Highly Selective Thioselenation of Vinylcyclopropanes with a $(PhS)_2$−$(PhSe)_2$ Binary System and Its Application to Thiotelluration

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Received June 2, 1998

A novel, highly selective method for introducing organic sulfur, selenium, and tellurium functions into vinylic cyclopropanes has been developed on the basis of the relative reactivities of organic dichalcogenides and chalcogen-centered radicals. Upon irradiation with the light of wavelength over 300 nm, the reaction of vinylcyclopropanes with diphenyl disulfide and diphenyl diselenide proceeds smoothly to provide the corresponding γ-(selenoethyl)allylic sulfides regioselectively in good yields. Similarly, vinylcyclopropanes undergo regioselective thiotelluration by use of a novel $(PhS)_2$−$(PhTe)_2$ binary system, affording the corresponding ring-opened thiotelluration product in good yields. Furthermore, the scope and limitations of this $(PhS)_2$−$(PhTe)_2$ binary system are discussed.

Introduction

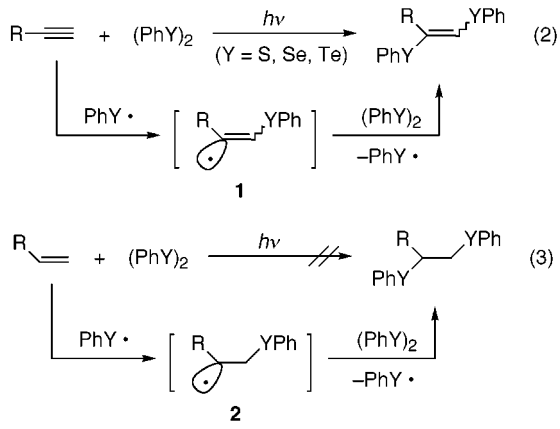
Since organic disulfides, diselenides, and ditellurides undergo homolytic cleavage by irradiation with ultraviolet, near-UV, and visible light, respectively, generating the corresponding chalcogen-centered radicals (eq 1),[1] the photolysis of organic dichalcogenides in the presence of carbon−carbon unsaturated compounds may effect radical addition of dichalcogenides to unsaturated bonds.

$$(PhY)_2 \underset{}{\overset{h\nu}{\rightleftharpoons}} 2\,PhY\cdot \qquad (1)$$

Y = S	λ_{max} = 250 nm
Se	330 nm
Te	406 nm

However, examples of the radical addition of organic dichalcogenides to carbon−carbon multiple bonds have been limited to a few cases, including the addition of $(RY)_2$ to acetylenes (Y = S,[2] Se,[3] and Te[4]) and allenes (Y = Se[5]), and until very recently, there have been no reported examples of the efficient radical addition of organic dichalcogenides to olefins (eqs 2−3).[6]

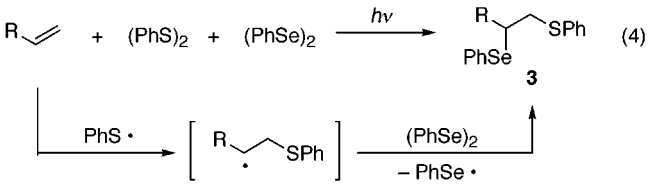
The addition to acetylenes proceeds via the formation of a β-chalcogen-substituted vinylic radical (**1**) by the terminal attack of PhY• to the triple bond, followed by the S_H2 reaction between **1** and $(PhY)_2$. Similarly, if the radical addition to olefins takes place, a β-chalcogen-substituted alkyl radical (**2**) may be formed as a key intermediate. Since the rate constants for the addition of PhY• to olefins are assumed to be comparable with those for the addition to acetylenes,[2] the reverse reaction from **2** to give the starting olefin and PhY• is probably much faster than that from **1**; conceivably, this contributes to the inefficiency of the radical addition of dichalcogenides to olefins.



