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Novel Photoreaction Using Diphenyl Disulfide Derivatives: Photoinduced Oxidation of Allyl Alcohol

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Allyl alcohols are oxidized to acrylaldehydes using diphenyl disulfide derivatives upon photoirradiation. The reaction occurs via α-hydrogen abstraction by a sulfanyl radical. Interestingly, the oxidation reaction occurs in moderate yield when a dendrimer disulfide is used as a mediator.

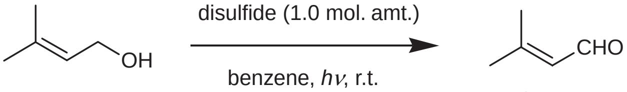
Photoreactivity of diphenyl disulfide derivatives has attracted scientific attention in the past few decades. Sulfanyl radicals generated by homolytic cleavage of the S–S bond play important roles in photoinitiated reactions such as sulfenylation of aryl halides[1a] and hindered phenols,[1b] and vinyl polymerization.[2] Ogawa and Sonoda reported that a binary system of organic dichalcogenides, i.e., a $(PhS)_2$–$(PhSe)_2$ system, provides the desired vicinal dichalcogenation of carbon–carbon unsaturated compounds[3a–3c] and double chalcogenation of isocyanides[3d] under photoirradiation. However, transformation of functional groups using photoreaction of disulfide is quite rare.[4] Meanwhile, dendrimers containing a photoreactive core have garnered considerable interest in the fields of material science and synthetic organic chemistry. In particular, there is an increasing emphasis on developing applications for dendrimer disulfide because of various interesting features in supramolecular chemistry,[5] host–guest chemistry,[6] stabilization of highly reactive species,[7] and material science.[8] Recently, we reported that a photoaddition reaction of C_{60} with a poly(amidoamine) dendrimer disulfide, of which the core is diphenyl disulfide, gave a new fullerodendrimer having fullerene–sulfur bonds as a linkage.[9] During our studies on dendrimer effects of dendrimer disulfides, we found a novel reaction of diphenyl disulfide derivatives, i.e., allyl alcohols were converted into acrylaldehydes in the presence of diphenyl disulfide derivatives upon photoirradiation. In this paper, we describe that diphenyl disulfide derivatives mediate oxidation of various allyl alcohols to give acrylaldehydes upon photoirradiation. In particular, an effective oxidation of allyl alcohol was accomplished by the use of dendrimer disulfides.

Results and Discussion

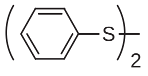
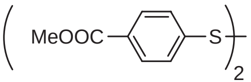
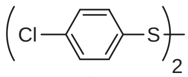
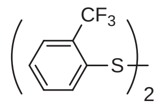
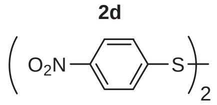
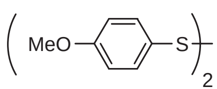
A benzene solution of 3-methyl-2-buten-1-ol (**1a**) in the presence of diphenyl disulfide (**2a**) was irradiated with a high-pressure mercury lamp ($\lambda > 300$ nm) through a Pyrex filter at room temperature under a nitrogen atmosphere for 80 min to give 3-methyl-2-butenal (**3a**) in 23% yield. Reactions in the dark or in the absence of diphenyl disulfide (**2a**) did not proceed. Complex mixtures were obtained when oxygen was passed through the reaction mixture during the reaction. These results indicate that oxidation of allyl alcohol **1a** is a photoreaction mediated by diphenyl disulfide (**2a**).

We carried out the same reaction in the presence of various diphenyl disulfide derivatives to obtain mechanistic insights into this oxidation (Table 1). Bis(p-nitrophenyl) disulfide (**2e**) was difficult to dissolve in benzene; instead, chloroform was used as the solvent in Entry 5. The use of diphenyl disulfides having electron-withdrawing substituents resulted in moderate yields of products (Entries 2–5). On the other hand, the use of bis(p-methoxyphenyl) disulfide (**2f**), an electron-rich disulfide,

Table 1. Oxidation of 3-Methyl-2-buten-1-ol (**1a**) Using Photolysis of Diphenyl Disulfide Derivatives



1a **3a**

Entry	Disulfide	Time	Conversion /%	Yield[a)] /%
1	 **2a**	80 min	63	23
2	 **2b**	30 min	45	31
3	 **2c**	1 h	58	44
4	 **2d**	30 min	85	37
5[b)]	 **2e**	1 h	48	30
6	 **2f**	2.5 h	56	trace

a) GC yield (based on consumed starting material). b) $CHCl_3$ was used as a solvent.

