Highly Regioselective Thioselenation of Acetylenes by Using a $(PhS)_2$−$(PhSe)_2$ Binary System

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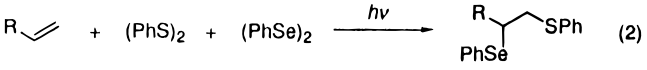
The absorption maximum of organic disulfides and diselenides lies in the ultraviolet and near-UV regions, respectively;[1] therefore, irradiation with the corresponding lights causes homolytic cleavage of the chalcogen−chalcogen bonds to generate the corresponding chalcogen-centered radicals as label species (eq 1).[2] Accordingly, if

$$(PhY)_2 \underset{}{\overset{h\nu}{\rightleftharpoons}} 2\,PhY\bullet \quad (Y = S, Se) \qquad (1)$$

the photolysis of dichalcogenides is performed in the presence of carbon−carbon unsaturated compounds, the formed chalcogen-centered radicals may add to the unsaturated bonds, producing a variety of organic chalcogen compounds conveniently. However, the chalcogen-centered radicals are less reactive compared to oxygen radicals and are liable to reform the starting dichalcogenides, so the radical addition of dichalcogenides to unsaturated bonds is an inefficient reaction. In practice, examples of radical addition of organic disulfides and diselenides to carbon−carbon unsaturated bonds are limited to the addition to acetylenes[3] and allenes,[4] and, heretofore, no report of efficient radical addition to olefins has been made.

However, we have recently disclosed that a binary system of organic dichalcogenides, *i.e.*, a $(PhS)_2$−$(PhSe)_2$ system, successfully effects the desired vicinal dichalcogenation of olefins under radical conditions (eq 2).[5]



(2)

Some kinetic data reported in the literature indicate the relative reactivities between $(PhS)_2$ and $(PhSe)_2$ and between PhS• and PhSe•, *i.e.*, $(PhSe)_2$ is more reactive toward alkyl radicals compared with $(PhS)_2$ [$k_{(PhSe)_2}/k_{(PhS)_2}$ = ca. 160],[6] whereas PhS• is relatively reactive toward carbon−carbon double bonds compared with PhSe• [$k_{PhS\bullet}/k_{PhSe\bullet} = 10-50$].[7] Accordingly, the use of a binary system makes it possible to employ the higher reactivities of both $(PhSe)_2$ and PhS• for the desired radical addition to olefins. Described herein is a highly selective thioselenation of acetylenes by using a $(PhS)_2$−$(PhSe)_2$ binary system.

Radical-addition to acetylenes by using a $(PhS)_2$−$(PhSe)_2$ binary system was conducted as follows: upon irradiation through Pyrex with a tungsten lamp ($h\nu$ > 300 nm), the reaction of phenylacetylene with equimolar amounts of diphenyl disulfide and diphenyl diselenide proceeded very smoothly with excellent regio- and stereoselectivity to give (*E*)-α-(phenylseleno)-*β*-(phenylthio)-styrene (**2a**) in almost quantitative yield (Scheme 1). Formation of the $(PhS)_2$ adduct, the $(PhSe)_2$ adduct, and the regioisomer of the thioselenation products was not detected at all. A similar reaction of terminal alkynes such as 1-octyne also provided the desired thioselenation product in good yield, although the reaction required prolonged irradiation and was accompanied with the formation of the *Z*-isomer and a trace amount of the $(PhS)_2$ adduct (Scheme 2).

The difference in reactivity between phenylacetylene and 1-octyne is most probably due to the difference in stability of vinylic radicals formed as the intermediate. Phenylthio radical (PhS•), which is formed directly by the photolysis of $(PhS)_2$ and/or by the S_H2 reaction of $(PhS)_2$ with PhSe•, attacks at the sterically less hindered terminal position of acetylenes to generate vinylic radicals. In general, vinyl radicals are believed to be a stereoisomeric mixture of *σ*-radicals as shown in Scheme 2, and a fast equilibrium is present between the stereoisomers.[8] Contrary to this, α-aryl-substituted vinylic radicals are assumed to be *π*-radicals and are more stable than alkyl-substituted vinylic *σ*-radicals.[9] Accordingly, the formation of a vinylic *π*-radical from phenylacetylene proceeds more smoothly compared with the case of 1-octyne.