On the contrary, we recently disclosed that a binary system of organic dichalcogenides, i.e., a $(PhS)_2$−$(PhSe)_2$ system, successfully effects the desired radical addition to olefins upon irradiation with near-UV or visible light, providing the corresponding thioselenation products (**3**) regioselectively in high yields (eq 4).[7]

(1) Schmidt, U.; Müller, A.; Markau, K. *Chem. Ber.* **1964**, *97*, 405.
(2) Heiba, E. I.; Dessau, R. M. *J. Org. Chem.* **1967**, *32*, 3837.
(3) (a) Back, T. G.; Krishna, M. V. *J. Org. Chem.* **1988**, *53*, 2533. (b) Ogawa, A.; Yokoyama, H.; Yokoyama, K.; Masawaki, T.; Kambe, N.; Sonoda, N. *J. Org. Chem.* **1991**, *56*, 5721. (c) Ogawa, A.; Takami, N.; Sekiguchi, M.; Yokoyama, H.; Kuniyasu, H.; Ryu, I.; Sonoda, N. *Chem. Lett.* **1991**, 2241.
(4) (a) Ogawa, A.; Yokoyama, K.; Yokoyama, H.; Obayashi, R.; Kambe, N.; Sonoda, N. *J. Chem. Soc., Chem. Commun.* **1991**, 1748. (b) Ogawa, A.; Yokoyama, K.; Obayashi, R.; Han, L.-B.; Kambe, N.; Sonoda, N. *Tetrahedron* **1993**, *49*, 1177.
(5) Ogawa, A.; Yokoyama, K.; Yokoyama, H.; Sekiguchi, M.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1990**, *31*, 5931.
(6) For the free-radical selenosulfonation of olefins, see: (a) Back, T. G.; Collins, S. *Tetrahedron Lett.* **1980**, *21*, 2215. (b) Gancarz, R. A.; Kice, J. L. *Tetrahedron Lett.* **1980**, *21*, 4155. (c) Back, T. G.; Collins, S. *J. Org. Chem.* **1981**, *46*, 3249. (d) Gancarz, R. A.; Kice, J. L. *J. Org. Chem.* **1981**, *46*, 4899. For a review concerning the selenosulfonation, see: (e) Back, T. G. *Phosphorus Sulfur Silicon Relat. Elem.* **1992**, *67*, 203. For the selenothiocarbonylation of olefins, see: (f) Toru, T.; Seko, T.; Maekawa, E. *Tetrahedron Lett.* **1985**, *26*, 3263. (g) Toru, T.; Kanefusa, T.; Maekawa, E. *Tetrahedron Lett.* **1986**, *27*, 1583. (h) Toru, T.; Seko, T.; Maekawa, E.; Ueno, Y. *J. Chem. Soc., Perkin Trans. 1* **1988**, 575. (i) Toru, T.; Seko, T.; Maekawa, E.; Ueno, Y. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1927.

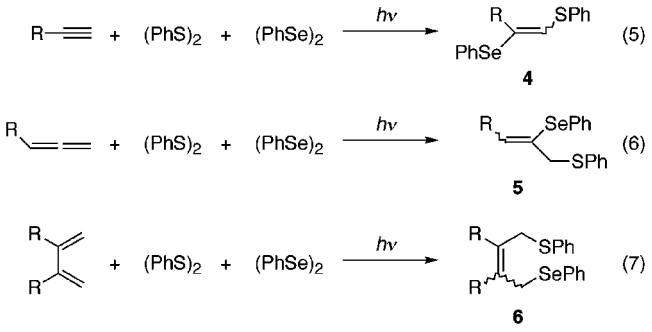
10.1021/jo981053q CCC: $18.00
Published on Web 12/11/1998



(4)

Some kinetic data are reported for the relative reactivities of chalcogen-centered radicals toward olefins as well as those of dichalcogenides toward carbon radicals: PhS• is relatively reactive toward carbon−carbon double bonds compared with PhSe• [$k_{PhS•}/k_{PhSe•} = 10-50$],[8] whereas $(PhSe)_2$ is more reactive toward alkyl radicals compared with $(PhS)_2$ [$k_{(PhSe)_2}/k_{(PhS)_2}$ = ca. 160].[9] 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.