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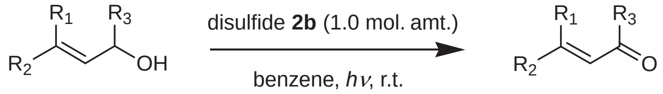
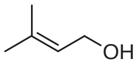
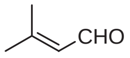
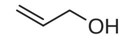
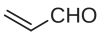
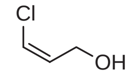
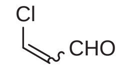
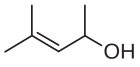
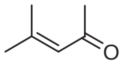
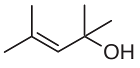
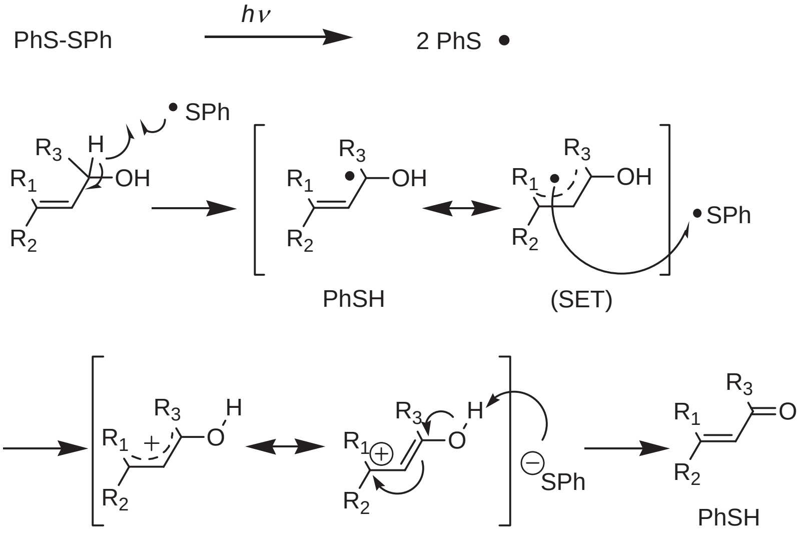
Table 2. Oxidation of Allyl Alcohols Using Photolysis of Disulfide **2b**



Entry	Allyl alcohol	Time	Conversion/%	Product	Yield/%
1	 **1a**	30 min	$45^{a)}$	 **3a**	$31^{a)}$
$2^{b)}$	 **1b**	30 min	$37^{c)}$	 **3b**	$7^{c)}$
$3^{b)}$	 **1c**	2 h	$28^{c)}$	 **3c**	$35^{c)}$ ($E/Z = 57/43$)$^{d),e)}$
4	 **1d**	30 min	$53^{a)}$	 **3d**	$25^{a)}$
5	 **1e**	20 min	$47^{a)}$		—

a) GC yield (based on consumed starting material). b) $CDCl_3$ was used as a solvent. c) NMR yield (based on consumed starting material). d) E/Z Ratio was determined by ^{1}H NMR. e) Starting allyl alcohol **1c** was recovered in 72%$^{c)}$, $E/Z = 54/46^{d)}$.



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

gave trace product (Entry 6). Various allyl alcohols were also employed for oxidation using bis(p-methoxycarbonylphenyl) disulfide (**2b**) (Table 2). Reaction of allyl alcohol having no substituent (**1b**) on the terminal olefin gave low yield of product **3b** (Entry 2). Although longer reaction time was required, oxidation of (Z)-3-chloro-2-propenol (**1c**) gave product **3c** in almost the same yield as the oxidation of allyl alcohol **1a** (Entry 3). The E–Z isomerization of recovered allyl alcohol **1c** (E/Z = 54:46) and product **3c** (E/Z = 57:43) indicates that carbon-centered radical intermediate might be formed in this reaction. The use of secondary alcohol **1d** afforded product **3d** in lower yield than the use of primary alcohol **1a** (Entry 4). The reaction of tertiary alcohol **1e** gave no oxidized product (Entry 5). These results show that the α-hydrogen of the alcohol is necessary to cause oxidation. In all cases of the above reactions, thiols corresponding to disulfides were obtained. For example, oxidation of 3-methyl-2-buten-1-ol (**1a**) using diphenyl disulfide (**2a**) gave thiophenol and unchanged diphenyl disulfide (**2a**) in 23% and 54% yield, respectively.

Based on the results described above, a plausible mechanism is proposed in Scheme 1. The reaction is triggered by the sulfanyl radical generated by photolysis of the diphenyl disulfide. Then, the abstraction of an α-hydrogen, which occurs from the allyl alcohol to the sulfanyl radical, produces the allylic radical and thiophenol. It is noteworthy that only a few reactions involving hydrogen abstraction by a sulfanyl radical have been reported.[4] Next, a single electron transfer (SET) occurs from the allylic radical to another sulfanyl radical, and an allylic cation is formed. Employing diphenyl disulfides **2b–2e** having electron-withdrawing substituent resulted in moderate yields, in marked contrast with the reaction by the use of electron-rich disulfide **2f**. Meanwhile, the reaction efficiency of allyl alcohol **1c** having electron-withdrawing chlorine group is quite low compared to **1a**, which has electron-donating methyl groups. These results might suggest that sulfanyl radical (or diphenyl disulfide) acts as an electron acceptor during the SET process. The thiolate anion, which is generated by SET, abstracts the proton of alcohol to give the oxidized product and thiophenol. However, the exact reaction mechanism is not completely clear. Efforts to obtain a better understanding of the reaction mechanism are in progress.

This oxidation gave only 23–44% yield of products. Polymerization of allyl alcohols initiated by the carbon-centered radical generated from the addition reaction of sulfanyl radical to the olefin probably causes decreased yield of the products. Gel permeation chromatography (GPC) analysis of the reaction mixture of 3-methyl-2-buten-1-ol (**1a**) and bis(2-trifluoromethylphenyl) disulfide (**2d**) showed several peaks in the high-molecular-weight region. Furthermore, trace amount of byproduct, which might be formed by the addition reaction of disulfide or thiol to the olefins, were observed by GC analysis. To decrease the rate of side reactions triggered by the addition of sulfanyl radical to unsaturated bonds, diphenyl disulfide having bulky substituents might be expected to be effective. Okazaki and Goto reported a stable aromatic *S*-nitrosothiol bearing a dendrimer steric protection group.[10] This protection group suppresses oxidative dimerization of the *S*-nitrosothiol without diminution of reactivity of the *S*-nitrosothiol core towards appropriate molecules such as thiols or alcohols. This result prompted us to investigate oxidation using dendrimer disulfides **4**[6] (Chart 1) or **5**.