The obtained thioselenation products have their absorption maximum in the near-UV region and, therefore, prolonged irradiation with near-UV causes isomerization between the *E*- and *Z*-isomers. Even in the case of phenylacetylene, indeed, irradiation for a long time led to a decrease of stereoselectivity.

Table 1 represents the thioselenation of various acetylenes by using a $(PhS)_2$−$(PhSe)_2$ binary system. Termi-

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(1) The UV−visible spectra of diphenyl disulfide and diphenyl disulfide are as follows: $(PhS)_2$: λ_{max} = 250 nm, ϵ_{max} = 500; $(PhSe)_2$: λ_{max} = 330 nm, ϵ_{max} = 1000.

(2) Schmidt, U.; Müller, A.; Markau, K. *Chem. Ber.* **1964**, *97*, 405.

(3) For the addition of disulfides to acetylenes, see: (a) Heiba, E. I.; Dessau, R. M. *J. Org. Chem.* **1967**, *32*, 3837. For the addition of diselenides to acetylenes, 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.

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

(5) (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.

(6) The rate constants for the S_H2 reaction of 5-hexenyl radical with $(PhS)_2$ and $(PhSe)_2$ are determined to be 7.6×10^4 M^{-1} s^{-1} 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.

(7) In the case of styrene, for example, the addition rate constants of PhS• and PhSe• are estimated to be 5.1×10^7 M^{-1} s^{-1} 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.

(8) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.

(9) Singer, L. A.; Chen, J. *Tetrahedron Lett.* **1969**, 4849.

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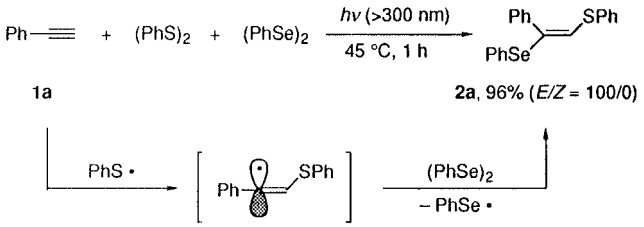
Scheme 1



Scheme 2

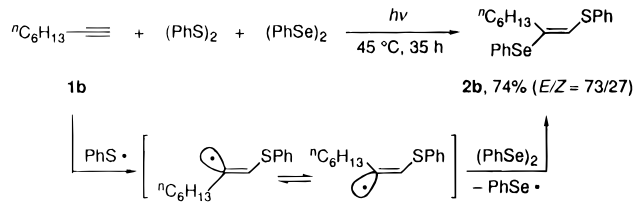


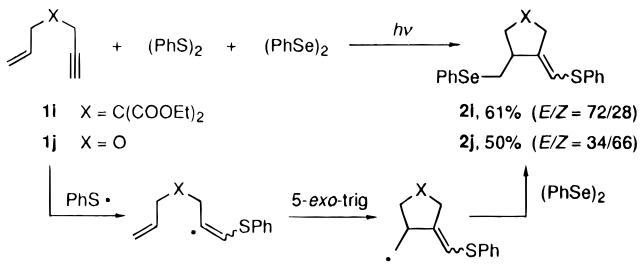
Table 1. Photo-Initiated Thioselenation of Acetylene with $(PhS)_2$–$(PhSe)_2$[a]

