A Novel Photoinduced Thioselenation of Allenes by Use of a Disulfide−Diselenide Binary System

Akiya Ogawa,*,† Ryoichi Obayashi,† Mikio Doi,† Noboru Sonoda,*,‡ and Toshikazu Hirao*,†

*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita,
Osaka 565, Japan, and Department of Applied Chemistry, Faculty of Engineering, Kansai University,
Suita, Osaka 564, Japan*

Dependent on the selection of the lights employed, the relative reactivities of organic dichalcogenides toward carbon radicals, and the thermodynamical stability of products, it has become apparent that two different chalcogeno groups can be introduced simultaneously into allenes with excellent selectivity. The $(PhS)_2$−$(PhSe)_2$ binary system is effective for the regioselective thioselenation of allenes, affording β-selenoallylic sulfides in good yields. Further investigation on the reaction of allenes with $(PhS)_2$ and $(PhTe)_2$ afforded no thiotelluration products, unfortunately, due to the instability of C−Te bonds under photoirradiated conditions. However, a novel telluride-catalyzed dithiolation reaction of allenes with disulfides has been developed successfully, while the use of a disulfide single system could not effect the radical dithiolation of allenes.

Introduction

The absorption maximum of organic dichalcogenides such as diphenyl disulfides, diselenides, and ditellurides lies in the ultraviolet, near-UV, and visible regions, respectively (Figure 1). Accordingly, upon irradiation with the corresponding lights, homolysis of dichalcogenides takes place to generate the chalcogen-centered radicals as labile species (eq 1).[1] Compared to oxygen-

$$RY\!-\!YR \xrightarrow[\text{Y = S, Se, Te}]{h\nu} 2\,RY\bullet \qquad (1)$$
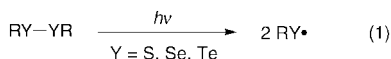
centered radicals, chalcogen-centered radicals such as PhS•, PhSe•, and PhTe• are generally less reactive, and the relative reactivities between the chalcogen-centered radicals decrease with increasing molecular weight (PhS• > PhSe• > PhTe•).[2]

In general, organic dichalcogenides cannot add to alkenes under radical conditions for the following reasons.[3] In the case of diselenides and ditellurides, seleno and telluro radicals can add to carbon−carbon unsaturated bonds, but the β-elimination reaction from the
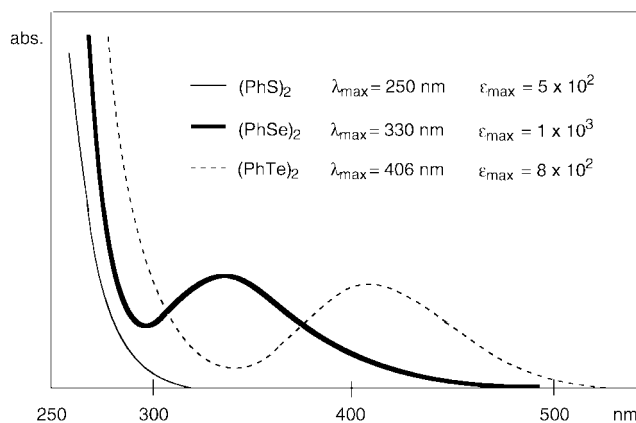

Figure 1. UV−vis spectra of $(PhS)_2$, $(PhSe)_2$, and $(PhTe)_2$.

resulting β-seleno and β-telluro carbon radicals is too rapid to allow trapping of them in most cases. The addition of PhY• (Y = S, Se, Te) to an alkene is reversible and the rate constant for elimination follows the sequence of Te > Se > S. This probably contributes to the inefficiency of the desired addition reactions of diselenides and ditellurides. In the case of disulfides, the capturing ability of organic disulfides toward carbon radicals is much lower than those of selenides and tellurides, so the polymerization reactions proceed preferentially.[4] Herein we report a novel radical addition reaction of organic dichalcogenides to allenes.

Results and Discussion

Photoinduced Addition to Allenes by Using Organic Dichalcogenide Single Systems. Upon irradiation with a tungsten lamp through Pyrex ($h\nu$ > 300 nm),