Dendrimer **5** was synthesized as shown in Scheme 2. A known compound **7** was selected as the starting material, which was prepared according to the literature.[11] Compound **7** was treated with NaOH in methanol under reflux for 1 day, and then acidified with HCl to obtain 5-sulfanylisophthalic acid (**8**). Fischer esterification of isophthalic acid **8** with meth-

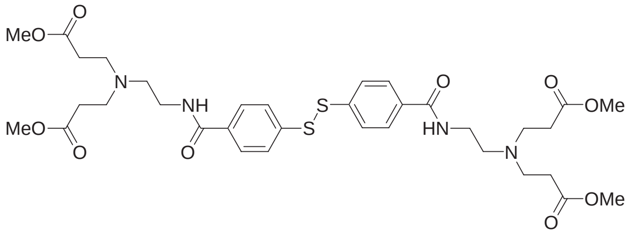


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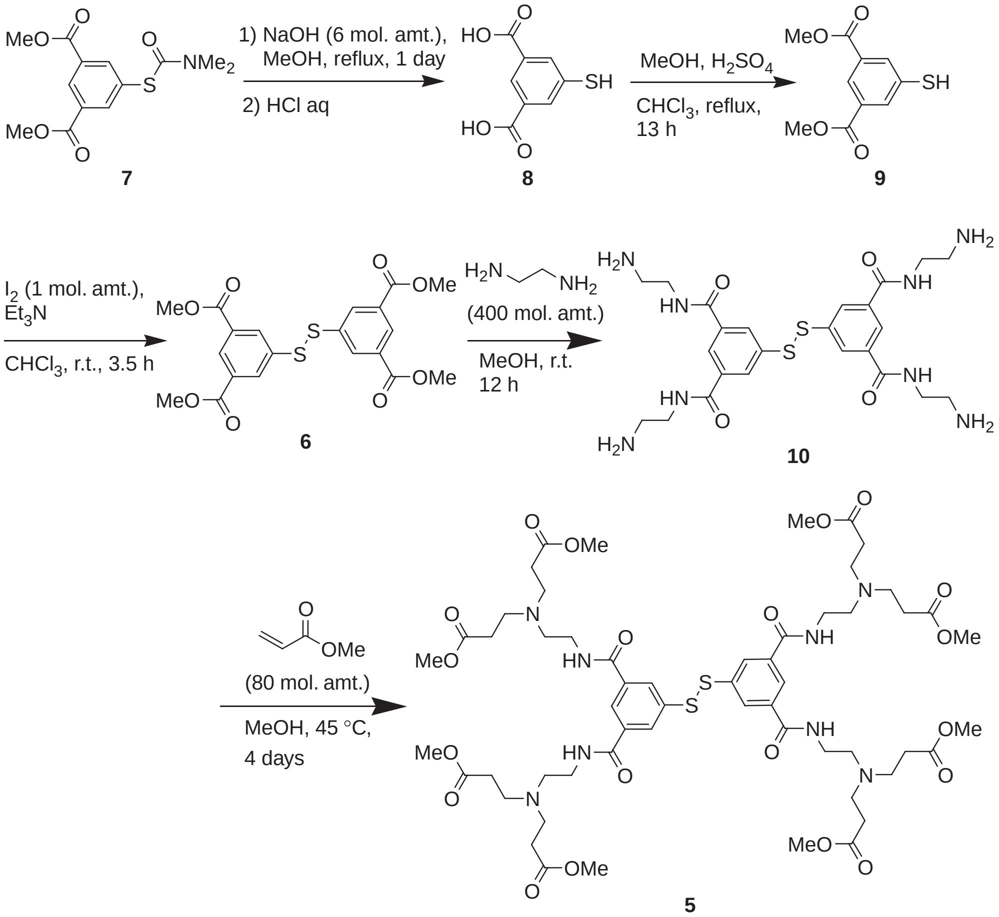
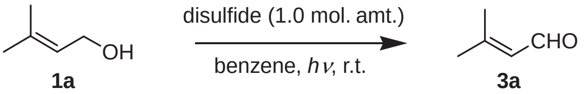
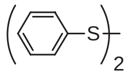
Chart 1.



Scheme 2. Synthesis of dendrimer disulfide **5**.

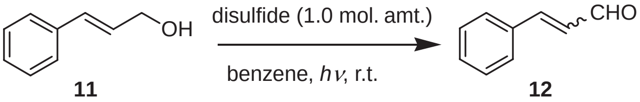
Table 3. Oxidation of 3-Methyl-2-buten-1-ol (**1a**) Using Photolysis of Dendrimer Disulfides

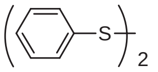


Entry	Disulfide	Time/h	Conversion/%	Yield$^{a)}$/%
1	 **2a**	1	63	23
2	Dendrimer **4**	2.5	59	63
3	Dendrimer **5**	2.5	58	51

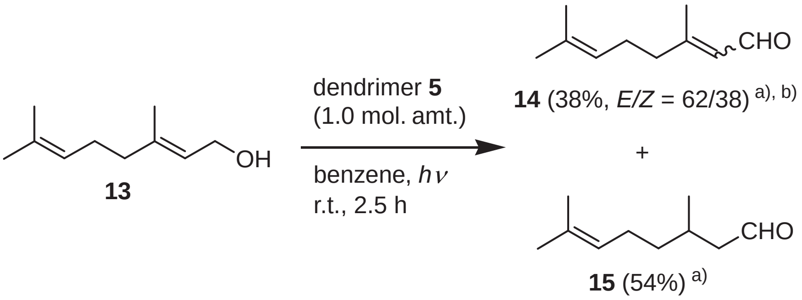
a) GC yield (based on consumed starting material).