Entry	Substrate	Conditions	Product	Yield, %[b] (*E*/*Z*)
1	HO— **1c**	40 °C, 30 h	HO, SPh, PhSe **2c**	74 (60/40)
2	^{t}Bu— **1d**	20 °C, 150 h	^{t}Bu, SPh, PhSe **2d**	31 (58/42)
3	Ph— ^{n}Pr **1e**	40 °C, 30 h	Ph, SPh, PhSe, ^{n}Pr **2e**	87 (86/14)
4	^{n}Pr— ^{n}Pr **1f**	40 °C, 250 h	^{n}Pr, SPh, PhSe, ^{n}Pr **2f**	76 (95/5)
5	**1g**	40 °C, 6 h	SPh, PhSe **2g**	71 (17/83)
6	MeO **1h**	20 °C, 3 h	MeO, SPh, PhSe **2h**	90[c] (30/70)

[a] Reactions were conducted under the conditions of 0.25mmol of acetylene, 0.25 mmol of $(PhS)_2$ and 0.25 mmol of $(PhSe)_2$. *hν*: tungsten lamp (500 W, Pyrex). [b] Isolated yield unless otherwise stated. [c] NMR yield.

nal acetylenes such as propargyl alcohol (**1c**) underwent thioselenation regioselectively (entry 1). The thioselenation of conjugate enynes (**1g** and **1h**) proceeded smoothly without affecting the olefinic units to provide the corresponding 1-(phenylthio)-2-(phenylseleno)alkenes (**2g** and **2h**) in good yields (entries 5 and 6). On the other hand, the thioselenation of *tert*-butylacetylene (**1d**) and 4-octyne (**1f**) required longer reaction time, probably due to the steric hindrance (entries 2 and 4). Interestingly, the thioselenation of 1-phenyl-1-pentyne (**1e**) as an inner acetylene proceeded with excellent regioselectivity (entry 3). All reactions listed in Table 1 were performed in higher concentrations of the substrates, because the dilution of the substrates markedly retards the thioselenation. It must be kept in mind that, if the thioselenation is performed in the absence of a solvent, the reaction

Scheme 3



temperature should be over 40 °C. This is because a mixture of acetylene, $(PhS)_2$, and $(PhSe)_2$ becomes homogeneous over that temperature. Although the radical addition of $(PhS)_2$ or $(PhSe)_2$ to acetylenes is known as mentioned already, the present thioselenation reaction of acetylenes involved only trace amounts of (PhS)-adducts as byproducts (which could easily be removed by column chromatography). These facts clearly indicate that the present thioselenation is a kinetically well-controlled system.

As an extension of our interest in the synthetic application of the $(PhS)_2$–$(PhSe)_2$ binary system, the thioselenation reaction of enynes via 5-*exo* radical cyclization[10] was demonstrated. The photoirradiated reaction of diethyl allylpropargylmalonate (**1i**) with $(PhS)_2$ and $(PhSe)_2$ successfully afforded the corresponding five-membered ring product (**2i**) bearing phenylthio and phenylseleno groups at both terminal positions regioselectively (Scheme 3).[11] Similar conditions can be employed with allyl propargyl ether (**1j**).[11] Both reactions proceeded via the selective addition of PhS• to the carbon–carbon triple bonds. The obtained five-membered cyclic thioselenation products may be accepted as synthetically useful intermediates, because the formed vinylic sulfide moiety can be converted to a formyl group[12] and the selenide moiety can be transferred into a hydrogen[13] and an olefinic moiety[14] by treatment with Bu_3SnH and by oxidation, respectively.

In conclusion, a novel, highly selective method for introducing organic sulfur and selenium functions into carbon–carbon triple bonds has been developed. Based on the relative reactivities between the thio and seleno radicals and between disulfide and diselenide, it has become apparent that two different chalcogeno-groups can be introduced simultaneously into carbon–carbon triple bonds with excellent selectivity. With enynes, thioselenation via radical cyclization is demonstrated successfully. We are currently examining applicability of this methodology to a variety of different classes of substrates.

