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Photoinduced Isomerization of Allyl Alcohols to Carbonyl Compounds Using Dendrimer Disulfide as Catalyst

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ABSTRACT: *Allyl alcohols were isomerized to carbonyl compounds using diphenyl disulfide derivatives upon photoirradiation. Especially, dendrimer disulfide catalyzed the isomerization of allyl alcohols. Photoinduced isomerization in water was also succeeded by the use of water-soluble dendrimer disulfide.* © 2009 Wiley Periodicals, Inc. Heteroatom Chem 20:1–11, 2009; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20504

INTRODUCTION

Photoreactivity of diphenyl disulfide derivatives has attracted scientific attention in the past few decades [1,2]. Sulfanyl radical generated by homolytic cleavage of the S–S bond plays important roles in photoinitiated reactions such as sulfenylation of aryl halides [3] and hindered phenols [4], vinyl polymerization [5], and vicinal dichalcogenation of unsaturated compounds [6–10]. A few examples of transformation of the functional groups using photoreaction of disulfide were also reported [11]. Recently, we have reported the photoinduced oxidation of allyl alcohols to acrylaldehydes using diphenyl disulfide derivatives [12]. However, much less is known about the transformation of functional groups using disulfide as a photocatalyst. Meanwhile, with a growing demand for environmentally benign reactions, catalytic reactions that are atom efficient receive increasing attention [13]. Isomerization of allyl alcohols forms an elegant shortcut to carbonyl compounds in a completely atom-economical process that offers several useful applications in natural-product syntheses and in bulk chemical processes [14]. Although many reports described isomerization of allyl alcohols using metal catalysts [15–18] such as Ru complexes [16,17] and Fe-carbonyl complexes [15,18], isomerization without metal catalyst was quite rare [19]. In this paper, we describe photoinduced isomerization of allyl alcohols to carbonyl compounds using diphenyl disulfide. Especially, dendrimer disulfide catalyzed the isomerization of allyl alcohols. Photoinduced isomerization in water by the use of water-soluble dendrimer disulfide is also examined.

RESULTS AND DISCUSSION

In previous work, we reported that diphenyl disulfide derivatives mediate oxidation of various allyl alcohols to give acrylaldehydes upon photoirradiation [12]. A plausible mechanism of photoinduced oxidation of allyl alcohol is shown in Scheme 1. The reaction was triggered by the sulfanyl radical generated by photolysis of the diphenyl disulfide. Then, the abstraction of an α-hydrogen, which occurred from the allyl alcohol to the sulfanyl radical, produced the allylic radical and thiophenol. Next, a single electron transfer (SET) occurred from the allylic radical to another sulfanyl radical, and an allylic cation was

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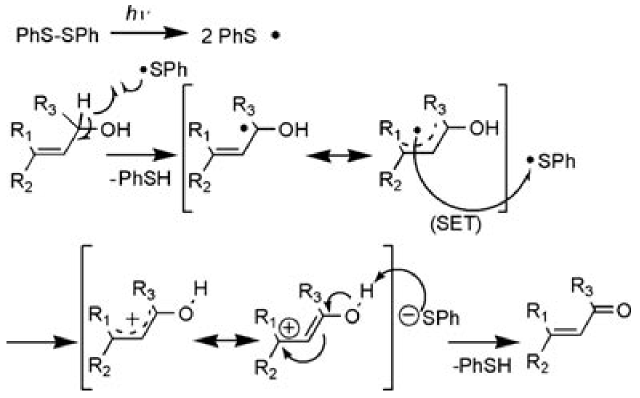
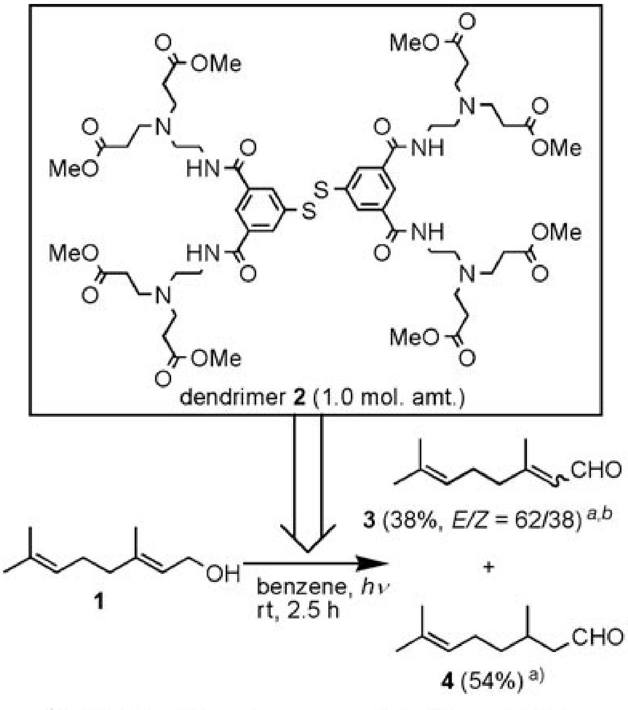
Contract grant number: 19010105.



SCHEME 1 Plausible mechanism of oxidation of allyl alcohol using photolysis of diphenyl disulfide.

formed. The thiolate anion, which was generated by SET, abstracted the proton of —OH group to give the oxidized product and thiophenol. Interestingly, photoirradiation of geraniol (**1**) in the presence of dendrimer disulfide (**2**) gave isomerization product, 3,7-dimethyl-6-octenal (citroneral, **4**), in 54% yield (Scheme 2).