Moreover, it has become apparent that this $(PhS)_2$−$(PhSe)_2$ binary system is available for highly selective introduction of both thio and seleno groups into a wide range of carbon−carbon multiple bonds. For example, the photoinduced reaction of acetylenes with organic disulfides and diselenides takes place smoothly to provide the corresponding vicinally thioselenated alkenes (**4**) regioselectively (eq 5).[10] The $(PhS)_2$−$(PhSe)_2$ binary system is also effective for the regioselective thioselenation of allenes[11] and 1,3-dienes,[7,12] affording β-selenoallylic sulfides (**5**) and γ-(selenomethyl)allylic sulfides (**6**), respectively, in good yields (eqs 6−7).



(5)

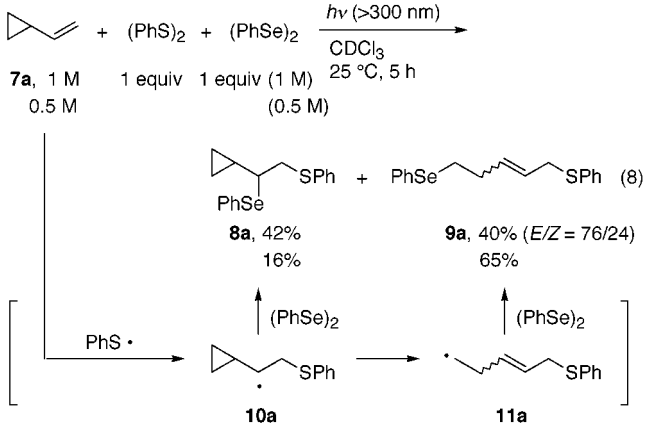
(6)

(7)

In this paper, we report the regioselective thioselenation of vinylcyclopropanes via ring-opening of the cyclopropylcarbinyl radical intermediates, and in addition, an application to the development of a disulfide−ditelluride binary system.[13]

Results and Discussion

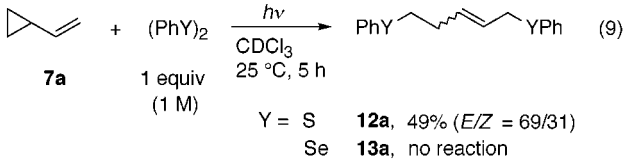
Thioselenation of Vinylcyclopropanes. When the reaction of vinylcyclopropane (**7a**, 1 M) with an equimolar amount of diphenyl disulfide and diphenyl diselenide in $CDCl_3$ was conducted upon irradiation through Pyrex with a tungsten lamp at 25 °C for 5 h, {2-(phenylthio)-1-(phenylseleno)ethyl}cyclopropane (**8a**) and 1-(phenylthio)-5-(phenylseleno)-2-pentene (**9a**) were obtained in 42 and 40% yields, respectively (eq 8). The reaction involves



(8)

the formation of a cyclopropylcarbinyl radical (**10a**) by the attack of PhS• at the terminal carbon of **7a**. If **10a** is captured directly by $(PhSe)_2$, the former adduct (**8a**) is formed. On the other hand, the latter adduct (**9a**) is produced by ring opening of **10a** to give the primary radical (**11a**) and subsequent S_H2 reaction of **11a** with $(PhSe)_2$. Decreasing the concentration of $(PhSe)_2$ by dilution with the solvent led to the formation of the ring-opened **9a** preferentially.