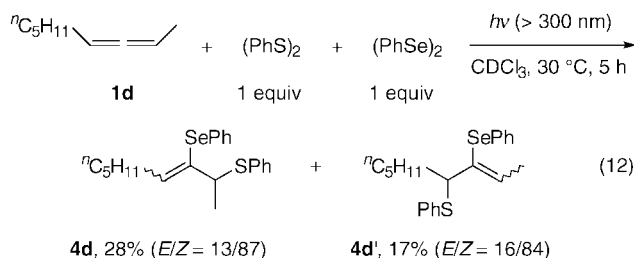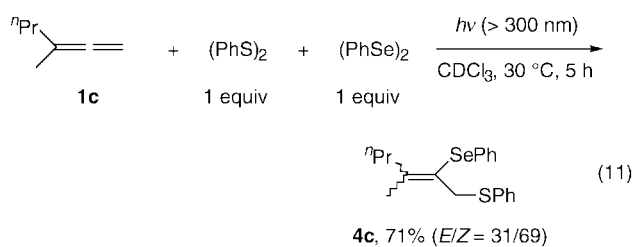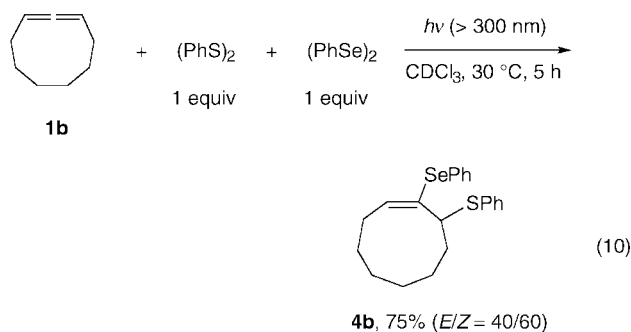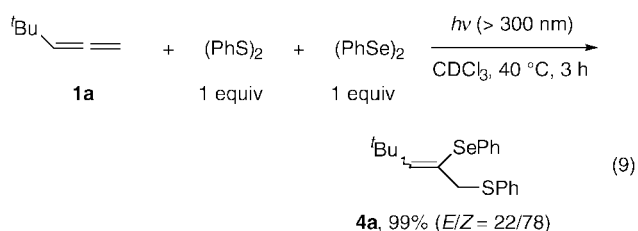† Osaka University.
‡ Kansai University.
(1) Schmidt, U.; Müller, A.; Markau, K. *Chem. Ber.* **1964**, *97*, 405.
(2) In the case of styrene, for example, the addition rate constants of PhS• and PhSe• are 2.0×10^7 and 2.2×10^6 M^{-1} s^{-1}, respectively. See: (a) Ito, O. *J. Am. Chem. Soc.* **1983**, *105*, 850. (b) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1979**, *101*, 1815. (c) Ito, O.; Matsuda, M. *J. Org. Chem.* **1984**, *49*, 17. (d) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1981**, *103*, 5871. (e) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1979**, *101*, 5732. (f) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1982**, *104*, 1701. (g) McPhee, D. J.; Campredon, M.; Lesage, M.; Griller, D. *J. Am. Chem. Soc.* **1989**, *111*, 7563.
(3) Organic dichalcogenides can add to acetylenes under radical conditions, providing vicinal dichalcogenoalkenes in good yields. For the addition of (RS)₂, see: (a) Heiba, E. I.; Dessau, R. M. *J. Org. Chem.* **1967**, *32*, 3837. For the addition of (RSe)₂, see: (b) Back, T. G.; Krishna, M. V. *J. Org. Chem.* **1988**, *53*, 2533. (c) Ogawa, A.; Yokoyama, H.; Yokoyama, K.; Masawaki, T.; Kambe, N.; Sonoda, N. *J. Org. Chem.* **1991**, *56*, 5721. (d) Ogawa, A.; Takami, N.; Sekiguchi, M.; Yokoyama, H.; Kuniyasu, H.; Ryu, I.; Sonoda, N. *Chem. Lett.* **1991**, 2241. For the addition of (RTe)₂, see: (e) Ogawa, A.; Yokoyama, K.; Yokoyama, H.; Obayashi, R.; Kambe, N.; Sonoda, N. *J. Chem. Soc., Chem. Commun.* **1991**, 1748. (f) Ogawa, A.; Yokoyama, K.; Obayashi, R.; Han, L.-B.; Kambe, N.; Sonoda, N. *Tetrahedron* **1993**, *49*, 1177.
(4) The rate constants for the S$_H$2 reaction of 5-hexenyl radical with (PhS)₂ and (PhSe)₂ are 7.6×10^4 and 1.2×10^7 M^{-1} s^{-1}, respectively. See: (a) Russell, G. A.; Tashtoush, H. *J. Am. Chem. Soc.* **1983**, *105*, 1398. (b) Perkins, M. J.; Turner, E. S. *J. Chem. Soc., Chem. Commun.* **1981**, 139. (c) Russell, G. A.; Ngoviwatchai, P.; Tashtoush, H. I.; Pla-Dalmau, A.; Khanna, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 3530.

the reaction of *tert*-butylallene (**1a**) with diphenyl disulfide was conducted at room temperature for 24 h, which afforded a complex mixture (eq 2). This is most probably due to the lower capturing ability of (PhS)$_2$ toward carbon radicals, which might permit the oligomerization of allenes.

$$^{t}Bu{=}{=} \;+\; (PhS)_2 \xrightarrow[\text{CDCl}_3,\ 15\ ^{\circ}C,\ 24\ h]{h\nu\ (>300\ nm)} \text{a complex mixture} \quad (2)$$

1a　　1 equiv

$$^{t}Bu{=}{=} \;+\; (PhSe)_2 \xrightarrow[\text{CDCl}_3,\ 15\ ^{\circ}C,\ 1\ h]{h\nu\ (>300\ nm)} {}^{t}Bu{-}\text{CH}{=}\text{C(SePh)CH}_2\text{SePh} \quad (3)$$

1a　　1 equiv　　　　　　　　　　　　　　　　**2a**, 82% ($E/Z = 28/72$)

$$^{t}Bu{=}{=} \;+\; (PhTe)_2 \xrightarrow[\text{CDCl}_3,\ 15\ ^{\circ}C,\ 1\ h]{h\nu\ (>300\ nm)} \text{no reaction} \quad (4)$$

1a　　1 equiv

In contrast, we have recently found that the photoinduced radical addition of diphenyl diselenide to allenes proceeds very smoothly, giving the corresponding β-selenoallylic selenides in high yields, as exemplified in eq 3.[5,6] Compared to (PhS)$_2$, (PhSe)$_2$ exhibits excellent carbon radical capturing ability [$k_{(PhSe)_2}/k_{(PhS)_2}$ = ca. 160],[4] which completely inhibits the oligomerization of allenes. On the other hand, diphenyl ditelluride did not add to allenes at all, as can be seen from eq 4.