(10) (a) Curran, D. P.; Porter, N. A.; Giese, B. *Stereochemistry of Radical Reactions*; VCH: Weinheim, 1996. (b) Fossey, J.; Lefort, D.; Sorba, J. *Free Radicals in Organic Chemistry*; Masson: Paris, 1995. (c) Curran, D. P. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 4, p 779. (d) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon Press: Oxford, 1986.

(11) The thioselenation of enynes was accompanied by the formation of acyclic thioselenation products: CH_2=$CHCH_2XCH_2C(SePh)$=$CHSPh$, X = $C(CO_2Et)_2$: 7% (*E*/*Z* = 79/21); X = O: 11% (*E*/*Z* = 79/21).

(12) Gröbel, B.-T.; Seebach, D. *Synthesis* **1977**, 357.

(13) Clive, D. L. J.; Chittattu, G.; Farina, V.; Kiel, W. A.; Menchen, S. M.; Russell, C. G.; Singh, A.; Wong, C. K.; Curtis, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 4438.

(14) Reich, H. J.; Wollowitz, S. *Org. React.* **1993**, *44*, 1.

Experimental Section

General Comments.[5a] Unless otherwise noted, acetylenes were used commercially and were purified by distillation. Diphenyl disulfide was purified by recrystallization from EtOH. Diphenyl diselenide[15] was prepared according to the literature and was recrystallized from hexane. Enynes[16] were synthesized according to the literature.

Thioselenation of Acetylenes: α-(phenylseleno)-β-(phenylthio)styrene (2a). In a Pyrex glass tube (ϕ = 5 mm) were placed phenylacetylene (**1a**) (0.25 mmol), diphenyl disulfide (0.25 mmol), and diphenyl diselenide (0.25 mmol). The tube was filled with Ar and was sealed under reduced pressure. The mixture was irradiated at 45 °C for 30 h with a tungsten lamp (500 W) positioned approximately 8 cm from the tube. Phenylacetylene unreacted was evaporated in vacuo, and the residue was chromatographed on silica gel eluted with hexane to remove diphenyl disulfide, diphenyl diselenide, and diphenyl seleno sulfide.[17] Changing the eluent to hexane/Et_2O = 10/1 yielded 91 mg (96%, *E*/*Z* = 100/0) of α-(phenylseleno)-β-(phenylthio)styrene (**2a**): a pale yellow oil; [*E*-isomer]: ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.86 (s, 1 H), 7.12−7.33 (m, 11 H), 7.41−7.53 (m, 4 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 126.92, 127.45, 128.15, 129.10, 129.16, 129.32, 129.74, 130.08, 130.54, 130.66, 132.13, 132.94, 135.81, 138.48; IR (NaCl) 3055, 1578, 1476, 1439, 1070, 1022, 763, 737, 710, 689, 669 cm^{-1}; MS (EI), *m*/*z* = 368 (M^+, 51); exact mass (M^+) calcd for $C_{20}H_{16}SSe$ 368.0138, found 368.0156.