Table 4. Oxidation of Cinnamyl Alcohol (**11**)



Entry	Disulfide	Time	Conversion/%	Yield$^{a)}$/%
1	 **2a**	70 min	52	44 ($E/Z > 95/5$)$^{b)}$
2	Dendrimer **4**	2.5 h	54	58 ($E/Z > 95/5$)$^{b)}$
3	Dendrimer **5**	2.5 h	42	46 ($E/Z > 95/5$)$^{b)}$

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



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

Scheme 3. Oxidation of geraniol (**13**).

anol under reflux for 13 h gave dimethyl 5-sulfanylisophthalate (**9**). Thiol **9** was oxidized with I_2 in the presence of triethylamine at room temperature for 3.5 h to afford bis(3,5-methoxycarbonylphenyl) disulfide (**6**) (58% yield, 3 steps). The treatment of disulfide **6** with ethylenediamine produced the core of dendrimer **10**. Subsequently, **10** was allowed to react with methyl acrylate to give a dendrimer disulfide **5** (33%, two steps).

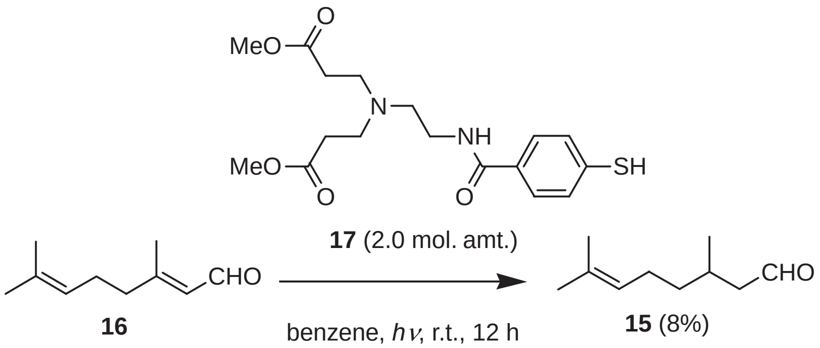
We then carried out oxidation of 3-methyl-2-buten-1-ol (**1a**) in the presence of dendrimer disulfides **4** or **5** (Table 3). Their use gave product **3a** in much better yields (63% or 51%) than by the use of diphenyl disulfide (**2a**) (23%), although the conversions of allyl alcohol **1a** were almost the same. This result indicated that the bulky dendritic substituent might inhibit side reactions. Dendrimer disulfides were also effective for oxidation of other allyl alcohols, such as cinnamyl alcohol (**11**) (Table 4). Oxidation of cinnamyl alcohol (**11**) in the presence of dendrimer disulfides **4** or **5** gave cinnamaldehyde (**12**) in 58% or 46% yields, respectively. On the other hand, the use of diphenyl disulfide (**2a**) afforded product **12** in 44% yield.

Furthermore, oxidation of geraniol (**13**) in the presence of dendrimer disulfide **5** gave citral (**14**) and 3,7-dimethyl-6-octenal (citronellal, **15**) in 38% and 54% yields (Scheme 3), respectively. The total amount of oxidation products, aldehydes **14** and **15**, reached 92% yield. This result might indicate that the polymerization initiated by the intermediate carbon-centered radical might be suppressed by the use of a bulky allyl alcohol. Although the reaction mechanism is not clear, citronellal (**15**) might be formed by reduction of citral (**14**). We followed the time course of this reaction by NMR and observed that citronellal (**15**) was not formed until 20 min after the start of the reaction. Furthermore, we confirmed that photoreaction of (E)-citral (**16**) in the presence of dendron thiol **17** gave citronellal (**15**) in 8% yield (Scheme 4).

Absorption maximums ($\lambda_{\max}$) and molar extinction coefficients (ε) of disulfides **2a**, **4**, and **5** are displayed in Table 5. All three disulfides gave the same absorption maximum at 276 nm and similar values of molar extinction coefficients. However, oxidations by the use of dendrimer disulfides **4** and **5** gave products in better yields than by the use of diphenyl disulfide (**2a**). Hence, the difference in reactivity between dendritic disulfide and nonsubstituted diphenyl disulfide might arise from not photoexcitation but the following reactions, which can be affected by the bulky dendritic substituent.

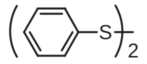
Conclusion

These results described herein show the first example of oxidation of allyl alcohol mediated by diphenyl disulfide derivatives upon photoirradiation. Since dendritic substituents were quite effective to inhibit unwanted side reactions of the intermediates, dendrimer disulfide was found to be a good mediator of this oxidation reaction. Further work is in progress to explore the application and advantages of photoreactivities of dendrimer disulfides.



Scheme 4. Photoirradiation of (*E*)-citral (**16**) in the presence of dendron thiol **17**.

Table 5. Absorption Data for Diphenyl Disulfide Derivatives

Disulfide	λ_{max}/nm[a)]	ε_{max}/M^{-1} cm^{-1} [a)]
Dendrimer **4**	276	1.66×10^4
Dendrimer **5**	276	5.69×10^3
 **2a**	276	2.86×10^3

a) In benzene.