Consideration of the radical addition reactions of PhYH (Y = S, Se, and Te) to allenes helps in understanding which carbons of allenes should be attacked by PhY$^{\bullet}$ (Y = S, Se, and Te). Pasto et al. reported the UV-irradiated addition of benzenethiol to *tert*-butylallene (**1a**), as shown in eq 5.[7] The result indicates that PhS$^{\bullet}$ attacks at both inner and terminal carbons of **1a** in the ratio of 75:25, respectively. On the other hand, we have recently revealed that PhSeH adds to **1a**, giving only vinylic selenides (eq 6).[8] This indicates that PhSe$^{\bullet}$ attacks only at the inner carbon of **1a**. Compared to PhSH and PhSeH, benzenetellurol is very unstable, especially under photoirradiation conditions; therefore, we examined the photoirradiated reaction of (PhTe)$_2$ with *tert*-butylallene (**1a**) in the presence of benzeneselenol, in place of the photoinduced reaction of PhTeH with **1a**. Since PhSeH has no absorption in the region of wavelength over 500 nm, irradiation with the light of wavelength over 500 nm induces homolysis of (PhTe)$_2$ selectively. As can be seen from eq 7, the addition of PhTe$^{\bullet}$ to **1a** proceeded selectively only at the inner carbon of **1a**, as well as in the case of PhSe$^{\bullet}$.

From the results of the addition of PhYH (Y = S, Se, and Te), the radical addition of (PhSe)$_2$ to allenes includes the addition of PhSe$^{\bullet}$ to the inner carbon of allenes and

(5) Ogawa, A.; Yokoyama, K.; Yokoyama, H.; Sekiguchi, M.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1990**, *31*, 5931.

(6) Similar conditions can be employed with a variety of allenes such as aromatic allenes, cyclic allenes, and internal allenes. For example, nona-1,2-diene (**1b**) provided 2,3-bis(phenylseleno)non-1-ene (**2b**) in almost quantitative yield ($E/Z = 91/9$).

(7) (a) Pasto, D. J.; Warren, S. E.; Morrison, M. A. *J. Org. Chem.* **1981**, *46*, 2837. See also: (b) Pasto, D. J.; L'Hermine, G. *J. Org. Chem.* **1990**, *55*, 685. (c) Griesbaum, K.; Oswald, A. A.; Quiram, E. R.; Naegele, W. *J. Org. Chem.* **1963**, *28*, 1952. (d) Van der Ploeg, H. J.; Knotnerus, J.; Bickel, A. F. *Recl. Trav. Chem. Pays-Bas* **1962**, *81*, 775. (e) Jacobs, T. L.; Illingworth, G. E., Jr. *J. Org. Chem.* **1963**, *28*, 2692.

(8) Masawaki, T.; Ogawa, A.; Kambe, N.; Ryu, I.; Sonoda, N. *Chem. Lett.* **1987**, 2407.

$$^{t}Bu{=}{=} \;+\; PhSH \xrightarrow{UV} {}^{t}Bu\text{-CH}{=}\text{C(SPh)CH}_3 \;+ \quad 37\%$$

$$^{t}Bu\text{C(SPh)}{=}\text{CH}_2 \;+\; {}^{t}Bu\text{-CH}{=}\text{CH-CH}_2\text{SPh} \quad (5)$$
38%　　　　　　25%

$$^{t}Bu{=}{=} \;+\; PhSeH \xrightarrow{h\nu\ (>300\ nm)} {}^{t}Bu\text{-CH}{=}\text{C(SePh)CH}_3 \;+ \quad 70\%$$

1 equiv

$$^{t}Bu\text{C(SePh)}{=}\text{CH}_2 \;+\; {}^{t}Bu\text{-CH}{=}\text{CH-CH}_2\text{SePh} \quad (6)$$
8%　　　　　　0%

$$^{t}Bu{=}{=} \;+\; (PhTe)_2 \;+\; PhSeH \xrightarrow[\text{CDCl}_3,\ 40\ ^{\circ}C,\ 1\ h]{h\nu\ (>500\ nm)}$$

1 equiv　　1 equiv

$$^{t}Bu\text{-CH}{=}\text{C(TePh)CH}_3 \;+\; {}^{t}Bu\text{C(TePh)}{=}\text{CH}_2 \quad (7)$$
34%　　　　　　16%

$$\left(\;+\; \text{adducts of PhSeH} \right)$$

the subsequent S$_H$2 reaction of the formed allylic radical (**3**) with (PhSe)$_2$. On the other hand, the reason that the radical addition of (PhTe)$_2$ to allenes does not proceed at all is most probably due to the instability of the desired allylic tellurides under the present photoirradiation (or radical) conditions.