1-(Phenylthio)-2-(phenylseleno)-1-octene (2b). The reaction of 1-octyne (**1b**) (0.25 mmol) with diphenyl disulfide (0.25 mmol) and diphenyl diselenide (0.25 mmol) was performed by irradiation at 45 °C for 35 h with a tungsten lamp (500 W) through Pyrex. The residual mixture was purified by flash chromatography on silica gel using hexane and then diethyl ether as eluents to provide 65 mg (74%, *E*/*Z* = 73/27) of 1-(phenylthio)-2-(phenylseleno)-1-octene (**2b**) as a mixture of *E*- and *Z*-isomers accompanied by a trace of disulfide adduct as byproduct. Owing to the similar polarities of (*E*)-**2b** and (*Z*)-**2b**, the isolation of each isomer failed, and so the following spectral and analytical data were obtained using the stereoisomeric mixture: a pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) [*E*-isomer]: δ 0.87 (t, 3 H, *J* = 6.8 Hz), 1.28 (m, 6 H), 1.54 (m, 2 H), 2.47 (t, 2 H, *J* = 7.3 Hz), 6.48 (s, 1 H), 7.13−7.41 (m, 8 H), 7.51−7.54 (m, 2 H). [*Z*-isomer]: δ 0.87 (t, 3 H, *J* = 6.8 Hz), 1.28 (m, 6 H), 1.54 (m, 2 H), 2.42 (t, 2 H, *J* = 7.3 Hz), 6.71 (s, 1 H), 7.13−7.41 (m, 8 H), 7.51−7.54 (m, 2 H). NOE experiment: Irradiation of the allyl triplet at δ 2.42 resulted in a 6.4% enhancement of the signal at δ 6.71 (vinyl singlet); ^{13}C NMR (68 MHz, $CDCl_3$) [*E*-isomer]: δ 14.09, 22.57, 28.50, 28.71, 31.60, 34.59, 123.87, 125.77, 126.41, 128.72, 129.04, 129.28, 131.48, 133.49, 135.53, 136.04. [*Z*-isomer]: δ 14.07, 22.47, 28.47, 28.70, 31.60, 36.41, 122.09, 127.02, 127.57, 129.27, 129.27, 131.07, 132.61, 132.94, 133.58, 135.81; IR (NaCl) 3058, 2954, 2927, 2855, 1579, 1477, 1438, 1022, 736, 690, 668 cm^{-1}; MS (EI), *m*/*z* = 376 (M^+, 100); exact mass (M^+) calcd for $C_{20}H_{24}SSe$ 376.0764, found 376.0778.

3-(Phenylthio)-2-(phenylseleno)-prop-2-en-1-ol (2c). The reaction of propargyl alcohol (**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 40 °C for 30 h with a tungsten lamp (500 W) through Pyrex. The residual mixture was purified by preparative TLC (silica gel, pentane/Et_2O = 5/1) to provide 45 mg (29%, *Z*-isomer) and 74 mg (47%, *E*-isomer) of 3-(phenylthio)-2-(phenylseleno)-2-propenol (**2c**): a pale yellow oil; [*E*-isomer]: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.77 (br s, 1 H), 4.16 (s, 2 H), 7.03 (s, 1 H), 7.20−7.47 (m, 10 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 65.49, 127.00, 127.47, 129.20, 129.38, 129.93, 130.39, 130.50, 132.77, 134.76, 134.82; IR (NaCl) 3376, 3058, 1581, 1478, 1439, 1090, 1024, 740, 690 cm^{-1}; MS (EI), *m*/*z* = 322 (M^+, 13); exact mass (M^+) calcd for $C_{15}H_{14}OSSe$ 321.9931, found 321.9942. [*Z*-isomer]: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.89 (br s, 1 H), 4.37 (s, 2 H), 6.69 (s, 1 H), 7.22−7.42 (m, 10 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 61.40, 127.24, 127.38, 129.26, 129.30, 129.53, 130.48, 130.51, 133.67, 133.89, 134.87; IR (NaCl) 3389, 3057, 1582, 1478, 1439, 1024, 739, 690 cm^{-1}; MS (EI), *m*/*z* = 322 (M^+, 11); exact mass (M^+) calcd for $C_{15}H_{14}OSSe$ 321.9931, found 321.9938.

