rather than the open-form **2A-(S, Se)**, whereas only the open-form **2A-O** is allowed for **1-O**. The stable bridged-form **2B-(S, Se)** increases the dissociation energy for the second C−X bond cleavage, **2** → **3**, which hinders the formation of **3**. Thus, the order in the yield of **5a** was reversed between **1-O** and **1-S**; the order of the yield between **1-Se** and **1-O** was not reversed probably because of the low dissociation energy of C−Se bond even in the bridged-form.

Effect of Laser Fluence. It is clear from Figure 2 that the consumption of **1-(O, S, Se)** and the formation of **6-(S, Se)** proceeded by one-photon processes, but a two-photon process was operating in the formation of **5a**, which is consistent with the mechanism shown in Scheme 1. The two-photon process is largely affected by the fluence of light since, theoretically, the yield of the two-photon product is proportional to the square of the light intensity. In the standard condition [type i mode] the result on the transmission of the KrF excimer laser at 10-mm optical path (*cf.* Table 2) showed that most of the photons were absorbed when **1-(S, Se)** was used, and about a half of the photons was absorbed in the case of **1-O**. This result indicates the presence of a large difference in the photon density between incident-side and exit-side of the photolysis cell; thus, the photon density near the exit-side of the laser becomes too low for conducting the two-photon processes. A simple calculation shows that, under this photolysis condition, the number of photons per molecule of **1** is 2.1 photons·molecule^{-1}·pulse^{-1}, which is not sufficient for the efficient formation of **5a**, although a large consumption of **1** was observed.

The simple way to improve the efficiency of the two-photon process is to increase the laser fluence. By increasing the laser fluence by 25-fold [type iii mode], *ca.* 2-fold increase in the yield of **5a** was achieved compared with that of the standard condition [Figure 3a *vs* 3c (**1-S**); Figure 3d *vs* 3f (**1-Se**)]. A simple calculation shows that the number of photons per molecule of **1** is 53 photons·molecule^{-1}·pulse^{-1}. However, such high fluence photolysis has disadvantage for practical purposes because the quartz window of the reaction vessel (or simply a quartz cuvett) is often damaged by such high fluence photolysis.

Another way to increase the efficiency is to decrease the optical path of the laser. When 1-mm optical path was used, 70−90% of photons are transmitted in most cases (*cf.* Table 2) so that the photon density at the exit-side is still sufficiently high for conducting efficient two-photon reactions. By decreasing the optical path to 1 mm [type iv mode] ca. 2-fold increase in the yield of **5a** was obtained compared with the standard condition [Figure 3a *vs* 4b (**1-S**); Figure 3d *vs* 4c (**1-Se**)] even with the low fluence (LF) laser photolysis; the effect of decreasing the optical path from 10 mm to 1 mm was similar to that of increasing the laser fluence by 25-fold [type iii mode]. A simple calculation shows that the number of photons per molecule of **1** is 21 photons·molecule^{-1}·pulse^{-1}; the number of photons is in the same order as that of the high fluence (HF) photolysis with 10-mm optical path [type ii mode].

Cycloaddition Reaction of *o*-Quinodimethane. Singlet diradical **3B** is in resonance with the ground state *o*-quinodimethane (**3A**), which undergoes cycloaddition reaction with the dienophiles. Triplet diradical **3B** and *o*-quinodimethane (**3A**) might be involved during the

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[24] Baff, L. *The chemistry of organic selenium and tellurium compounds*; Patai, S., Rappoport, Z., Ed.; Wiley: Chichester, 1986; vol. 1, chapter 4, p 159.

formation of singlet **3A/B**; however, intersystem crossing of triplet to singlet **3A/B** is expected to be fast.[25]

In the case of the reaction between **1-Se** and **4c**, the obtained cycloadduct was only **5c**; the result is the same as that obtained by thermal reactions.[9,12] According to the orbital-symmetry rules, this result indicates that cycloaddition of **3A** and dienophile **4** proceeded by a concerted thermal process because the stereoisomer **5b** should have been the major product if the reaction proceeded photochemically, and the mixture of **5b** and **5c** should have been obtained by stepwise processes. Two attempts were made in order to increase the efficiency of the thermal process and thus the yield of cycloaddition product **5**.

The first attempt was to increase the concentration of dienophile in order to facilitate the trapping of *o*-quinodimethane (**3A**) generated by the laser photolysis. However, the result obtained was found to be the opposite to the expectation; by the 10-fold increase of the concentration of **4a** [type ii mode], the rates of the consumption of **1-(S, Se)** and the formations of **5a** and **6-(S, Se)** have decreased compared with those of standard condition [type i mode] [Figure 3b *vs* 3a (**1-S**); Figure 3e *vs* 3d (**1-Se**)]. Furthermore, the final yield of **5a** have also decreased. These decreases are ascribed to the considerable absorption of the photons by dienophile **4a**. Although the molar absorptivity of **4a** is *ca.* 1/100 of that of **1-(S, Se)**, the total absorption of **4a** becomes comparable to that of **1-(S, Se)** in type ii mode because the concentration of **4a** is 100-fold higher than that of **1-(S, Se)**. Therefore, the effective fluence of the laser for the photolysis of **1-(S, Se)** is considered to be about a half of that of the standard condition [type i mode]. This is evidenced by the fact that the consumption rate of **1-(S, Se)**, which proceeds by an one-photon process, in type ii mode becomes about half of that of type i mode [Figure 3b *vs* 3a (**1-S**) and Figure 3e *vs* 3d (**1-Se**); at the first laser shot].