R-CH$\bullet$-C(SePh)=CH$_2$

3

Photoinduced Addition to Allenes by Using (PhS)$_2$–(PhSe)$_2$ Binary Systems. To construct the radical addition reactions of organic dichalcogenides to carbon–carbon unsaturated compounds, it is important to consider the relative reactivities of dichalcogenides toward carbon radicals as well as those of chalcogen-centered radicals toward unsaturated bonds. Some kinetic data reported in the literature indicate that (PhSe)$_2$ is more reactive toward alkyl radicals, compared to (PhS)$_2$ [$k_{(PhSe)_2}/k_{(PhS)_2}$ = ca. 160].[4] On the other hand, PhS$^{\bullet}$ is relatively reactive toward carbon–carbon double bonds, compared to PhSe$^{\bullet}$ [$k_{PhS^{\bullet}}/k_{PhSe^{\bullet}}$ = 10–50].[2] Thus, if the photoinduced addition to carbon–carbon unsaturated compounds is performed in the presence of both (PhS)$_2$ and (PhSe)$_2$, the selective attack of PhS$^{\bullet}$ to the double bonds and the selective trapping of the thus formed carbon radicals with (PhSe)$_2$ are expected to effect simultaneous introduction of two different chalcogeno groups into the carbon–carbon double bonds. In practice, we have recently developed a novel thioselenation of alkenes with the aid of the (PhS)$_2$–(PhSe)$_2$ binary system, as indicated in eq 8.[9]

$$R\text{-CH}{=}\text{CH}_2 \;+\; (PhS)_2 \;+\; (PhSe)_2 \xrightarrow{h\nu} R\text{-CH(SePh)-CH}_2\text{SPh} \quad (8)$$

Keeping the above kinetic considerations in mind, we examined the radical addition to allenes by using the $(PhS)_2–(PhSe)_2$ binary system. When the reaction of *tert*-butylallene (**1a**) with equimolar amounts of $(PhS)_2$ and $(PhSe)_2$ was conducted at 40 °C for 3 h upon irradiation with a tungsten lamp through Pyrex (>300 nm) (eq 9), the reaction proceeded very smoothly to afford the β-(phenylseleno)allylic sulfide (**4a**) in almost quantitative yield. Similarly, a cyclic allene (**1b**) also underwent thioselenation smoothly, as depicted in eq 10. With a terminal disubstituted allene (**1c**), the thioselenation took place regioselectively (eq 11). In contrast, inner allenes such as **1d** provided a regioisomeric mixture (**4d** and **4d′**) (eq 12). In each reaction, a phenylseleno group was introduced selectively into the central carbon of the allenes.

$$^tBu\diagup\!\!=\!\!=\quad+\quad (PhS)_2\quad+\quad (PhSe)_2\quad\xrightarrow[\text{CDCl}_3,\,40\,°C,\,3\,h]{h\nu\,(>300\,nm)}$$

1a   1 equiv   1 equiv

$$^tBu\diagup\!\!\diagdown\!\!\diagup^{SePh}_{SPh}\qquad (9)$$

4a, 99% (*E/Z* = 22/78)

$$\text{(cyclooctadiene)}\quad+\quad (PhS)_2\quad+\quad (PhSe)_2\quad\xrightarrow[\text{CDCl}_3,\,30\,°C,\,5\,h]{h\nu\,(>300\,nm)}$$

1 equiv   1 equiv

1b

$$\text{(cyclic)}^{SePh}_{SPh}\qquad (10)$$

4b, 75% (*E/Z* = 40/60)

$$^nPr\diagup\!\!=\!\!=\quad+\quad (PhS)_2\quad+\quad (PhSe)_2\quad\xrightarrow[\text{CDCl}_3,\,30\,°C,\,5\,h]{h\nu\,(>300\,nm)}$$

1c   1 equiv   1 equiv

$$^nPr\diagup\!\!\diagdown\!\!\diagup^{SePh}_{SPh}\qquad (11)$$

4c, 71% (*E/Z* = 31/69)

$$^nC_5H_{11}\diagdown\!\!=\!\!=\diagup\quad+\quad (PhS)_2\quad+\quad (PhSe)_2\quad\xrightarrow[\text{CDCl}_3,\,30\,°C,\,5\,h]{h\nu\,(>300\,nm)}$$

1d   1 equiv   1 equiv

$$^nC_5H_{11}\diagup\!\!\diagdown^{SePh}_{SPh}\quad+\quad ^nC_5H_{11}\diagup\!\!\diagdown^{SePh}_{PhS}\qquad (12)$$

4d, 28% (*E/Z* = 13/87)   **4d′**, 17% (*E/Z* = 16/84)

To gain insight into the mechanism of the present thioselenation of allenes, the reaction of *tert*-butylallene (**1a**) with $(PhS)_2$ and $(PhSe)_2$ was followed by the measurement of ^{1}H NMR spectra (Figure 2). Contrary to our