Experimental

Melting points (mp) were determined using a Mel-Temp II melting point apparatus, Laboratory Devices Inc., and are uncorrected. The NMR spectra were measured using a JEOL AL300 spectrometer. The IR and IR-attenuated total reflection (ATR) spectra were recorded on an Avatar 360T2 spectrometer, Thermo Nicolet Japan Inc. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) was performed on an Autoflex mass spectrometer, Bruker Daltonics Inc. Elemental analysis was carried out using a 2400 Series II CHNS/O elemental analyzer, Perkin-Elmer Inc. The GPC experiments were performed on an appropriate device (LC-918V; Japan Analytical Industry Co.) using JAIGEL 1H, 2H columns. Chloroform was used as the eluting solvent. Gas chromatography (GC) analyses were carried out on a GC18A gas chromatograph, Shimadzu Corp., 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.). The GC-MS analyses were performed on a GC-MS workstation (QP5000; Shimadzu Corp.) with a fused silica capillary column (30 m × 0.25 mm i.d., coating TC-5; GL Science Co., Ltd.). 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.) was used as the light source. Unless otherwise noted, the reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Kogyo Co., Ltd., Kanto Kagaku, or Aldrich Chemical Co., Inc. The Et_2O used in reactions was further purified using general methods. Other solvents and reagents were used as received without further purification. Dendrimer **4** was synthesized according to a previously reported method.[6] Compound **7** was prepared using a method reported by Portnoy et al.[11]

For comparison of reaction rates, the conversion of allyl alcohol was set between ca. 40–60%. In the case of the reaction using bis(2-trifluoromethylphenyl) disulfide (**2d**), allyl alcohol was rapidly consumed.

Preparation of 2,4-Dimethyl-3-penten-2-ol (1e). A solution of 4-methyl-3-penten-2-one (**3d**) (1.00 g, 10.2 mmol) in Et_2O (20 mL) was added dropwise to a stirred solution of 0.93 M methyl magnesium bromide in THF (32.9 mL, 30.6 mmol) diluted with Et_2O (50 mL). After stirring at room temperature for 1 h, aqueous saturated NH_4Cl (30 mL) was added. The mixture was extracted with Et_2O, dried over $MgSO_4$, and the solvent evaporated under ice cooling. The residue was distilled to afford 2,5-dimethyl-3-penten-2-ol (**1e**) (0.49 g, 4.29 mmol), bp 42 °C (13 mmHg), as a colorless liquid in 42% yield, with spectral data being identical to that of an authentic sample:[12] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 6H), 1.70 (s, 3H), 1.85 (s, 3H), 5.33 (s, 1H).

Preparation of Bis(4-methoxycarbonylphenyl) Disulfide (2b). Sulfuric acid (1.6 mL) was added dropwise to a mixture of 4-sulfanylbenzoic acid (1.60 g, 10.4 mmol), methanol (2.52 mL, 62.2 mmol), and chloroform (6.4 mL). After stirring at 75 °C for 13 h, the solution was extracted with chloroform. The organic layer was washed with aqueous saturated $NaHCO_3$, dried over $MgSO_4$, and the solvent evaporated to afford methyl 4-sulfanylbenzoate as a yellow solid in 86% yield: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.63 (s, 1H), 3.67 (s, 3H), 7.04 (d, $J = 8.4$ Hz, 2H), 7.63 (d, $J = 8.4$ Hz, 2H).

Solutions of methyl 4-sulfanylbenzoate (1.40 g, 8.33 mmol) in chloroform (20 mL) and iodine (1.58 g, 6.24 mmol) in chloroform (50 mL) were added separately and simultaneously over 1 h to a vigorously stirred solution of triethylamine (1.74 mL, 12.49 mmol) in chloroform (20 mL). After stirring at room temperature for 1.5 h, the solution was washed with aqueous saturated $Na_2S_2O_3$, dried over $MgSO_4$, and the solvent evaporated. The residue was purified by silica-gel column chromatography (eluent, chloroform) and recrystallization from benzene–ethanol (1:1) to afford bis(4-methoxycarbonylphenyl) disulfide (**2b**) (1.14 g, 3.36 mmol) as a white crystalline solid in 81% yield, spectral data being identical to that of an authentic sample:[13] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.90 (s, 6H), 7.53 (d, $J = 8.8$ Hz, 4H), 7.97 (d, $J = 8.6$ Hz, 4H).

Preparation of Bis(2-trifluoromethylphenyl) Disulfide (2d). Solutions of *o*-trifluoromethylbenzenethiol (0.54 g, 3.03 mmol) in chloroform (10 mL) and iodine (0.58 g, 2.27 mmol) in chloroform (20 mL) were added separately and simultaneously over 1 h to a vigorously stirred solution of triethylamine (0.63 mL, 4.55 mmol) in chloroform (10 mL). After stirring at room temperature for 4 h, the solution was washed with aqueous saturated $Na_2S_2O_3$, dried over $MgSO_4$, and the solvent evaporated. The residue was purified by silica-gel column chromatography (eluent, chloroform/hexane = 1/4) and recrystallized from methanol to afford bis(2-trifluoromethylphenyl) disulfide (**2d**) (0.26 g, 0.73 mmol) as pale yellow plates in 48% yield, with spectral data being identical to that of an authentic sample:[14] mp 60 °C (lit. 62 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (t, $J = 7.5$ Hz, 1H), 7.49 (t, $J = 7.4$ Hz, 3H), 7.64 (d, $J = 7.5$ Hz, 3H), 7.84 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 121.8, 125.4, 126.6, 126.7, 127.1, 129.5, 132.5.