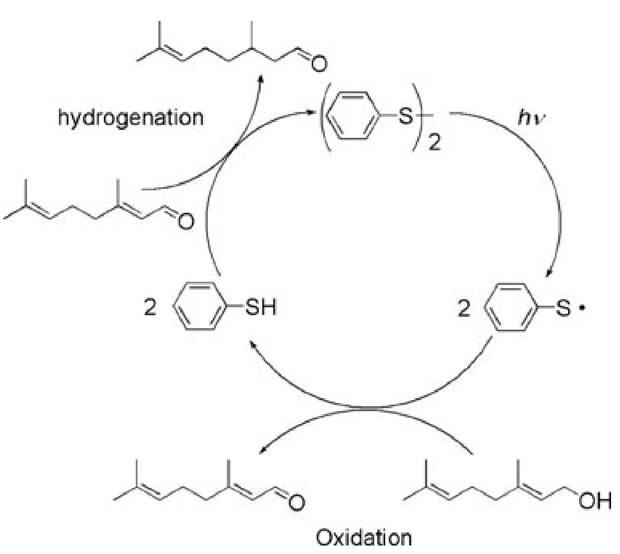


[a] Isolated yield (based on consumed starting material).
[b] E/Z Ratio was determined by ^{1}H NMR.

SCHEME 2 Photoinduced oxidation of geraniol (**1**) using dendrimer disulfide **2**.

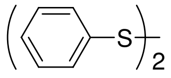
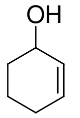
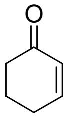
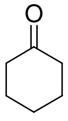
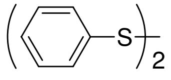
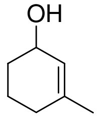
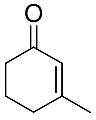
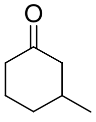
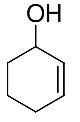
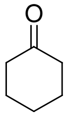
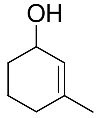
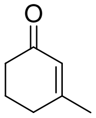
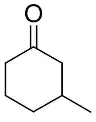
We followed the time course of this reaction by an NMR and observed that citronellal (**4**), isomerized product, was not formed until 20 min after the start of the reaction, although oxidized product, citral (**3**), was observed immediately after the start of the reaction [12]. A catalytic cycle was proposed to explain this isomerization result as Scheme 3. The first step was photolysis of disulfide. Subsequent oxidation of allyl alcohols yields acrylaldehydes and thiols. Final hydrogenation of acrylaldehydes produces isomerized products and disulfides.

Komiya reported that isomerization of 2-cyclohexene-1-ol using Ru catalyst gave higher yield of isomerized product than yields of products of the isomerization of 3-buten-2-ol or 1-phenylallyl alcohol [16]. This result prompted us to investigate isomerization of 2-cyclohexene-1-ol using diphenyl disulfide derivatives. A benzene solution of 2-cyclohexene-1-ol (**5**) in the presence of diphenyl disulfide (**6**) was irradiated with a high-pressure mercury lamp (λ > 300 nm) through a Pyrex filter at room temperature under an argon atmosphere for 5.5 h to give 2-cyclohexenone (**7**) and cyclohexanone (**8**) in 14% and 56% yields, respectively (Table 1, entry 1). Reactions in the dark or in the absence of diphenyl disulfide (**6**) did not proceed. Hence, the isomerization is a photoreaction mediated by diphenyl disulfide (**6**). Isomerization of 3-methyl-2-cyclohexene-1-ol (**9**) was also examined, since photoinduced oxidation of trisubstituted allyl alcohol gave higher yield of oxidized product than



SCHEME 3 Catalytic cycle of photoinduced isomerization of allyl alcohol.

TABLE 1 Photoinduced Isomerization of Allyl Alcohols Using Diphenyl Disulfide Derivatives[a]

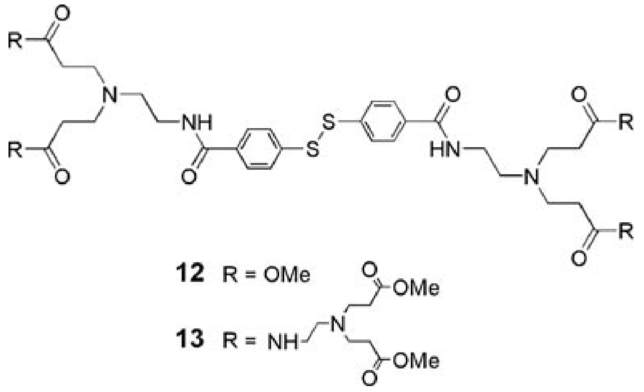
Entry	*Disulfide*	*Allyl Alcohol*	*Time*	*Conversion*	*Product*	*Yield*[b]
1	 **6**	 **5**	5.5 h	>99%	 **7**	14%
					 **8**	56%
2	 **6**	 **9**	5.5 h	>99%	 **10**	trace
					 **11**	60%
3	Dendrimer **12**	 **5**	2.5 h	>99%	 **8**	81%
4	Dendrimer **12**	 **9**	2.5 h	>95%	 **10**	16%
					 **11**	79%

[a]Reactions initiated with UV-light (high-pressure mercury lamp, $\lambda > 300$ nm) in benxene at rt.

[b]GC yield (based on consumed starting material).

the result of oxidation of nonsubstituted allyl alcohol [12]. Photoinduced isomerization of allyl alcohol **9** using diphenyl disulfide (**6**) gave trace amount of 3-methyl-2-cyclohexenone (**10**) and 60% yield of 3-methylcyclohexanone (**11**) (entry 2). Trace amount of by-products, which might be formed by the addition reaction of disulfide or thiol to the olefins, was observed in each photoreactions by GC analysis.