3,3-Dimethyl-1-(phenylthio)-2-(phenylseleno)-1-butene (2d). The reaction of 3,3-dimethyl-1-butyne (**1d**) (0.25 mmol) with diphenyl disulfide (0.25 mmol) and diphenyl diselenide (0.3 mmol) in $CDCl_3$ (0.5 mL) was performed by irradiation at 20 °C for 150 h with a tungsten lamp (500 W) through Pyrex. Measurement of the NMR spectrum at this point indicated the recovery of **1d** (50%). The residual mixture was purified by preparative TLC (silica gel, hexane) to provide 9 mg (13%, *Z*-isomer) and 13 mg (18%, *E*-isomer) of 3,3-dimethyl-1-(phenylthio)-2-(phenylseleno)-1-butene (**2d**): a pale yellow oil; [*E*-isomer]: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.38 (s, 9 H), 6.49 (s, 1 H), 7.17−7.31 (m, 8 H), 7.53 (dd, 2 H, *J* = 7.3, 7.8 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 29.27, 39.49, 126.64, 127.10, 128.39, 129.01, 129.12, 129.29, 131.52, 132.83, 136.90, 140.35; MS (EI), *m*/*z* = 348 (M^+, 100); exact mass (M^+) calcd for $C_{18}H_{20}SSe$ 348.0451, found 348.0462. [*Z*-isomer]: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.23 (s, 9 H), 7.03 (s, 1 H), 7.17−7.34 (m, 6 H), 7.39 (dd, 2 H, *J* = 6.4, 7.8 Hz), 7.42 (dd, 2 H, *J* = 6.8, 8.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 29.76, 40.44, 125.85, 127.07, 129.04, 129.09, 129.18, 129.35, 130.33, 135.38, 135.92, 139.56; MS (EI), *m*/*z* = 348 (M^+, 100); exact mass (M^+) calcd for $C_{18}H_{20}SSe$ 348.0451, found 348.0460.

1-Phenyl-1-(phenylseleno)-2-(phenylthio)-1-pentene (2e). The reaction of 1-phenyl-1-pentyne (**1e**) (0.5 mmol) with diphenyl disulfide (0.5 mmol) and diphenyl diselenide (0.5 mmol) in $CDCl_3$ (0.5 mL) was performed by irradiation at 40 °C for 15 h with a tungsten lamp (500 W) through Pyrex. The residual mixture was purified by flash chromatography on silica gel using hexane and then diethyl ether as eluents to provide 172 mg (87%, *E*/*Z* = 86/14) of 1-phenyl-1-(phenylseleno)-2-(phenylthio)-1-pentene (**2e**) as a mixture of *E*- and *Z*-isomers. Owing to the similar polarities of (*E*)-**2e** and (*Z*)-**2e**, 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 (270 MHz, $CDCl_3$) [*E*-isomer]: δ 0.93 (t, 3 H, *J* = 7.3 Hz), 1.67 (sextet, 2 H, *J* = 7.4 Hz), 2.63 (t, 2 H, *J* = 7.8 Hz), 6.93−7.34 (m, 15 H). [*Z*-isomer]: δ 0.64 (t, 3 H,

(15) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.
(16) Billington, D. C.; Willson, D. *Tetrahedron. Lett.* **1984**, *25*, 4041.
(17) When a mixture of $(PhS)_2$ and $(PhSe)_2$ (1:1) was irradiated with a tungsten lamp, PhSSePh was formed in situ (the ratio of $(PhS)_2$/$(PhSe)_2$/PhSSePh was ca. 1/1/1.4 during the thioselenation of olefins).

J = 7.3 Hz), 1.44 (sextet, 2 H, J = 7.4 Hz), 2.09 (t, 2 H, J = 7.8 Hz), 6.93−7.34 (m, 15 H); MS (EI), m/z = 410 (M^+, 55); exact mass (M^+) calcd for $C_{23}H_{22}SSe$ 410.0607, found 410.0620.