Preparation of Bis(4-nitrophenyl) Disulfide (2e). Solutions of *p*-nitrobenzenethiol (1.00 g, 6.44 mmol) in chloroform (25 mL) and iodine (1.63 g, 6.44 mmol) in chloroform (40 mL) were added separately and simultaneously over 1 h to a vigorously stirred solution of triethylamine (1.35 mL, 9.66 mmol) in chloroform (25 mL). After stirring at room temperature for 4 h, the solution was washed with aqueous saturated $Na_2S_2O_3$, dried over $MgSO_4$, and the solvent evaporated. The residue was washed with methanol to afford bis(4-nitrophenyl) disulfide (**2e**) (0.74 g, 2.40 mmol) as a yellow powder in 37% yield, with spectral data identical to that of an authentic sample:[15] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, $J = 9.6$ Hz, 4H), 8.20 (d, $J = 9.6$ Hz, 4H).

Preparation of Bis(4-methoxyphenyl) Disulfide (2f). Solutions of *p*-methoxybenzenethiol (1.00 g, 7.13 mmol) in chloroform (25 mL) and iodine (1.81 g, 7.13 mmol) in chloroform (40 mL) were added separately and simultaneously over 1 h to a vigorously stirred solution of triethylamine (1.49 mL, 10.7 mmol) in chloroform (25 mL). After stirring at room temperature for 1.5 h, the solution was washed with aqueous saturated $Na_2S_2O_3$, dried over $MgSO_4$, and the solvent evaporated. The residue was purified by silica-gel column chromatography (eluent, chloroform/hexane = 7/1) to afford bis(4-methoxyphenyl) disulfide (**2f**) (0.94 g, 3.38 mmol) as a yellow liquid in 95% yield, spectral data being identical to that of an authentic sample:[15] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.79 (s, 3H), 6.83 (d, $J = 9.0$ Hz, 2H), 7.40 (d, $J = 8.2$ Hz, 1H).

Preparation of Bis(3,5-methoxycarbonylphenyl) Disulfide (6). Dimethyl 5-(dimethylcarbamoylthio) isophthalate (**7**) (1.32 g, 4.44 mmol) was added a 1 M solution (27 mL) of NaOH in methanol. After stirring at 75 °C for 19 h, the solution was cooled, diluted with ice water (160 mL), and acidified with 6 M HCl (44 mL). The yellow precipitate was filtered and dried to obtain the crude product of 5-sulfanylisophthalic acid (**8**) (0.72 g) as a yellow powder, which was used for the following reaction without further purification.

Sulfuric acid (1 mL) was added dropwise to a mixture of **8**, methanol (1.76 mL, 43.6 mmol) and chloroform (5.3 mL). After stirring at 75 °C for 13 h, the solution was extracted with chloroform. The organic layer was washed with aqueous saturated $NaHCO_3$, dried over $MgSO_4$, and the solvent evaporated to afford crude dimethyl 5-sulfanylisophthalate (**9**) (0.71 g) as a pale yellow solid, which was used for the following reaction without further purification.

Solutions of **9** (710 mg, 3.14 mmol) in chloroform (25 mL) and iodine (800 mg, 3.14 mmol) in chloroform (40 mL) were added separately and simultaneously over 1 h to a vigorously stirred solution of triethylamine (0.66 mL, 4.71 mmol) in chloroform (25 mL). After stirring at room temperature for 3.5 h, the solution was washed with aqueous saturated $Na_2S_2O_3$, dried over $MgSO_4$, and the solvent evaporated. The residue was purified by silica-gel column chromatography (eluent, chloroform) and recrystallized from benzene–ethanol (1:2) to afford bis(3,5-methoxycarbonylphenyl) disulfide (**6**) (580 mg, 1.29 mmol) as a white crystalline solid in 58% yield: mp 156 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.94 (s, 6H), 8.34 (s, 2H), 8.53 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.5, 129.7, 131.7, 132.6, 137.8, 165.3; IR (KBr) 1724, 1586, 1436 cm^{-1}. Anal. Found: C, 53.16; H, 4.07%. Calcd for $C_{20}H_{18}O_8S_2$: C, 53.32; H, 4.05%.

Preparation of Dendrimer Disulfide 5. A suspension of **6** (620 mg, 1.38 mmol) in methanol (37 mL) was added dropwise to ethylenediamine (37.3 mL, 558 mmol) under ice-cooling. The mixture was stirred at room temperature for 12 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 **10**, which was used for the following reaction without further purification.

A mixture of **10**, methyl acrylate (9.94 mL, 110 mmol) and methanol (30 mL) was stirred at 45 °C for 4 days. After removal of the solvent, the residue was purified by silica-gel column chromatography (eluent, chloroform/methanol = 30/1) and GPC with chloroform as eluent to afford the dendrimer disulfide **5** (560 mg, 0.45 mmol) as a thick yellow oil in 33% yield: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.44 (t, $J = 6.5$ Hz, 8H), 2.65 (t, $J = 5.7$ Hz, 4H), 2.77 (t, $J = 6.5$ Hz, 8H), 3.54 (q, $J = 5.7$ Hz, 4H), 3.57 (s, 12H), 7.44 (t, $J = 5.3$ Hz, 2H), 8.16 (s, 1H), 8.22 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.4, 37.7, 48.9, 51.6, 52.6, 124.7, 129.6, 135.9, 137.7, 165.8, 173.1; ATR (neet) 1732, 1660, 1529, 1437 cm^{-1}. MALDI-TOF-MS (matrix, dithranol): *m/z* 1251.51 ($[M + H]^+$). Calcd for $C_{56}H_{82}N_8O_{20}S_2$: *m/z* 1252.43.