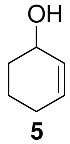
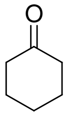
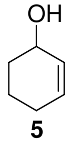
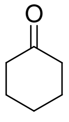
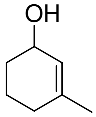
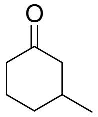
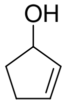
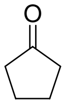
Although UV–vis spectra ($\lambda_{\max}$ and ε) of dendrimer disulfide is almost the same as diphenyl disulfide, dendrimer disulfide is a good mediator of photoinduced oxidation reaction of allyl alcohols because dendritic substituents are quite effective to inhibit side reactions initiated by the addition of sulfanyl radical to unsaturated bonds [12]. Hence, we carried out the isomerization using dendrimer disulfide **12**. Surprisingly, photoinduced isomerization of allyl alcohol **5** using dendrimer disulfide **12** gave ketone **8** as a sole product in 81% yield (entry 3). The reaction of allyl alcohol **9** afforded product **11** in 79% yield (entry 4). In this case, enone **10**, a product of oxidation of allyl alcohol **9**, was also obtained in 16% yield. These results indicated dendrimer disulfide **12** was effective for photoinduced isomerization.



Because of the high reactivity, dendrimer disulfide **12** was expected to catalyze the isomerization of allyl alcohols. We carried out the isomerization using 10 mol % of dendrimer disulfide **12**. Results were shown in Table 2. Isomerization of 2-cyclohexene-1-ol (**5**) using 10 mol % of dendrimer disulfide **12** afforded cyclohexanone (**8**) in 90% yield (entry 1). This result proved that the photoinduced isomerization was a catalytic reaction. Unfortunately, photoreaction in the presence of 1 mol % of dendrimer disulfide was not completed (entry 2). Even though longer reaction time was required, isomerization of 3-methyl-2-cyclohexene-1-ol (**9**) using 10 mol % of dendrimer disulfide **12** gave 3-methylcyclohexanone (**11**) in 91% yield (entry 3). Furthermore, isomerization of 2-cyclopentene-1-ol (**14**) using 10 mol % of dendrimer **12** gave corresponding cyclopentanone (**15**) in 90% yield (entry 4).

Although the exact reaction mechanism is not completely clear, a plausible mechanism of the catalytic isomerization was shown in Scheme 4. The oxidation step of isomerization was triggered by the sulfanyl radical generated by the photolysis of the diphenyl disulfide. Then, the abstraction of an α-hydrogen, which occurred from the allyl alcohol to the sulfanyl radical, produced the allylic radical and thiophenol. Next, a single electron transfer (SET) occurred from the allylic radical to another sulfanyl radical, and an allylic cation was formed. The thiolate anion, which was generated by SET, abstracted the proton of alcohol to give the oxidized product and thiophenol. The hydrogenation step of isomerization was initiated by the addition of sulfanyl radical to the C=C bond of enone, a product of oxidation. Next, the abstraction of hydrogen occurred from the thiol to the carbon radical, and a sulfide was formed (path A). This sulfide could also be formed by the ionic addition reaction in the dark (path B). After the tautomerization from keto-form to enol-form, another sulfanyl radical (path C) or thiolate anion (path D) attacked C–S bond to form disulfide. Finally, the abstraction of hydrogen (path C) or proton (path D) occurred from the thiol and hydrogenated product was formed. Recently, Ogawa

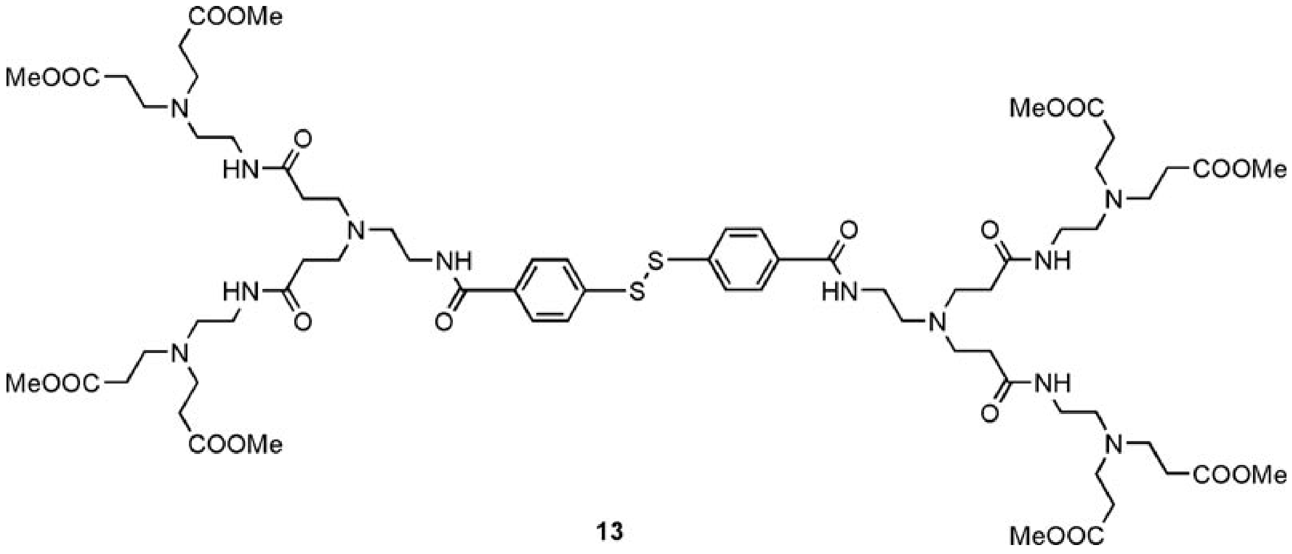
TABLE 2 Photoinduced Isomerization of Allyl Alcohols Using Dendrimer Disulfide **12** As Catalysts[a]