(9) (a) Ogawa, A.; Tanaka, H.; Yokoyama, H.; Obayashi, R.; Yokoyama, K.; Sonoda, N. *J. Org. Chem.* **1992**, *57*, 111. (b) Ogawa, A.; Sonoda, N. *Phosphorus, Sulfur, Silicon* **1994**, *95–96*, 331. (c) Ogawa, A.; Obayashi, R.; Ine, H.; Tsuboi, Y.; Sonoda, N.; Hirao, T. *J. Org. Chem.* **1998**, *63*, 881.
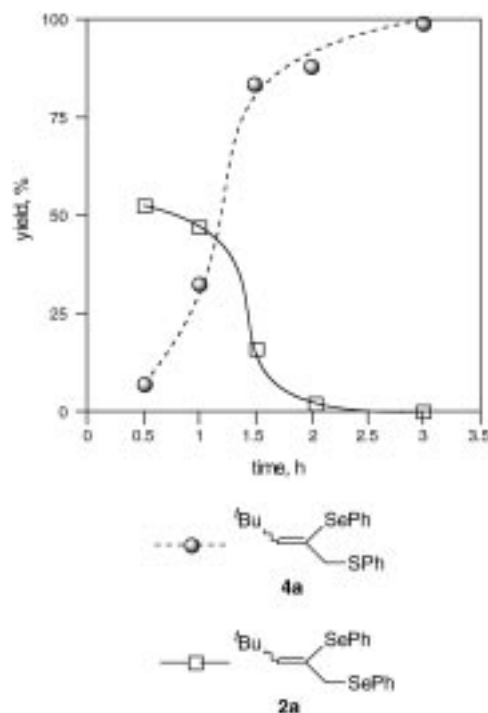
Figure 2. Plots of the yields of **2a** and **4a** against time.

Scheme 1. A Possible Reaction Path for the Thioselenation of Allenes
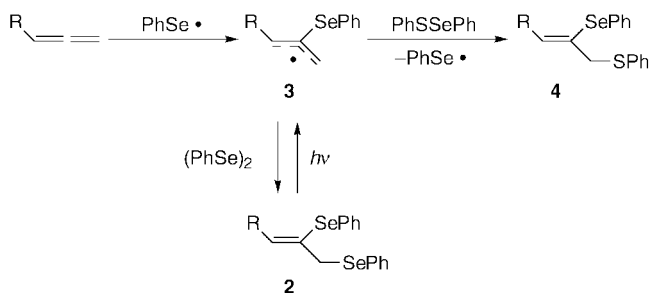
prediction that PhS• preferentially attacks at the allene, the results clearly indicates the initial formation of the $(PhSe)_2$ adduct (**2a**) via the exclusive addition of PhSe• to the allene. Then, the $(PhSe)_2$ adduct (**2a**) was converted into the thioselenation product (**4a**) via the selective displacement of the terminal phenylseleno group of **2a** with a phenylthio group under photoirradiation conditions. Indeed, the isolated $(PhSe)_2$ adduct (**2a**) was converted into the corresponding thioselenation product (**4a**) upon treatment with $(PhS)_2$ under the photoirradiation conditions.

Accordingly, the $(PhSe)_2$ adduct (**2**) is a kinetic product, whereas the thioselenation product (**4**) is a thermodynamic one, as indicated in Scheme 1. These results can be accounted for as follows: (i) As can be seen from Figure 1, the irradiation through Pyrex with a tungsten lamp ($h\nu$ > 300 nm) causes the homolysis of $(PhSe)_2$ preferentially, generating PhSe•. (ii) Although PhSe• may attack at $(PhS)_2$ to form PhS• and PhSSePh, the addition of PhSe• to **1a** proceeds faster, giving the allylic radical (**3a**). (iii) Since allylic selenide (**2a**) is in equilibrium with allylic radical (**3**) under photoirradiation conditions, **2a** converts into the thermodynamically more stable **4a** with the lapse of time.

Next, we attempted the thiotelluration of allenes by using a $(PhS)_2–(PhTe)_2$ binary system, because $(PhTe)_2$

Scheme 2. A Catalytic Cycle for the Dithiolation of *tert*-Butylallene
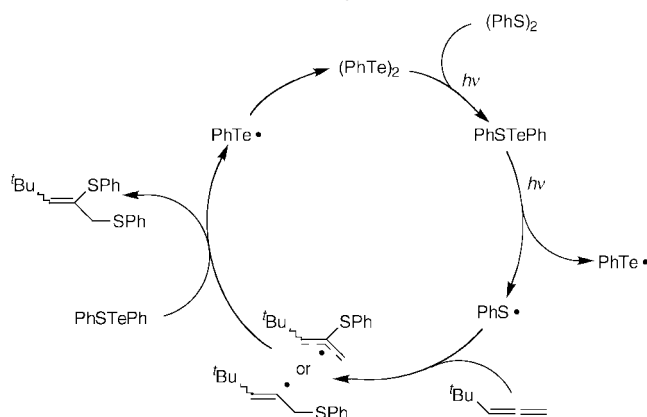
has higher capturing ability toward carbon radicals, compared to $(PhSe)_2$ $[k_{(PhTe)_2}/k_{(PhSe)_2} = $ ca. 4].[4] When a mixture of *tert*-butylallene (**1a**), $(PhS)_2$, and $(PhTe)_2$ was irradiated through filters with a tungsten lamp ($h\nu > 400$ nm) at 40 °C for 20 h, the desired thiotelluration product was not formed at all, but surprisingly, the $(PhS)_2$ adduct (**5a**) was obtained in moderate yield, as indicated in eq 13.