In contrast to the thioselenation by a $(PhS)_2$−$(PhSe)_2$ binary system, the photoinduced reaction of vinylcyclopropane (**7a**) with $(PhS)_2$ alone provided only the ring-opened product, 1,5-bis(phenylthio)-2-pentene (**12a**), selectively (eq 9). This result suggests that the S_H2 reaction



(9)

of the secondary carbon radical (**10a**) with $(PhS)_2$ is much slower compared with the case of $(PhSe)_2$. On the other hand, the reaction of vinylcyclopropane with diphenyl diselenide did not proceed at all under similar photoirradiated conditions. The lower reactivity of PhSe• may contribute to the inefficiency of the diselenation of vinylcyclopropane (eq 9).

The thioselenation of various vinylcyclopropanes (**7b**−**f**) was examined by using a $(PhS)_2$-$(PhSe)_2$ binary system and the results are shown in Table 1. The thioselenation of (2-propenyl)cyclopropane (**7b**) afforded the ring-opening product (**9b**) as the sole product in high yield (Table

(7) (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 Relat. Elem.* **1994**, *95*−*96*, 331. (c) Ogawa, A. *J. Synth. Org. Chem. Jpn.* **1995**, *53*, 869. (d) Ogawa, A.; Sonoda, N. *J. Synth. Org. Chem. Jpn.* **1996**, *54*, 894. (e) Ogawa, A.; Hirao, T. *Rev. Heteroat. Chem.* **1998**, *18*, 1.

(8) In the case of styrene, for example, the addition rate constants of PhS• and PhSe• are estimated to be 2.0×10^7 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.

(9) 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.

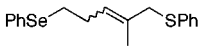
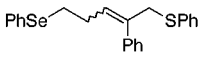
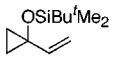
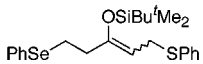
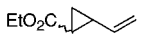
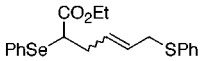
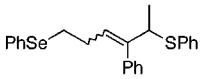
(10) Ogawa, A.; Obayashi, R.; Ine, H.; Tsuboi, Y.; Sonoda, N.; Hirao, T. *J. Org. Chem.* **1998**, *63*, 881.

(11) Ogawa, A.; Obayashi, R.; Doi, M.; Sonoda, N.; Hirao, T. *J. Org. Chem.* **1998**, *63*, 4277.

(12) Ogawa, A.; Obayashi, R.; Sonoda, N.; Hirao, T. *Tetrahedron Lett.* **1998**, *39*, 1577.

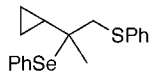
(13) Back, T. G.; Muralidharan, K. R. *J. Org. Chem.* **1989**, *54*, 121.

Table 1. Photoinitiated Thioselenation of Vinylcyclopropanes[a]

entry	substrate	time, h	product	yield, %[b] (*E*/*Z*)
1	 **7b**	17	 **9b**	86 (67/33)
2	 **7c**	5	 **9c**	90 (40/60)
3	 **7d**	6[c]	 **9d**	88 (53/47)[d]
4	 **7e**[e]	1	 **9e**	97 (80/20)
5	 **7f**[f]	35	 **9f**	35 (90/10)

[a] Reaction conditions : substrate (0.5 mmol, 1 M), $(PhS)_2$ (1 equiv, 1 M), $(PhSe)_2$ (1 equiv, 1 M), $CDCl_3$ (0.5 mL), 40 °C. [b] Isolated yield. [c] At 25 °C. [d] NMR yield. [e] *cis*/*trans* = 1/99. [f] Neat, *cis*/*trans* = 52/48.

1, entry 1). The cyclopropyl thioselenation product (**8b**) was not formed at all, most probably due to the lower reactivity of $(PhSe)_2$ toward tertiary carbon radicals.