Entry	*Disulfide (mol %)*	*Allyl Alcohol*	*Time*	*Conversion*	*Product*	*Yield*[b]
1	Dendrimer **12** (10 mol %)	 **5**	2.5 h	>99%	 **8**	90%
2	Dendrimer **12** (1 mol %)	 **5**	12 h	54%	 **8**	34%
3	Dendrimer **12** (10 mol %)	 **9**	12 h	>99%	 **11**	91%
4	Dendrimer **12** (10 mol %)	 **14**	2.5 h	>99%	 **15**	90%

[a] Reactions initiated with UV-light (high-pressure mercury lamp, $\lambda > 300$ nm) in benzene at rt.
[b] GC yield (based on consumed starting material).

and coworkers have been reported photoinduced reduction of conjugate dienes using a PhSH-$(PhSe)_2$ binary system [20]. The reaction mechanism of the reduction of diene was similar to the plausible mechanism of hydrogenation step of our isomerization. There could be alternative pathways, that is, direct isomerizations via the formation of cation radical of allyl alcohol by photoinduced SET process or the hydrogen atom donation from a thiol to an allyl radical instead of SET process [21,22]. However, since we observed the enone as an intermediate, the alternative pathway might be excluded.

On the contrary to dendrimer **12**, higher generation dendrimer disulfide **13** was not so effective to mediate photoinduced isomerization (Table 3, entries 3 and 4). This result might indicate that dendrimer having too bulky dendritic wedge inhibited not only side reactions but also isomerization reaction.

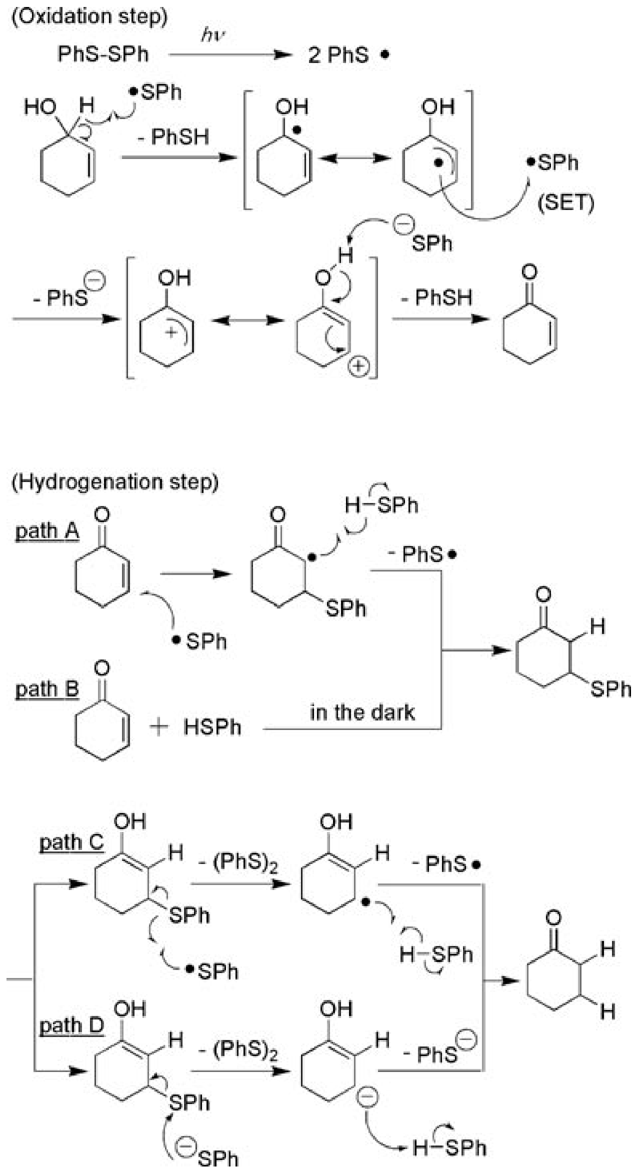


13

It is notable that the products of the photoreaction, oxidized product or isomerized product, do not depend on the reaction conditions but depend on ΔG° of the reaction, that is, the difference of thermodynamic stability between allyl alcohols (starting materials), carbonyl compounds (oxidized products), and saturated carbonyl compounds (isomerized products). The heats of formation (ΔH_f) of allyl alcohols, allyl carbonyl compounds, and carbonyl compounds derived from PM3 calculations were shown in Fig. 1. The change in the ΔH_f before and after photoinduced isomerization proved stabilization by the photoinduced isomerization. The stabilization by isomerization from 2-cyclohexene-1-ol (**5**) to cyclohexanone (**8**) is −59.86 kJ mol^{-1}, and that from 3-methyl-2-cyclohexene-1-ol (**9**) to 3-methylcyclohexanone (**11**) is −43.92 kJ mol^{-1}. The stabilization by isomerization from geraniol (**1**) to citroneral (**4**) is −27.96 kJ mol^{-1}, which is the smallest value among these three examples. These calculated results are in good accordance with the difference of reactivity among 2-cyclohexene-1-ol (**5**), 3-methyl-2-cyclohexene-1-ol (**9**), and geraniol (**1**).

To extend the scope of the reaction, we carried out the photoinduced isomerization using water-soluble dendrimer disulfide as a catalyst in water. Water-soluble dendrimer disulfide **16**, which has sugar moiety at the terminals, was synthesized as Scheme 5. The treatment of dendrimer disulfide **12** with ethylenediamine produced dendrimer disulfide **17**. Subsequently, **17** was allowed to react with glucono-δ-lactone to give dendrimer disulfide **16** (66%, two steps). The structure of dendrimer disulfide **16** was confirmed by ^{1}H NMR spectroscopy and MALDI-TOF-MS. The MALDI-TOF-MS spectrum of dendrimer disulfide **16** showed the parent peak at *m*/*z* 1559.34, which was consistent with the calculated data (1559.64 [MH^+]), as shown in Fig. 2.