5a, 50% (*E*/*Z* = 24/76)
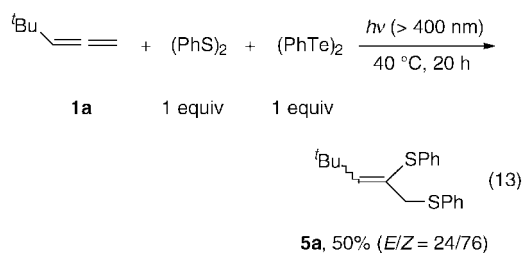
Since the photoinitiated reaction of allenes with $(PhS)_2$ gave rise to a complex mixture as mentioned above, it seems likely that diphenyl ditelluride inhibits the oligomerization of allenes. Thus, a catalytic dithiolation of allenes with $(PhS)_2$ was demonstrated in the presence of a small amount of $(PhTe)_2$ (30 mol %). The reaction successfully afforded the $(PhS)_2$ adduct (**5a**) in good yield with excellent regioselectivity (eq 14).

5a, 62% (*E*/*Z* = 14/86)
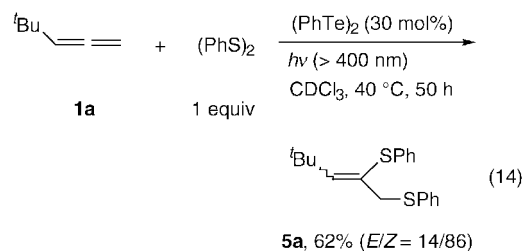
Scheme 2 indicates a possible reaction path, which includes the following: (i) the photoinduced comproportionation of $(PhTe)_2$ and $(PhS)_2$ to give PhSTePh; (ii) the generation of PhS• by the photolysis of PhSTePh; (iii) the formation of allylic and vinylic radical intermediates by the attack of PhS• at the internal and terminal carbons of *tert*-butylallene, respectively; (iv) the S_H2 reaction of the radical intermediates with PhSTePh, affording the $(PhS)_2$ adduct.

In conclusion, a highly selective and efficient introduction of two different chalcogen functions, i.e., PhS and PhSe groups, into allenes has been accomplished by using

a $(PhS)_2$–$(PhSe)_2$ binary system. Furthermore, a novel dithiolation of allenes, which could not proceed by the radical reaction of $(PhS)_2$ alone, has been achieved in the presence of a catalytic amount of $(PhTe)_2$. We believe that the procedure described here is synthetically promising for producing a variety of allylic and vinylic chalcogen intermediates conveniently.

Experimental Section

General Comments. Diphenyl disulfide was obtained commercially and was purified by recrystallization from EtOH. Diphenyl diselenide[11] and diphenyl ditelluride[12] were prepared according to the literature and recrystallized from hexane. Allenes[13] were synthesized according to the literature and purified by distillation.

^{1}H NMR spectra of CDCl$_3$ solutions were recorded with JEOL JNM-GSX-270 (270 MHz) and Varian Mercury 300 (300 MHz) spectrometers. Me$_4$Si served as the internal standard. ^{13}C NMR spectra of CDCl$_3$ solutions were recorded with JEOL JNM-GSX-270 (68 MHz) and Varian Mercury 300 (75 MHz) spectrometers. Chemical shifts in the ^{13}C NMR spectra were determined relative to CDCl$_3$ but are reported in ppm downfield from Me$_4$Si (δ(CDCl$_3$) = 76.9 ppm). IR spectra were recorded with a Perkin-Elmer Model 1600 spectrometer. Mass spectra were recorded with a JEOL JMS-DX303. Elemental analyses were performed in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University.

Representative Procedure for the Regioselective Thioselenation of Allenes: 1-(Phenylthio)-2-(phenylseleno)-4,4-dimethyl-2-pentene (4a). In a Pyrex glass tube were placed *tert*-butylallene (**1a**, 0.25 mmol), diphenyl disulfide (0.25 mmol), diphenyl diselenide (0.25 mmol), and CDCl$_3$ (0.25 mL). The tube was filled with Ar, and the mixture was irradiated at 40 °C for 3 h with a tungsten lamp (500 W). The solvent was evaporated in vacuo, and the residue was purified by preparative TLC on silica gel (hexane) to provide 90 mg (99%, *E*/*Z* = 28/78) of 1-(phenylthio)-2-(phenylseleno)-4,4-dimethyl-2-pentene (**4a**): a yellow oil; ^{1}H NMR (270 MHz, CDCl$_3$) [*E*-isomer] δ 1.13 (s, 9 H), 3.92 (s, 2 H), 6.15 (s, 1 H), 7.22−7.33 (m, 8 H), 7.47−7.48 (m, 2 H); [*Z*-isomer] δ 1.14 (s, 9 H), 3.52 (s, 2 H), 5.96 (s, 1 H), 7.22−7.33 (m, 8 H), 7.47−7.48 (m, 2 H); NOE experiment; irradiation of the allyl singlet at δ 3.52 resulted in a 17% enhancement of the signal at δ 5.96 (vinyl singlet); ^{13}C NMR (68 MHz, CDCl$_3$) [*E*-isomer] δ 30.74, 35.59, 38.87, 126.18, 126.62, 127.08, 128.78, 129.13, 130.77, 132.68, 133.85, 136.37, 151.40; [*Z*-isomer] δ 30.49, 33.62, 45.16, 124.69, 126.78, 127.21, 128.62, 129.17, 129.72 131.90, 133.20, 135.34, 147.25; IR (NaCl) 3057, 2958, 2902, 2864, 1578, 1475, 1438, 1361, 1228, 1206, 1066, 1023, 958, 737, 691, 669 cm^{-1}; MS (EI), *m*/*z* = 362 (M$^+$, 26). Anal. Calcd for C$_{19}$H$_{22}$SSe: C, 63.14; H, 6.14. Found: C, 63.49; H, 6.27.