Preparation of Dendron Thiol 17. $NaBH_4$ (61.6 mg, 1.6 mmol) was added to a solution of dendrimer disulfide **4** (399 mg, 0.54 mmol) in ethanol (5.4 mL) at room temperature under Ar atmosphere. After stirring for 2 h, water was added. The mixture was extracted with chloroform. The organic layer was washed with brine, dried over $MgSO_4$, and the solvent evaporated to afford the dendron thiol **17** (367 mg, 1.00 mmol) as a thick yellow oil in 92% yield: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.44 (t, $J = 6.3$ Hz, 4H), 2.62 (t, $J = 5.6$ Hz, 2H), 2.75 (t, $J = 6.3$ Hz, 4H), 3.51–3.57 (m, 9H), 7.21 (brs, 1H), 7.28 (d, $J = 8.1$ Hz, 2H), 7.77 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.3, 37.0, 48.6, 51.2, 52.5, 127.7, 128.0, 131.5, 135.4, 166.3, 172.9; MALDI-TOF-MS (matrix, α-cyano-4-hydroxycinnamic acid): *m/z* 368.91 ($[M + H]^+$). Calcd for $C_{17}H_{24}N_2O_5S$: *m/z* 369.15.

Photoirradiation of a 3-Methyl-2-buten-1-ol (1a) and Diphenyl Disulfide (2a) Mixture. A mixture of 3-methyl-2-butene-1-ol (**1a**) (16 mg, 0.19 mmol) and diphenyl disulfide (**2a**) (41 mg, 0.19 mmol) in benzene (3.2 mL) was irradiated with a high-pressure mercury lamp for 80 min at room temperature. The resulting mixture was analyzed by GC. Decane was used as the internal standard.

Photoirradiation of a 3-Methyl-2-buten-1-ol (1a) and Bis(4-methoxycarbonylphenyl) Disulfide (2b) Mixture. A mixture of 3-methyl-2-buten-1-ol (**1a**) (16 mg, 0.19 mmol) and bis(4-methoxycarbonylphenyl) disulfide (**2b**) (64 mg, 0.19 mmol) in benzene (3.2 mL) was irradiated with a high-pressure mercury lamp for 30 min at room temperature. The resulting mixture was analyzed by GC. Decane was used as the internal standard.

Photoirradiation of a 3-Methyl-2-buten-1-ol (1a) and Bis(4-chlorophenyl) Disulfide (2c) Mixture. A mixture of 3-methyl-2-buten-1-ol (**1a**) (16 mg, 0.19 mmol) and bis(4-chlorophenyl) disulfide (**2c**) (53 mg, 0.19 mmol) in benzene (3.2 mL) was irradiated with a high-pressure mercury lamp for 1 h at room temperature. The resulting mixture was analyzed by GC. Decane was used as the internal standard.

Photoirradiation of a 3-Methyl-2-buten-1-ol (1a) and Bis(2-trifluoromethylphenyl) Disulfide (2d) Mixture. A mixture of 3-methyl-2-buten-1-ol (**1a**) (16 mg, 0.19 mmol) and bis(2-trifluoromethylphenyl) disulfide (**2d**) (67 mg, 0.19 mmol) in benzene (3.2 mL) was irradiated with a high-pressure mercury lamp for

30 min at room temperature. The resulting mixture was analyzed by GC. Decane was used as the internal standard.

Photoirradiation of a 3-Methyl-2-buten-1-ol (1a) and Bis(4-nitrophenyl) Disulfide (2e) Mixture. A mixture of 3-methyl-2-buten-1-ol (**1a**) (15 mg, 0.18 mmol) and bis(4-nitrophenyl) disulfide (**2e**) (56 mg, 0.18 mmol) in chloroform (3.0 mL) was irradiated with a high-pressure mercury lamp for 1 h at room temperature. The resulting mixture was analyzed by GC. Decane was used as the internal standard.

Photoirradiation of a 3-Methyl-2-buten-1-ol (1a) and Bis(4-methoxyphenyl) Disulfide (2f) Mixture. A mixture of 3-methyl-2-buten-1-ol (**1a**) (16 mg, 0.19 mmol) and bis(4-methoxyphenyl) disulfide (**2f**) (53 mg, 0.19 mmol) in benzene (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. Decane was used as the internal standard.

Photoirradiation of a 3-Methyl-2-buten-1-ol (1a) and Dendrimer Disulfide 4 Mixture. A mixture of 3-methyl-2-buten-1-ol (**1a**) (15 mg, 0.18 mmol) and dendrimer **4** (13 mg, 0.18 mmol) in benzene (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. Decane was used as the internal standard.

Photoirradiation of a 3-Methyl-2-buten-1-ol (1a) and Dendrimer Disulfide 5 Mixture. A mixture of 3-methyl-2-buten-1-ol (**1a**) (15 mg, 0.18 mmol) and dendrimer **5** (22 mg, 0.18 mmol) in benzene (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. Decane was used as the internal standard.