We then carried out photoinduced isomerization of allyl alcohols using dendrimer disulfide **16** in water (Scheme 6). Photoirradiation of 2-cyclohexene-1-ol (**5**) in the presence of 10 mol % of dendrimer disulfide **16** gave cyclohexanone (**8**) in 60% yield. 3-Methyl-2-cyclohexene-1-ol (**9**) was also employed for this reaction to achieve stereoselective isomerization. However, racemic 3-methylcyclohexanone (**11**) was obtained in 56% yield.



SCHEME 4 Plausible mechanism of photoinduced isomerization.

CONCLUSION

In summary, we disclosed a novel photoinduced isomerization of allyl alcohols mediated by diphenyl disulfide. In particular, an effective isomerization of allyl alcohol was accomplished by the use of dendrimer disulfides as catalysts. The reaction using water-soluble dendrimer disulfide in water was also succeeded. Further work is in progress to explore the applications and advantages of photoinduced isomerization using dendrimer disulfide.

EXPERIMENTAL SECTION

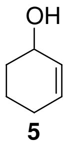
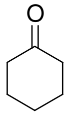
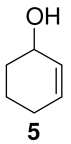
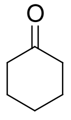
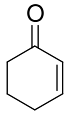
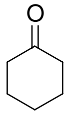
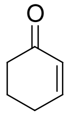
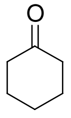
General Method

The NMR spectra was measured using a spectrometer (AL300; JEOL, Tokyo, Japan). Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) was performed on a mass spectrometer (Autoflex; Bruker Daltonics Inc., Tokyo, Japan). Gas chromatography (GC) analyses were carried out on a gas chromatograph (GC18A; Shimadzu Corp., Tokyo, Japan) equipped with an FID detector and a fused silica capillary column (30 m × 0.53 mm i.d., coating DB-1; J&W Scientific Inc., Tokyo, Japan). The oven was maintained at 40°C for 5 min, programmed at 2°C min^{-1} between 40 and 100°C, and programmed at 20°C min^{-1} between 100 and 270°C. The GC-MS analyses were performed on a GC-MS workstation (QP5000; Shimadzu Corp., Tokyo, Japan) with a fused silica capillary column (30 m × 0.25 mm i.d., coating TC-5; GL Science Co. Ltd., Tokyo, Japan). Optical rotations were recorded on a polarimeter (SEPA-300; HORIBA Corp., Tokyo, Japan, $\lambda = 589$ nm). Photoirradiation was carried out using a Pyrex reactor. Prior to irradiation, solvents were degassed with nitrogen for 30 min. A 500 W high-pressure mercury lamp (EHB-500; Eikosha Corp., Osaka, Japan) was used as the light source. Unless otherwise noted, the reagents were obtained from Wako Pure Chemical Industries Ltd. (Tokyo, Japan), Tokyo Kasei Kogyo Co. Ltd. (Tokyo, Japan), Kanto Kagaku (Tokyo, Japan), or Aldrich Chemical Co. Inc. (Tokyo, Japan). The Et_2O used in reactions was further purified using a general method. Other solvents and reagents were used as received without further purification. Dendrimer disulfide **12** and **13** were synthesized according to the previously reported method [10,12].

*3-Methyl-2-cyclohexen-1-ol (**10**)*

3-Methylcyclohexen-1-one (**11**) (5.00 g, 45.4 mmol) in dry Et_2O (5 mL) was added simultaneously over 20 min to lithium aluminum hydride (0.86 g, 22.7 mmol) in dry Et_2O (10 mL) at −50°C. After stirring at −50°C for 1 h, ice-cold water (1.5 mL), 4 N aqueous solution of NaOH (1.5 mL), and water (7 mL) were added in order. The aqueous slurry was extracted with Et_2O. Et_2O layer was washed with brine, dried over $MgSO_4$, and evaporated under ice cooling. The residue was purified using distillation (bp 52°C) and silica gel column chromatography (eluent, chloroform:methanol = 40:1) to afford 3-methyl-2-cyclohexen-1-ol (**10**) (1.34 g, 11.9 mmol) as a colorless liquid in 26% yield, identically to that of an authentic sample [23]: ^{1}H NMR (300 MHz, $CDCl_3$)

TABLE 3 Photoinduced Isomerization of Allyl Alcohols Using Dendrimer **12** and Higher Generation Dendrimer **13**[a]

Entry	*Disulfide (mol%)*	*Allyl Alcohol*	*Time*	*Conversion*	*Product*	*Yield*[b]
1	Dendrimer **12** (100 mol %)	 **5**	2.5 h	>99%	 **8**	90%
2	Dendrimer **12** (10 mol %)	 **5**	2.5 h	>99%	 **8**	90%
3	Dendrimer **13** (100 mol %)		2.5 h	55%	 **7**	trace
					 **8**	66%
4	Dendrimer **13** (10 mol %)		2.5 h	27%	 **7**	trace
					 **8**	72%

[a] Reactions initiated with UV-light (high-pressure mercury lamp, λ > 300 nm) in benxene at rt.
[b] GC yield (based on consumed starting material).

δ 1.33 (dd, $J = 2.7$ and 9.0 Hz, 1H), 1.50–1.61 (m, 2H), 1.69 (s, 3H), 1.74–1.80 (m, 2H), 1.87–1.96 (m, 2H), 4.17 (s, 1H), 5.50 (s, 1H).