The second attempt is to raise the reaction temperature. However, the increase of the reaction temperature, from room temperature to 60 °C, showed practically no effect on the rate of the consumption of **1-Se** and the yields of **5a** and **6-Se**.

Conclusions

o-Quinodimethane (**3A**) was generated effectively by excimer laser photolyses of 1,2-bis(phenoxymethyl)benzene (**1-O**), 1,2-bis[(phenylthio)methyl]benzene (**1-S**), and 1,2-[bis(phenylseleno)methyl]benzene (**1-Se**) in acetonitrile solutions *via* a two-photon process. Cycloaddition of **3A** was conducted with several dienophiles—maleic anhydride (**4a**), dimethyl maleate (**4b**), dimethyl fumarate (**4c**), fumaronitrile (**4d**), and dimethyl acetylenedicarboxylate (**4e**)—which gave corresponding cycloadducts **5a**−**e**. Four kinds of reaction conditions were tested by using a KrF excimer laser: (i) standard condition, (ii) high dienophile concentration, (iii) high laser fluence, and (iv) short optical path. The results obtained from these conditions revealed that the photon density was the most important factor for the efficient formation of **5**; the increase of laser fluence and the decrease of the optical path showed the same effect on the yield of **5**. The type of the heteroatoms (O, S, Se) in the leaving groups also showed a significant difference in the yield of **5**; this difference was interpreted in terms of the participation of a stable bridged-form monoradical as an intermediate, which hindered the second bond cleavage and thus giving a lower yield of **5**. The phenylseleno group was found to be the best among the three heteroatoms tested. Three kinds of excimer lasers—KrF, XeCl, and XeF lasers—were tested, and the maximum yield of the cycloadduct, 48%, was obtained by the use of KrF laser.

Experimental Section

Detailed descriptions on the preparation of the starting materials **1-(O, S, Se)** and the authentic compounds **5a**−**e** and **7** are given as Supporting Information.

Excimer Laser Photolyses. Laser photolyses were conducted in acetonitrile solution [**1**: 10^{-4} M; **4**: 10^{-3} M (LC) and 10^{-2} M (HC)] under a nitrogen gas atmosphere. High-fluence photolyses (HF, 3.12×10^{22} photons·m^{-2}·pulse^{-1}) were conducted by using an *ca.* 15-mm glass capillary of 1-mm diameter, one of whose ends was closed. A 10-μL aliquot of the solution was placed into a horizontally placed capillary, and the laser light was focused at the opening of the capillary. Low-fluence photolyses (LF, 1.25×10^{21} photons·m^{-2}·pulse^{-1}) were conducted on ca. 0.5-mL solution with 10-mm optical path or on ca. 0.1-mL solution with 1-mm optical path under a nitrogen gas atmosphere by using synthetic quartz cuvettes of 10-mm width. The experiments on the laser fluence dependence were conducted on ca. 0.5-mL solution (**1**: 10^{-4} M; **4a**: 10^{-3} M) under a nitrogen gas atmosphere by using a synthetic quartz cuvette of 10-mm width and 10-mm optical path. The excimer lasers used were Lambda Physik EMG 201 MSC [pulse width (fwhm) 30 ns (KrF) and 26 ns (XeF)] and Lambda Physik EMG 102 MSC [pulse width (fwhm) 14 ns (XeCl)]. The laser pulse energy was measured by means of a Gentec joulemeter ED-500 and a Tektronix T912 10 MHz storage oscilloscope.

Analysis of the Photolysis Products. The yields of the two-photon products **5a**−**e**, diphenyl disulfide (**6-S**), diphenyl diselenide (**6-Se**), and the consumption of the starting material **1-(O, S, Se)** were determined by HPLC analysis and their retention times compared with the authentic samples.

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

Supporting Information Available: Preparation of compounds **1-O**, **1-S**, **1-Se**, **5a-e**, and **7**; KrF laser fluence dependence on the reaction of **1-(S, Se)** and **5a** with 1-mm optical path; photolyses of **1-(S, Se)** and high concentration **4a** by high fluence KrF laser with 10-mm optical path; photolyses of **1-(S, Se)** and **4d** by high and low fluence KrF lasers with 10-mm optical path; photolyses of **1-Se** and **4b** by low fluence KrF laser with 10-mm optical path; original data on the photolysis of **1-(O, S)** and **4a** by low fluence XeCl laser with 1-mm optical path; original data on the photolysis of **1-Se** and **4a** by low fluence XeF laser with 1-mm optical path; original data on the photolyses of **1-Se** and **4b-e** by low fluence KrF laser with 1-mm optical path at room temperature; original data on the photolyses of **1-Se** and **4a-e** by low fluence KrF laser with 1-mm optical path at 60 °C (29 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[25] Wintgens, V.; Netto-Ferreira, J. C.; Casal, H. L.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 2363−2367.