KrF excimer laser photolysis of 1,2-bis(substituted-methyl)benzenes in the presence of alkenes and acetylene; two-photon formation of *o*-quinodimethane and its cycloaddition with dienophiles

Akihiko Ouchi*† and Yoshinori Koga

National Institute of Materials and Chemical Research, AIST, MITI, 1-1, Higashi, Tsukuba, Ibaraki 305, Japan

***o*-Quinodimethane 3 is generated effectively by KrF excimer laser (248 nm) photolysis of 1,2-bis(phenoxymethyl)-, 1,2-bis(phenylthiomethyl)- and 1,2-bis(phenylselenomethyl)-benzene *via* a two-photon process; cycloaddition of 3 with several dienophiles gives corresponding adducts in a maximum yield of 48%.**

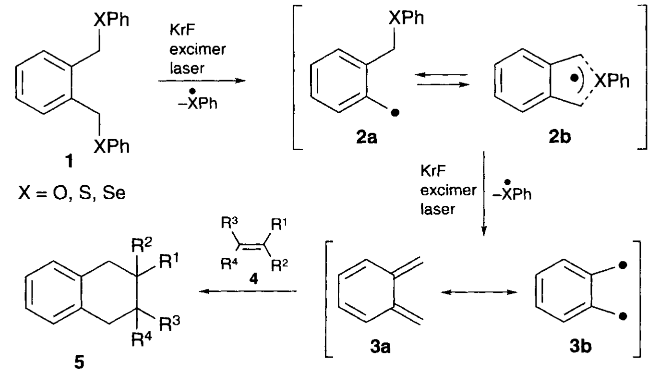
o-Quinodimethane [**3**, 5,6-bis(methylene)cyclohexa-1,3-diene] is a useful reactive species which is frequently used in organic synthesis as a building block. Several methods for its generation and applications have been reported.[1] However, many of the methods require long synthetic steps for the preparation of its precursors and/or a long reaction time. Here we report a fast and simple synthesis of **3** from easily accessible precursors by KrF excimer laser-induced photolysis of 1,2-bis(phenoxymethyl)benzene **1-O**, 1,2-bis(phenylthiomethyl)benzene **1-S** and 1,2-bis(phenylselenomethyl)benzene **1-Se**‡ (Scheme 1). Diradical **3b** is the expected intermediate initially formed by a double homolytic cleavage of C–X (X = O, S, Se) bonds§ by a two-photon process which can easily isomerize to the resonance form **3a** ⟷ **3b**.[2,3] *o*-Quinodimethane **3** was then trapped with various dienophiles **4** to give the corresponding cycloaddition products **5**.

The photolysis was conducted in acetonitrile (**1**: 10^{-4} mol dm^{-3}; **4**: 10^{-3} mol dm^{-3}) under a nitrogen atmosphere at room temperature using a synthetic-quartz cell of 10 mm width and 1 mm optical path. A KrF excimer laser [248 nm, 100 mJ cm^{-2} pulse^{-1}, pulsewidth 26 ns (fwhm)] was irradiated on the solution (1, 2, 3 and 5 laser pulses). The dienophiles used were maleic anhydride **4a**, dimethyl maleate **4b**, dimethyl fumarate **4c**, fumaronitrile **4d** and dimethyl acetylenedicarboxylate **4e**. The experiments on the fluence dependence were conducted similarly with a single laser pulse by using a synthetic-quartz cell of 10 mm optical path. The conversion of **1** and the yield of the reaction products **5** were analysed by HPLC in comparison with the authentic samples.¶

The molar absorptivities of **1** and **4** in acetonitrile at 248 nm were measured by a UV spectrometer: 670 (**1-O**), 13 600 (**1-S**), 16 780 (**1-Se**), 160 (**4a**), 470 (**4b**), 400 (**4c**), 0 (**4d**) and 230 (**4e**) dm^3 mol^{-1} cm^{-1}. This result indicates that, in the cases of **1-S** and **1-Se**, most of the photons are absorbed by **1** and not by the existing dienophiles **4**. The chromophores of **1** are two PhX moieties and an *ortho*-dialkylbenzene moiety. The PhX leaving groups are expected to absorb the laser energy more effectively.[4]

Fig. 1 shows the fluence dependence on the reaction between **1-O**, **1-S**, **1-Se** and maleic anhydride **4a** in 20–140 mJ cm^{-2} pulse^{-1} in the 10 mm optical-path cell. As seen from Fig. 1, the slope of the consumption of **1** *vs.* laser fluence for a double-logarithmic plot was unity, whereas that of the yields of **5a** was two. This result indicates that the consumption of **1** proceeds by a one-photon process but the formation of **3** is by a two-photon process. The saturation of the consumptions of **1-S**, **1-Se** and the yield of **5a** in the reaction with **1-Se** was, however, observed at the high laser fluence.||

As seen in Fig. 1, the rate of the consumption of **1** was in the order **1-Se** ≈ **1-S** > **1-O**. The order is parallel to that of the molar absorptivities of **1-O**, **1-S** and **1-Se**; the molar absorptivities of **1-S** and **1-Se** showed almost the same value but that of **1-O** was two orders in magnitude smaller than the others. In contrast to the consumption of **1**, an irregular trend was observed in the yield of **5a**, in which **1-O** falls out from the line, *i.e.* **1-Se** > **1-O** > **1-S**. This tendency seems to reflect the facility of the second bond cleavage. A naive comparison of C–X (X = O, S, Se) bond dissociation energies[5] gives the expected order, **1-Se** > **1-S** > **1-O**. However, MO calculations** showed that monoradicals **2-S** and **2-Se** favour the bridged forms **2b-S** and **2b-Se**, whereas the **2-O** can only take the open form **2a-O**. Participation of the stable bridged form **2b-S** and **2b-Se** increases the dissociation energy for the second leaving