Photoirradiation of an Allyl Alcohol (1b) and Bis(4-methoxycarbonylphenyl) Disulfide (2b) Mixture. A mixture of allyl alcohol (**1b**) (3.4 mg, 0.059 mmol) and bis(4-methoxycarbonylphenyl) disulfide (**2b**) (20 mg, 0.059 mmol) in $CDCl_3$ (1.0 mL) was irradiated with a high-pressure mercury lamp for 30 min at room temperature. The resulting mixture was analyzed by NMR. *t*-Butyl acetate was used as the internal standard.

Photoirradiation of a (*Z*)-3-Chloro-2-propen-1-ol (1c) and Bis(4-methoxycarbonylphenyl) Disulfide (2b) Mixture. (*Z*)-3-Chloro-2-propen-1-ol (**1c**) was prepared using a method reported by Alami et al.[16] A mixture of (*Z*)-3-chloro-2-propen-1-ol (**1c**) (18 mg, 0.19 mmol) and bis(4-methoxycarbonylphenyl) disulfide (**2b**) (64 mg, 0.19 mmol) in $CDCl_3$ (3.2 mL) was irradiated with a high-pressure mercury lamp for 2 h at room temperature. The resulting mixture was analyzed by NMR. *t*-Butyl acetate was used as the internal standard.

Photoirradiation of a 4-Methyl-3-penten-2-ol (1d) and Bis-(4-methoxycarbonylphenyl) Disulfide (2b) Mixture. 4-Methyl-3-penten-2-ol (**1d**) was prepared using a method reported by Cain.[17] A mixture of 4-methyl-3-penten-2-ol (**1d**) (19 mg, 0.19 mmol) and bis(4-methoxycarbonylphenyl) disulfide (**2b**) (64 mg, 0.19 mmol) in benzene (3.2 mL) was irradiated with a high-pressure mercury lamp for 30 min at room temperature. The resulting mixture was analyzed by GC. Decane was used as the internal standard.

Photoirradiation of a 2,4-Dimethyl-3-penten-2-ol (1e) and Bis(4-methoxycarbonylphenyl) Disulfide (2b) Mixture. A mixture of 2,4-dimethyl-3-penten-2-ol (**1e**) (22 mg, 0.19 mmol) and bis(4-methoxycarbonylphenyl) disulfide (**2b**) (64 mg, 0.19 mmol) in benzene (3.2 mL) was irradiated with a high-pressure mercury lamp for 20 min at room temperature. The resulting mixture was analyzed by GC. Decane was used as the internal standard.

Photoirradiation of a Cinnamyl Alcohol (11) and Diphenyl Disulfide (2a) Mixture. A mixture of cinnamyl alcohol (**11**) (25 mg, 0.19 mmol) and diphenyl disulfide (**2a**) (41 mg, 0.19 mmol) in benzene (3.2 mL) was irradiated with a high-pressure mercury lamp for 70 min at room temperature. After removal of the solvent, the resulting mixture was purified by silica-gel column chromatography (eluent, chloroform/hexane = 2/1) to afford cinnamaldehyde (**12**) (5.8 mg, 0.044 mmol) in 44% yield (based on consumed starting material).

Photoirradiation of a Cinnamyl Alcohol (11) and Dendrimer Disulfide 4 Mixture. A mixture of cinnamyl alcohol (**11**) (17 mg, 0.13 mmol) and dendrimer **4** (160 mg, 0.13 mmol) in benzene (2.2 mL) was irradiated with a high-pressure mercury lamp for 2.5 h at room temperature. After removal of the solvent, the resulting mixture was purified by silica-gel column chromatography (eluent, chloroform) to afford cinnamaldehyde (**12**) (7.3 mg, 0.055 mmol) in 58% yield (based on consuming starting material).

Photoirradiation of a Cinnamyl Alcohol (11) and Dendrimer Disulfide 5 Mixture. A mixture of cinnamyl alcohol (**11**) (21 mg, 0.16 mmol) and dendrimer **5** (120 mg, 0.16 mmol) in benzene (2.7 mL) was irradiated with a high-pressure mercury lamp for 2.5 h at room temperature. After removal of the solvent, the resulting mixture was purified using silica-gel column chromatography (eluent, chloroform) to afford cinnamaldehyde (**12**) (3.3 mg, 0.025 mmol) in 46% yield (based on consumed starting material).

Photoirradiation of a Geraniol (13) and Dendrimer Disulfide 5 Mixture. A mixture of geraniol (**13**) (22 mg, 0.14 mmol) and dendrimer **5** (170 mg, 0.14 mmol) in benzene (2.4 mL) was irradiated with a high-pressure mercury lamp for 2.5 h at room temperature. After removal of the solvent, the resulting mixture was purified by silica-gel column chromatography (eluent, chloroform) to afford citral (**14**) (3.4 mg, 0.022 mmol) and citronellal (**15**) (5.0 mg, 0.032 mmol) in 38% and 54% yield, respectively (based on consumed starting material).

Photoreaction of (*E*)-Citral (16) with Dendron Thiol 17. (*E*)-Citral (**16**) was prepared by oxidation of geraniol (**13**) using MnO_2. A mixture of (*E*)-citral (**16**) (66 mg, 0.43 mmol) and dendron thiol **17** (312 mg, 0.85 mmol) in benzene (7.1 mL) was irradiated with a high-pressure mercury lamp for 12 h at room temperature. After removal of the solvent, the resulting mixture was purified by silica-gel column chromatography (eluent, chloroform) to afford citronellal (**15**) (5.5 mg, 0.036 mmol) in 8% yield.

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Supporting Information

Copies of NMR spectra. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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