Preparation of the Dendrimer Disulfide 16

A solution of dendrimer disulfide **12** (511 mg, 0.70 mmol) in methanol (38 mL) was added dropwise to ethylenediamine (38 mL, 556 mmol) under ice cooling. The mixture was stirred at room temperature for 13 h. After removal of the solvent under reduced pressure at 45°C, the residue was reprecipitated from a methanol–ether solution to obtain dendrimer disulfide **17**, which was used for the following reaction without further purification.

A solution of **17** in methanol (5 mL) was added to a vigorously stirred solution of Glucono-δ-lactone (2.48 g, 13.9 mmol) in methanol (139 mL) at 50°C. After stirring at 50°C for 2 h, the reaction mixture was cooled at <0°C for 18 h. A white precipitate was filtered, washed with Et_2O, and dried to afford the dendrimer disulfide **16** (725 mg, 0.46 mmol) as a white solid in 66% yield: ^{1}H NMR (300 MHz, D_2O) δ 2.29 (m, 4H), 2.50–2.80 (m, 7H), 3.00–3.20 (m 8H), 3.23 (s, 2H), 3.30–3.75 (m, 12H), 3.96 (s, 2H), 4.17 (s, 2H), 7.51 (d, $J = 8.4$ Hz, 2H), 7.59 (d, $J = 7.8$ Hz, 2H); MALDI-TOF-MASS (matrix, sinapic acid): m/z 1559.34 ([MH]$^+$). Calcd. for $C_{142}H_{238}N_{28}O_{46}S_2$: m/z 1559.64; $[\alpha]_D^{22} = +19.1$ ($c = 1.06$, water).

Photoinduced Isomerization of the 2-Cyclohexene-1-ol (5) Using 100 mol % of Diphenyl Disulfide (6)

A mixture of 2-cyclohexene-1-ol (**5**) (18.4 mg, 0.19 mmol) and diphenyl disulfide (**6**) (41.5 mg, 0.19 mmol) in benzene (3.2 mL) was irradiated with a high-pressure mercury lamp for 5.5 h at

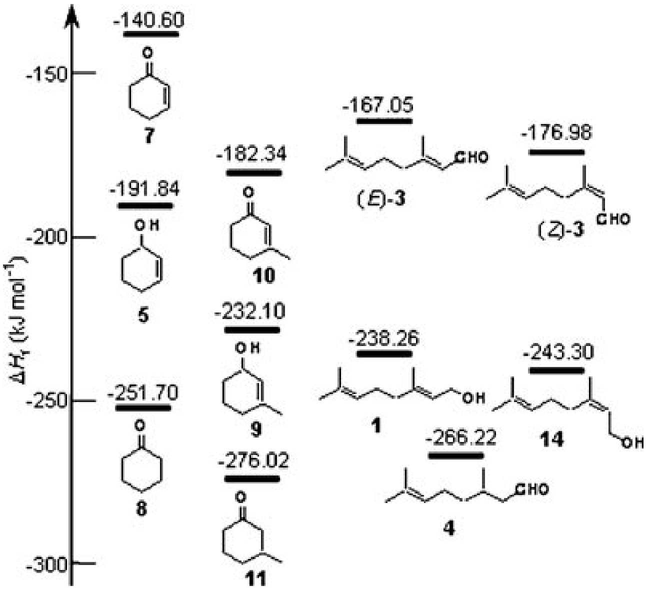


FIGURE 1 Heats of formation (ΔH_f) of allyl alcohols, α,β-unsaturated carbonyl compounds, and saturated carbonyl compounds derived from PM3 calculations.

room temperature. The resulting mixture was analyzed by GC. Decane was used as the internal standard. Three compounds were identified with the following retention times: (a) retention time 9.0 min, cyclohexanone (**8**) (56%); (b) retention time 9.4 min, 2-cyclohexene-1-ol (**5**) (trace); (c) retention time 11.0 min, 2-cyclohexenone (**7**) (14%).

Photoinduced Isomerization of the 3-Methyl-2-cyclohexene-1-ol (9) Using 100 mol % of Diphenyl Disulfide (6)

A mixture of 3-methyl-2-cyclohexene-1-ol (**9**) (21.3 mg, 0.19 mmol) and diphenyl disulfide (**6**) (41.5 mg, 0.19 mmol) in benzene (3.2 mL) was irradiated with a high-pressure mercury lamp for 6 h at room temperature. The resulting mixture was analyzed by GC. Decane was used as the internal standard. Two compounds were identified with the following retention times: (a) retention time 12.7 min, 3-methylcyclohexanone (**11**) (60%); (b) retention time 19.7 min, 3-methyl-2-cyclohexenone (**10**) (trace).

Photoinduced Isomerization of the 2-Cyclohexene-1-ol (5) Using 100 mol % of Dendrimer Disulfide 12

A mixture of 2-cyclohexene-1-ol (**5**) (15.0 mg, 0.15 mmol) and dendrimer disulfide **12** (110 mg, 0.15 mmol) in benzene (2.5 mL) was irradiated with a high-pressure mercury lamp for 2.5 h at room temperature. The resulting mixture was analyzed by GC. Decane was used as the internal standard. Cyclohexanone (**8**) was identified with the retention time 9.0 min (81%).

Photoinduced Isomerization of the 2-Cyclohexene-1-ol (5) Using 10 mol % of Dendrimer Disulfide 12

A mixture of 2-cyclohexene-1-ol (**5**) (34.8 mg, 0.36 mmol) and dendrimer disulfide **12** (26.1 mg, 0.036 mmol) in benzene (6 mL) was irradiated with a high-pressure mercury lamp for 2.5 h at room temperature. The resulting mixture was analyzed by GC. Decane was used as the internal standard. Cyclohexanone (**8**) was identified with the retention time 9.0 min (90%).