Scheme 1

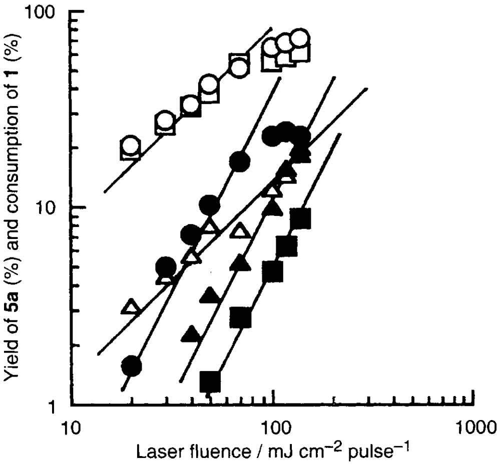


Fig. 1 Laser fluence dependence on the consumption of **1** and yield of **5a** as a function of KrF excimer laser fluence. **1-O**, **1-S**, **1-Se** open symbols and **5a** closed symbols. Substrates: ▲, △ (**1-O**); ■, □ (**1-S**); ●, ○ (**1-Se**). Concentration: 10^{-4} mol dm^{-3} **1** and 10^{-3} mol dm^{-3} **4a** in acetonitrile. Optical path: 10 mm. The results are the average of two independent runs.

group, which hinders the cleavage for the formation of **3**, and thus reversing the order for the yield of **5a** between **1-O** and **1-S**; the order between **2-Se** and **2-O** was not reversed, which is due to the weak C–Se bond even in the bridged form.

Runs 1–3 in Table 1 show the reaction between **1-O**, **1-S**, **1-Se** and **4a** with 1 mm optical path. The result shows that both the conversion of **1** and the yield of **5a** increased with the decrease of the optical path (Table 1, runs 1–3 *vs*. Fig. 1 at 100 mJ cm^{-2} pulse^{-1}). The reactions with other dienophiles are shown in runs 4–7. As seen in runs 3–7, the consumption of **1-Se** was not dependent on the type of the dienophiles present, which is consistent with the fact that most of the photons were absorbed by **1-Se** due to the large difference in the molar absorptivities. In spite of the large conversions of **1** the yield of **5** was lower than expected, which implies insufficient formation of **3** from **2**. It suggests the existence of side reactions from **2** leading to some stable products; this is supported by the detection of some by-products in the HPLC analyses, which also appeared in the absence of the dienophiles.

Table 1 Consumption of **1** and yield of cycloadducts **5**[a]

Run	Precursor **1**	Dienophile **4**	No. of laser pulses	Yield of **5** (%)	Consumption of **1** (%)
1	**1-O**	**a**	1	13 ± 0.3	30 ± 1.9
			5[b]	28 ± 1.4	77 ± 2.9
2	**1-S**	**a**	1	13 ± 0.6	90 ± 0.2
			3[b]	30 ± 2.3	99 ± 0.1
3	**1-Se**	**a**	1	43 ± 2.2	91 ± 0.7
			5[b]	48 ± 0.6	~ 100 ± 0.3
4	**1-Se**	**b**	1[b]	4.7 ± 0.3	89 ± 1.7
5	**1-Se**	**c**	1	16 ± 1.9[c]	88 ± 1.6
			5[b]	20 ± 2.8[c]	~ 100 ± 0.1
6	**1-Se**	**d**	1[b]	39 ± 4.2	93 ± 0.4
7	**1-Se**	**e**	1	2.3 ± 0.3	94 ± 0.8
			5[b]	4.0 ± 0.1	~ 100 ± 0.2

[a] KrF excimer laser fluence: 100 mJ cm^{-2} pulse^{-1}; optical path: 1 mm; concentration: 10^{-4} mol dm^{-3} **1** and 10^{-3} mol dm^{-3} **4** in acetonitrile; the results are the average of two independent runs. [b] Highest yield of **5** obtained among 1-, 2-, 3- and 5-laser-pulse photolyses. [c] Yield of **5b**; 2.4 ± 0.3% (1 pulse), 3.2 ± 1.0% (5 pulses).

Footnotes

† E-mail:ouchi@nimc.go.jp

‡ Compounds **1-O**, **1-S** and **1-Se** were synthesized in one step from commercially available 1,2-bis(bromomethyl)benzene in good yields.

§ Similar bond cleavage with a KrF excimer laser have been reported in the reaction of 1,8-bis(substituted-methyl)naphthalenes, which formed acenaphthene.[4]

¶ Authentic samples **5a-e** were synthesized by conventional procedures; ^{1}H and ^{13}C NMR, IR and mass spectra of each sample were identical with the reported data.

|| In the case of the photolyses with 1 mm optical path, the saturation of the consumption of **1** and the yield of **5a** was observed even from the low fluence.

** Calculated by using the PM3 method (RHF, CI) in MOPAC ver. 6.0 [*cf.* J. J. P. Stewart, *QCPE Bull.*, 1989, **9**, 10]. The calculation showed the heats of formation of 80.9 and 72.1 kcal mol^{-1} (1 cal = 4.184 J) 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}; however, the calculation starting from the bridged form **2b-O** did not give stable structure but lead to the open form **2a-O**.

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