4-(Phenylthio)-5-(phenylseleno)-4-octene (2f). The reaction of 4-octyne (**1f**) (0.5 mmol) with diphenyl disulfide (0.8 mmol) and diphenyl diselenide (0.8 mmol) in $CDCl_3$ (0.5 mL) was performed by irradiation at 40 °C for 250 h with a tungsten lamp (500 W) through Pyrex. The residual mixture was purified by HPLC ($CHCl_3$ as an eluent) to provide 159 mg (76%, E/Z = 95/5) of 4-(phenylthio)-5-(phenylseleno)-4-octene (**2f**) as a mixture of *E*- and *Z*-isomers. Isolation of the major isomer (*E*-isomer) was performed by flash chromatography on silica gel using hexane and then diethyl ether as eluents. Mp 59.5 °C (a white solid); [*E*-isomer]: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.80 (t, 3 H, J = 7.3 Hz), 0.84 (t, 3 H, J = 7.3 Hz), 1.51 (sextet, 2 H, J = 8.3 Hz), 1.52 (sextet, 2 H, J = 8.3 Hz), 2.53 (t, 2 H, J = 7.3 Hz), 2.59 (t, 2 H, J = 7.6 Hz), 7.18−7.32 (m, 8 H), 7.50 (dd, 2 H, J = 5.9, 7.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.50, 13.59, 22.37, 22.77, 38.04, 38.56, 126.22, 127.33, 128.91, 128.95, 129.15, 129.70, 130.17, 133.44, 135.83, 139.14; IR (KBr) 2959, 2931, 2870, 1576, 1476, 1439, 1023, 736, 692 cm^{-1}; MS (EI), m/z = 376 (M^+, 100); exact mass (M^+) calcd for $C_{20}H_{24}SSe$ 376.0763, found 376.0744.

1-[1′-(Phenylseleno)-2′-(phenylthio)ethenyl]cyclohexene (2 g). The reaction of 1-ethynylcyclohexene (**1g**) (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 40 °C for 6 h with a tungsten lamp (500 W) through Pyrex. The residual mixture was purified by HPLC ($CHCl_3$ as an eluent) to provide 65 mg (71%) of 1-[1′-(phenylseleno)-2′-(phenylthio)ethenyl]-1-cyclohexene (**2g**) as a mixture of *E*- and *Z*-isomers (E/Z = 17/83). a pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) [*E*-isomer]: δ 1.47−1.64 (m, 4 H), 2.06 (br s, 2 H), 2.21 (br s, 2 H), 5.80 (t like, 1 H), 6.55 (s, 1 H), 7.21−7.51 (m, 10 H). [*Z*-isomer]: δ 1.47−1.64 (m, 4 H), 2.07 (br s, 2 H), 2.25 (br s, 2 H), 6.28 (s, 1 H), 7.01 (s, 1 H), 7.10−7.44 (m, 10 H). NOE experiment: Irradiation of the allylic broad singlet at δ 2.25 resulted in a 4.5% enhancement of the signal at δ 7.01 (vinyl singlet); ^{13}C NMR (68 MHz, $CDCl_3$) [*E*-isomer]: δ 21.85, 22.60, 25.40, 27.69, 126.50, 126.59, 127.27, 129.01, 129.01, 129.07, 130.35, 131.01, 133.16, 133.64, 135.75, 136.45; [*Z*-isomer]: δ 22.05, 22.77, 22.97, 27.02, 126.14, 127.09, 128.97, 129.10, 129.35, 130.159, 130.37, 131.41, 131.52, 133.02, 135.35, 135.87; IR (NaCl) 3057, 2926, 2856, 1578, 1476, 1438, 1069, 1023, 882, 864, 799, 735, 689, 668 cm^{-1}; MS (EI), m/z = 372 (M^+, 45); exact mass (M^+) calcd for $C_{20}H_{20}SSe$ 372.0449, found 372.0450.