2-(Phenylseleno)-3-(phenylthio)cyclononene (4b). The reaction of cyclonona-1,2-diene (**1b**, 0.25 mmol) with diphenyl disulfide (0.25 mmol) and diphenyl diselenide (0.25 mmol) in CDCl$_3$ (0.5 mL) was performed by irradiation at 30 °C for 5 h with a tungsten lamp (500 W) through Pyrex. The residual mixture was purified by flash chromatography on silica gel using pentane and then diethyl ether as eluents to provide 73 mg (75%, *E*/*Z* = 40/60) of 3-(phenylthio)-2-(phenylseleno)cyclononene (**4b**) as a mixture of *E*- and *Z*-isomers. Owing to the similar polarities of (*E*)-**4b** and (*Z*)-**4b**, the isolation of each isomers did not meet success, and so the following spectral and analytical data were obtained using the *E*,*Z*-mixture: mp 84−85 °C (a light yellow crystal); ^{1}H NMR (270 MHz, CDCl$_3$)

(10) For the diselenide-catalyzed dithiolation of 1,3-dienes with $(PhS)_2$, see: Ogawa, A.; Obayashi, R.; Sonoda, N.; Hirao, T. *Tetrahedron Lett.* **1998**, *39*, 1577.

(11) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.

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[*E*-isomer] δ 1.12 (m, 2 H), 1.47 (m, 6 H), 1.60 (m, 2 H), 2.08 (m, 2 H), 4.53 (dd, J = 3.9, 11.2 Hz, 1 H), 5.56 (t, J = 8.8 Hz, 1 H), 7.13−7.28 (m, 4 H), 7.56−7.62 (m, 4 H), 7.39−7.42 (d like, 2 H); [*Z*-isomer] δ 1.12 (m, 2 H), 1.47 (m, 6 H), 1.60 (m, 2 H), 2.08 (m, 2 H), 4.53 (dd, J = 3.9, 11.2 Hz, 1 H), 5.65 (t, J = 8.8 Hz, 1 H), 7.13−7.28 (m, 6 H), 7.56−7.62 (m, 4 H); ^{13}C NMR (68 MHz, CDCl$_3$) [*E*-isomer] δ 23.73, 26.03, 26.13, 27.45, 28.93, 32.96, 50.37, 126.55, 127.87, 128.69, 129.09, 130.67, 130.70, 133.20, 136.01; [*Z*-isomer] δ 25.11, 25.97, 26.24, 27.65, 29.01, 33.80, 47.50, 127.33, 127.82, 128.85, 129.09, 130.46, 130.50, 134.02, 135.64; IR (KBr) 3052, 2914, 2852, 1578, 1479, 1437, 1020, 738, 689 cm^{-1}; MS (EI), m/z = 388 (M$^+$, 11); exact mass (M$^+$) calcd for C$_{21}$H$_{24}$SSe 388.0764, found 388.0772.

3-Methyl-2-(phenylseleno)-1-(phenylthio)-2-hexene (4c). The reaction of 3-methyl-1,2-hexadiene (**1c**, 0.25 mmol) with diphenyl disulfide (0.25 mmol) and diphenyl diselenide (0.25 mmol) in CDCl$_3$ (0.5 mL) was performed by irradiation at 30 °C for 5 h with a tungsten lamp (500 W) through Pyrex. The residual mixture was purified by HPLC (CHCl$_3$ as an eluent) to provide 63 mg (71%, *E*/*Z* = 31/69) of 3-methyl-2-(phenylseleno)-1-(phenylthio)-2-hexene (**4c**) as a mixture of *E*- and *Z*-isomers. Owing to the similar polarities of (*E*)-**4c** and (*Z*)-**4c**, the isolation of each isomer did not meet success, and so the following spectral and analytical data were obtained using the *E*,*Z*-mixture: a pale yellow oil; ^{1}H NMR (300 MHz, CDCl$_3$) [*E*-isomer] δ 0.90 (t, J = 7.3 Hz, 3 H), 1.40 (sextet, J = 7.6 Hz, 2 H), 1.98 (s, 3 H), 2.12 (t, J = 7.3 Hz, 2 H), 3.93 (s, 2 H), 7.13−7.28 (m, 4 H), 7.05−7.60 (m, 10 H); [*Z*-isomer] δ 0.89 (t, J = 7.3 Hz, 3 H), 1.37 (sextet, J = 7.6 Hz, 2 H), 1.72 (s, 3 H), 2.40 (t, J = 7.6 Hz, 2 H), 3.87 (s, 2 H), 7.19−7.32 (m, 4 H), 7.40 (d, J = 6.3 Hz, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$) [*E*-isomer] δ 14.19, 21.82, 23.57, 36.65, 41.40, 121.13, 126.28, 126.33, 128.53, 128.96, 131.17, 131.34, 135.98, 147.15; [*Z*-isomer] δ 14.07, 18.77, 21.76, 40.56, 41.40, 121.13, 126.44, 126.51, 128.53, 128.96, 130.53, 131.25, 131.63, 147.03; IR (NaCl) 3139, 3059, 2959, 2930, 2868, 1579, 1474, 1438, 1376, 1212, 1090, 1068, 1023, 911, 737, 692 cm^{-1}; MS (EI), m/z = 362 (M$^+$, 17); exact mass (M$^+$) calcd for C$_{19}$H$_{22}$SSe 362.0607, found 362.0622.