Photoinduced Isomerization of the 2-Cyclohexene-1-ol (5) Using 1 mol % of Dendrimer Disulfide 12

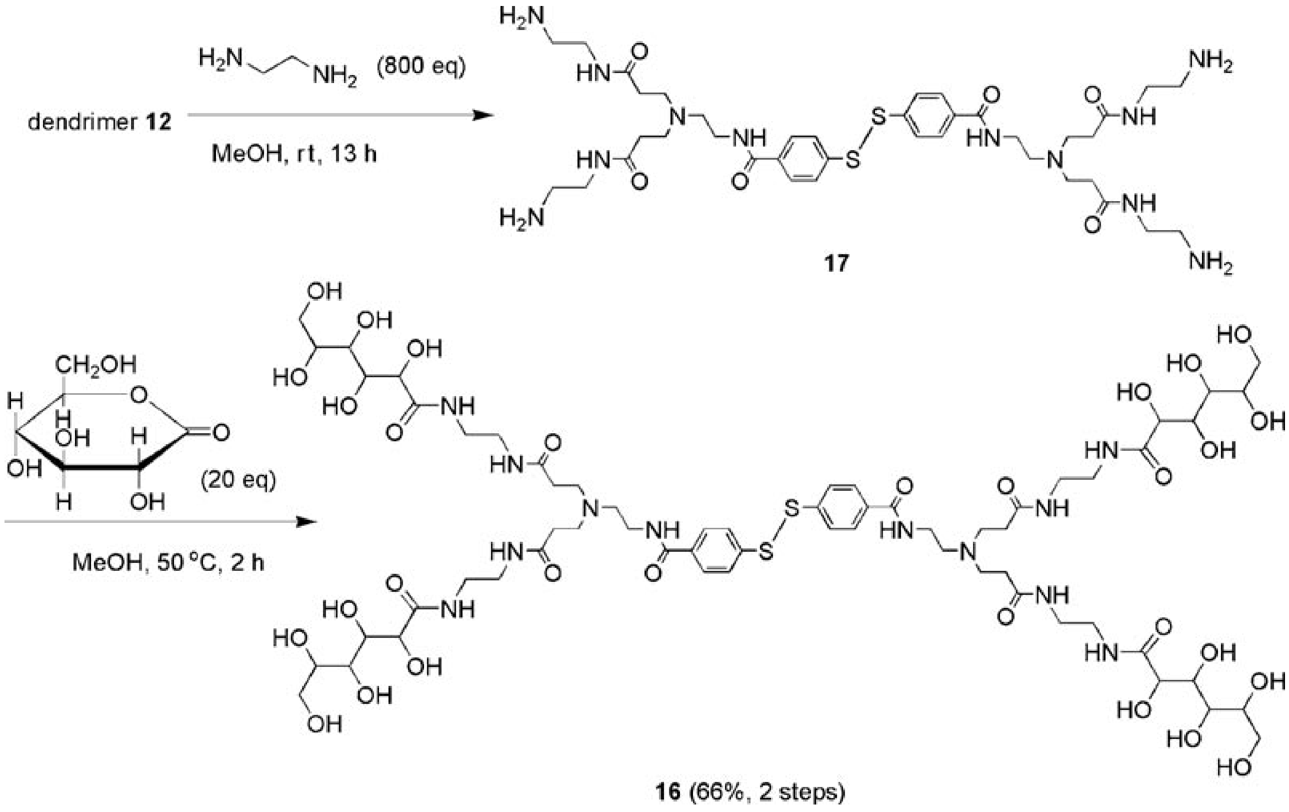
A mixture of 2-cyclohexene-1-ol (**5**) (33.4 mg, 0.34 mmol) and dendrimer disulfide **12** (2.5 mg, 3.4×10^{-3} mmol) in benzene (5.7 mL) was irradiated with a high-pressure mercury lamp for 12 h at room temperature. The resulting mixture was analyzed by GC. Decane was used as the internal standard. Two compounds were identified with the following retention times: (a) retention time 9.0 min, cyclohexanone (**8**) (18%); (b) retention time 9.4 min, 2-cyclohexene-1-ol (**5**) (46%).

Photoinduced Isomerization of the 3-Methyl-2-Cyclohexene-1-ol (9) Using 100 mol % of Dendrimer Disulfide 12

A mixture of 3-methyl-2-cyclohexene-1-ol (**9**) (38 mg, 0.34 mmol) and dendrimer disulfide **12** (249 mg, 0.34 mmol) in benzene (5.7 ml) was irradiated with a high-pressure mercury lamp for 2.5 h at room temperature. The resulting mixture was analyzed by GC. Decane was used as the internal standard. Three compounds were identified with the following retention times: (a) retention time 12.7 min, 3-methylcyclohexanone (**11**) (75%); (b) retention time 15.5 min, 3-methyl-2- cyclohexene-1-ol (**9**) (5%); (c) retention time 19.7 min, 3-methyl-2-cyclohexenone (**10**) (15%).

Photoinduced Isomerization of the 3-Methyl-2-Cyclohexene-1-ol (9) Using 10 mol % of Dendrimer Disulfide 12

A mixture of 3-methyl-2-cyclohexene-1-ol (**9**) (35.1 mg, 0.31 mmol) and dendrimer disulfide **12**



SCHEME 5 Synthesis of water-soluble dendrimer disulfide **16**.

(23.0 mg, 0.031 mmol) in benzene (5.3 mL) was irradiated with a high-pressure mercury lamp for 12 h at room temperature. The resulting mixture was analyzed by GC. Decane was used as the internal standard. 3-Methylcyclohexanone (**11**) was identified with the retention time 12.7 min (91%).