1-Methoxy-3-(phenylseleno)-4-(phenylthio)-1,3-butadiene (2h). The reaction of *cis*-1-methoxy-but-1-en-3-yne (**1h**) (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 40 °C for 3 h with a tungsten lamp (500 W) through Pyrex. The NMR yield of the thioselenation product (90%, E/Z = 30/70) was determined by ^{1}H NMR measurement of the reaction mixture using trioxane (δ = 5.09) as an internal standard: ^{1}H NMR (270 MHz, $CDCl_3$) [*E*-isomer]: δ 3.52 (s, 3 H), 5.65 (d, 1 H, J = 12.2 Hz), 6.78 (s, 1 H), 6.92 (d, 1 H, J = 12.2 Hz), 7.16−7.51 (m, 10 H). [*Z*-isomer]: δ 3.60 (s, 3 H), 6.00 (d, 1 H, J = 11.7 Hz), 6.58 (s, 1 H), 7.14 (d, 1 H, J = 11.7 Hz), 7.16−7.51 (m, 10 H). Unfortunately, attempted isolation by preparative TLC or HPLC failed because the vinyl ether moiety of **2h** underwent hydrolysis easily.

Radical Cyclization of Enyne 1i. In a Pyrex glass tube were placed 4,4-bis(ethoxycarbonyl)hept-1-en-6-yne (**1i**) (0.3 mmol), diphenyl disulfide (0.18 mmol), diphenyl diselenide (0.3 mmol), and $CDCl_3$ (0.5 mL). The mixture was irradiated at 40 °C for 25 h with a tungsten lamp (500 W). The solvent was then evaporated in vacuo, and the residue was purified by preparative TLC on silica gel (hexane/Et_2O = 5/1) to provide 82 mg (61%, E/Z = 72/28) of cyclic thioselenation product **2i** and 9 mg (7%, E/Z = 83/17) of acyclic 1,2-addition product **2i′**. Cyclic product **2i**: a pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.22 (t, 3 H, J = 7.2 Hz), 1.25 (t, 3 H, J = 7.2 Hz), 2.10 (dd, 1 H, J = 9.3, 13.2 Hz), 2.73 (dd, 1 H, J = 6.8, 12.7 Hz), 2.91−3.23 (m, 5 H), 4.17 (q, 2 H, J = 7.2 Hz), 4.19 (q, 2 H, J = 7.2 Hz), 6.08 (s, 1 H), 7.18−7.30 (m, 8 H), 7.47−7.54 (m, 2 H); MS (EI), m/z = 504 (M^+, 11); exact mass (M^+) calcd for $C_{25}H_{28}O_4SSe$ 504.0874, found 504.0891.

Radical Cyclization of Enyne 1j. The reaction of allyl propargyl ether (**1j**) (0.3 mmol) with diphenyl disulfide (0.18 mmol) and diphenyl diselenide (0.3 mmol) in $CDCl_3$ (0.5 mL) was performed by irradiation at 40 °C for 18 h with a tungsten lamp (500 W) through Pyrex. The solvent was then evaporated in vacuo, and the residue was purified by preparative TLC on silica gel (hexane/Et_2O = 20/1) to provide 54 mg (50%, E/Z = 34/66) of cyclic thioselenation product **2j** and 12 mg (11%, E/Z = 79/21) of acyclic 1,2-addition product **2j′**. Cyclic product **2j**: a pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.96 (m, 2 H), 3.14 (dd, 1 H, J = 5.4, 10.5 Hz), 3.82 (dd, 1 H, J = 5.4, 8.8 Hz), 4.08 (dd, 1 H, J = 5.9, 8.8 Hz), 4.35 (br s, 2 H), 6.42 (s, 1 H), 7.25−7.31 (m, 6 H), 7.44 (d, 2 H, J = 7.8 Hz), 7.51 (d, 2 H, J = 7.3 Hz); IR (NaCl) 3054, 2930, 2850, 1578, 1477, 1437, 1071, 1022, 927, 736, 690 cm^{-1}; MS (EI), m/z = 362 (M^+, 6); exact mass (M^+) calcd for $C_{25}H_{28}O_4SSe$ 362.0423, found 362.0236.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **2a**, **2b**, **2c**, **2d**, **2e**, **2f**, **2g**, **2i**, and **2j** (13 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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