4-(Phenylthio)-3-(phenylseleno)-2-nonene (4d′) and 2-(Phenylthio)-3-(phenylseleno)-3-nonene (4d). The reaction of 2,3-nonadiene (**1d**, 0.25 mmol) with diphenyl disulfide (0.25 mmol) and diphenyl diselenide (0.25 mmol) in CDCl$_3$ (0.5 mL) was performed by irradiation at 30 °C for 5 h with a tungsten lamp (500 W) through Pyrex. The residual mixture was purified by HPLC (CHCl$_3$ as an eluent) to provide 43 mg (28%) of **4d** (*E*/*Z* = 13/87) and 17% of **4d′** (*E*/*Z* = 16/84) as a mixture of **4d** and **4d′** (a pale yellow oil). Further purification by preparative TLC (silica gel) provided a mixture of *Z*-**4d** and *Z*-**4d′**: ^{1}H NMR (270 MHz, CDCl$_3$) [*Z*-**4d**] δ 0.82 (t, 3 H, J =

6.8 Hz), 1.08−1.41 (m, 6 H), 1.47 (d, 3 H, J = 6.8 Hz), 2.13 (q, 2 H, J = 7.6 Hz), 3.91 (q, 1 H, J = 6.8 Hz), 5.96 (t, 1 H, J = 6.4 Hz), 7.16−7.34 (m, 10 H); [*Z*-**4d′**] δ 0.84 (t, 3 H, J = 6.8 Hz), 1.08−1.41 (m, 6 H), 1.71 (d, 3 H, J = 6.4 Hz), 1.84 (q, 2 H, J = 7.5 Hz), 3.76 (t, 1 H, J = 7.1 Hz), 5.97 (q, 1 H, J = 6.3 Hz), 7.16−7.34 (m, 10 H); ^{13}C NMR (75 MHz, CDCl$_3$) [*Z*-**4d**] δ 14.05, 20.99, 22.51, 28.53, 31.28, 31.84, 53.00, 126.07, 127.12, 128.48, 128.88, 130.75, 131.32, 132.93, 133.40, 133.99, 134.59, 138.65; [*Z*-**4d′**] δ 14.10, 17.80, 22.55, 27.12, 31.51, 34.22, 58.93, 126.07, 126.88, 128.44, 128.82, 130.83, 130.92, 132.56, 133.19, 133.33, 133.89, 134.91; IR (NaCl) 3149, 3054, 2938, 2858, 1579, 1470, 1371, 1202, 1070, 1020, 909, 837, 738, 693 cm^{-1}; MS (EI), m/z = 390 (M$^+$, 43); exact mass (M$^+$) calcd for C$_{21}$H$_{24}$SSe 390.0920, found 388.0772.

Ditelluride-Catalyzed Dithiolation of Allenes: 1,2-Bis(phenylthio)-4,4-dimethyl-2-pentene (5a). In a Pyrex glass tube were placed *tert*-butylallene (**1a**, 0.25 mmol), diphenyl disulfide (0.3 mmol), diphenyl ditelluride (0.08 mmol), and CDCl$_3$ (0.5 mL). The tube was filled with Ar, and the mixture was irradiated at 40 °C for 50 h through a filter (>400 nm) with a tungsten lamp (500 W). The solvent was evaporated in vacuo. Purification by flash chromatography on silica gel using hexane and then diethyl ether as eluents yielded 49 mg (62%, *E*/*Z* = 14/86) of 1,2-bis(phenylthio)-4,4-dimethyl-2-pentene (**5a**): a yellow oil; ^{1}H NMR (270 MHz, CDCl$_3$) [*E*-isomer] δ 1.16 (s, 9 H), 3.80 (s, 2 H), 6.13 (s, 1 H), 7.16−7.33 (m, 10 H); [*Z*-isomer] δ 1.13 (s, 9 H), 3.47 (s, 2 H), 5.87 (s, 1 H), 7.18−7.35 (m, 10 H); NOE experiment; irradiation of the allyl singlet at δ 3.47 resulted in a 18.4% enhancement of the signal at δ 5.87 (vinyl singlet); ^{13}C NMR (68 MHz, CDCl$_3$) [*E*-isomer] δ 30.73, 34.84, 36.65, 126.51, 126.54, 128.23, 128.78, 128.98, 129.93, 130.53, 135.57, 136.61, 151.18; [*Z*-isomer] δ 30.39, 33.37, 43.43, 126.40, 126.92, 127.11, 128.58, 128.67, 129.01, 129.34, 130.00, 132.08, 149.15; IR (NaCl) 3057, 2957, 2901, 2864, 1583, 1478, 1438, 1361, 1230, 1207, 1088, 1068, 1025, 962, 740, 691 cm^{-1}; MS (EI), m/z = 314 (M$^+$, 93); exact mass (M$^+$) calcd for C$_{19}$H$_{22}$S$_2$ 314.1163, found 314.1186.