*Photoinduced Isomerization of the 2-Cyclopentene-1-ol (**14**) Using 10 mol % of Dendrimer Disulfide **12***

A mixture of 2-cyclopentene-1-ol (**14**) (33.7 mg, 0.40 mmol) and dendrimer disulfide **12** (29.7 mg, 0.040 mmol) in benzene (5.0 mL) was irradiated with a high-pressure mercury lamp for 2.5 h at room temperature. The resulting mixture was analyzed by GC. Decane was used as the internal standard. Cyclopentanone (**15**) was identified with the retention time 7.2 min (90%).

*Photoinduced Isomerization of the 2-Cyclohexene-1-ol (**5**) Using 100 mol % of Dendrimer Disulfide **13***

A mixture of 2-cyclohexene-1-ol (**5**) (17.1 mg, 0.17 mmol) and dendrimer disulfide **13** (268 mg, 0.17 mmol) in benzene (2.9 mL) was irradiated with a high-pressure mercury lamp for 2.5 h at room temperature. The resulting mixture was analyzed by GC. Decane was used as the internal standard. Three compounds were identified with the following retention times: (a) retention time 9.0 min, cyclohexanone (**8**) (18%); (b) retention time 9.4 min, 2-cyclohexene-1-ol (**5**) (73%); (c) retention time 11.0 min, 2-cyclohexenone (**7**) (trace).

*Photoinduced Isomerization of the 2-Cyclohexene-1-ol (**5**) Using 10 mol % of Dendrimer Disulfide **13***

A mixture of 2-cyclohexene-1-ol (**5**) (34.8 mg, 0.36 mmol) and dendrimer disulfide **13** (26.1 mg, 0.036 mmol) in benzene (6 mL) was irradiated with a high-pressure mercury lamp for 2.5 h at room temperature. The resulting mixture was analyzed by GC. Decane was used as the internal standard. Three compounds were identified with the following retention times: (a) retention time 9.0 min, cyclohexanone (**8**) (36%); (b) retention time 9.4 min, 2-cyclohexene-1-ol (**5**) (45%); (c) retention time 11.0 min, 2-cyclohexenone (**7**) (trace).

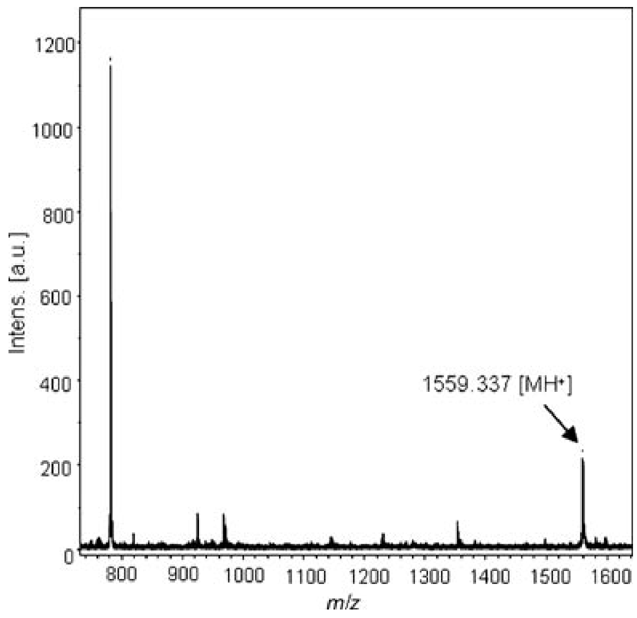
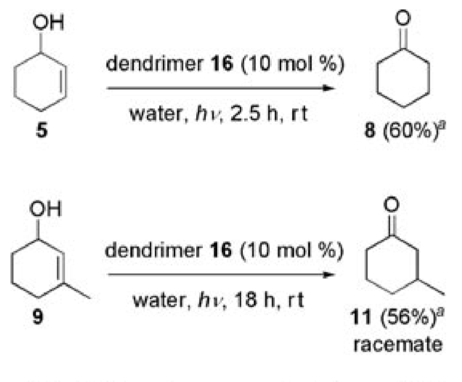


FIGURE 2 MALDI-TOF-MS spectrum of dendrimer sulfide **16**.

*Photoinduced Isomerization of the 2-Cyclohexene-1-ol (**5**) Using 10 mol % of Dendrimer Disulfide Having Sugar Moiety **15***

A mixture of 2-cyclohexene-1-ol (**5**) (18.6 mg, 0.19 mmol) and dendrimer disulfide **15** (29.6 mg, 0.019 mmol) in deionized water (3.2 mL) was irradiated with a high-pressure mercury lamp for 2.5 h at room temperature. The resulting mixture was analyzed by GC. 4-Methyl-3-pentene-2-one was used as the internal standard. Two compounds were identified with the following retention times: (a) retention time 9.0 min, cyclohexanone (**8**) (47%); (b) retention time 9.4 min, 2-cyclohexene-1-ol (**5**) (22%).



[a] GC yield (based on consumed starting material).

SCHEME 6 Photoinduced isomerization using dendrimer **16** in water.

*Photoinduced Isomerization of the 3-Methyl-2-cyclohexene-1-ol (**9**) Using 10 mol % of Dendrimer Disulfide Having Sugar Moiety **15***

A mixture of 3-methyl-2-cyclohexene-1-ol (**9**) (21.3 mg, 0.19 mmol) and dendrimer disulfide **15** (30.0 mg, 0.019 mmol) in deionized water (3.2 mL) was irradiated with a high-pressure mercury lamp for 18 h at room temperature. The resulting mixture was analyzed by GC. Cyclohexanone was used as the internal standard. 3-Methylcyclohexanone (**11**) was identified with the retention time 12.7 min (56%).

Calculations

The semiempirical calculations by the PM3 method were performed using MOPAC version 6.02 [24] with parameters in Ref. [25]. In the calculation, totally optimized molecular geometries in the ground state were used.

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