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)
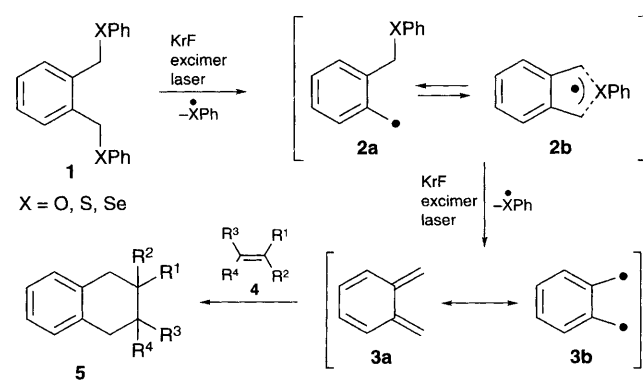
dm^3 mol^{-1} cm^{-1}. This result indicates that, in the cases of 1-S and 1-Se, most of the photons are absorbed by 1 and not by the existing dienophiles 4. The chromophores of 1 are two PhX moieties and an *ortho*-dialkylbenzene moiety. The PhX leaving groups are expected to absorb the laser energy 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
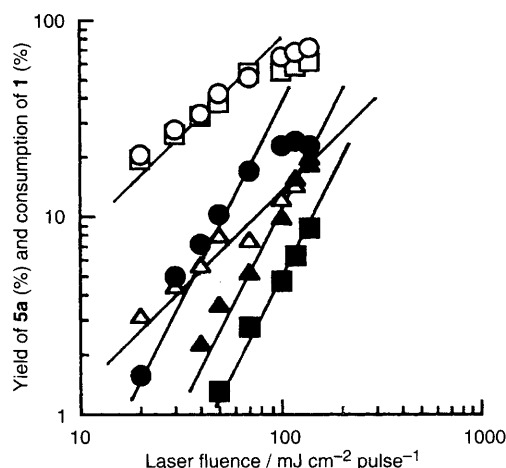

Fig. 1 Laser fluence dependence on the consumption of 1 and yield of 5a as a function of KrF excimer laser fluence. 1-O, 1-S, 1-Se open symbols and 5a closed symbols. Substrates: ▲, △ (1-O); ■, □ (1-S); ●, ○ (1-Se). Concentration: 10^{-4} mol dm^{-3} 1 and 10^{-3} mol dm^{-3} 4a in acetonitrile. Optical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

Scheme 1

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**

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).

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.

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**.

References

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