8b

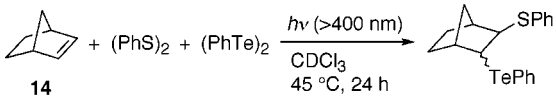
10' (R = CH_3)
10'' (R = Ph)

Since the cyclopropylcarbinyl radical (**10″**) bearing a phenyl group at the α-position is more stable than the corresponding α-methyl-substituted cyclopropylcarbinyl radical (**10′**), the rate of ring-opening is relatively slow (i.e., $k < 1.0 \times 10^6$ s^{-1} (at 37 °C) for **10″**; $k = 7.0 \times 10^7$ s^{-1} (at 37 °C) for **10′**).[14] Nevertheless, the thioselenation of 1-cyclopropylstyrene (**7c**) proceeded successfully to provide 1-(phenylthio)-2-phenyl-5-(phenylseleno)-2-pentene (**9c**) as the sole product (Table 1, entry 2).

On the other hand, introduction of a siloxy group or a carbonyl group into the cyclopropane ring accelerates the ring-opening to give the corresponding 3-(*tert*-butyldimethylsiloxy)- and 5-(ethoxycarbonyl)-1-(phenylthio)-5-(phenylseleno)-2-pentenes (**9d** and **9e**), respectively, in excellent yields (Table 1, entries 3 and 4). In the case of inner alkenes such as 1-cyclopropyl-1-phenylpropene (**7f**) prolonged irradiation is required and again, the ring-opening product (**9f**) was obtained exclusively (Table 1, entry 5).

Since the rate constant for the ring-opening of 1-(cyclopropyl)ethyl radical (**10′**) into a 1-pent-3-enyl radical is determined to be 7.0×10^7 s^{-1} (at 37 °C),[14,15] we can estimate roughly the rate for the S_H2 reaction of secondary alkyl radicals with $(PhSe)_2$ by conducting the reaction of vinylcyclopropane (**7a**) with $(PhS)_2$ and $(PhSe)_2$. Thus, we examined the reaction of vinylcyclopropane (1 M) with $(PhS)_2$ (1 M) and $(PhSe)_2$ (1 M) upon irradiation through Pyrex with a tungsten lamp at 25 °C. When the conversion was 9%, the product ratio of **9a**/**8a** was 1.13. Accordingly, the rate constant for the S_H2 reaction of secondary carbon radicals by $(PhSe)_2$ is estimated roughly as ca. 3×10^7 M^{-1} s^{-1} (25 °C), which is similar to the literature value obtained by using a 5-hexenyl radical clock system (2.6×10^7 M^{-1} s^{-1} (25 °C)).[9]

Thiotelluration of Vinylcyclopropanes. Compared with diphenyl diselenide, diphenyl ditelluride is reported to possess further excellent capturing ability toward carbon radicals [$k_{(PhTe)_2}/k_{(PhSe)_2}$ = ca. 4].[9] This suggests strongly that, if the reaction of olefins is performed by using a disulfide−ditelluride binary system, a novel thiotelluration of olefins may take place. Thus, we examined the visible-light-irradiated reaction of a variety of olefins with equimolar amounts of diphenyl disulfide and diphenyl ditelluride. However, the desired vicinal thiotelluration did not proceed at all, except for a special case such as norbornene (**14**), which underwent thiotelluration efficiently, as indicated in eq 10.

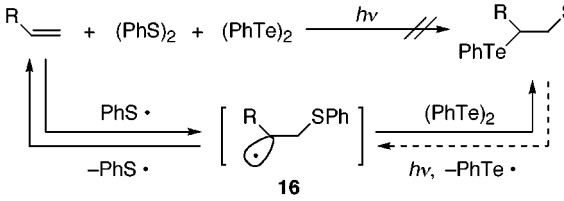


(10)

14

15, 74% [*exo*/*endo* = 51/49]

Although the reason the thiotelluration of olefins did not proceed is unclear, a photoinduced reverse process is probably operative to regenerate β-(phenylthio)alkyl radicals (**16**),[16] which easily decompose to the starting olefins and PhS• (eq 11). Accordingly, suppression of the reverse process may be required for achievement of the desired thiotelluration. Thus, we examined the thiotelluration of vinylcyclopropanes, because the initially formed β-(phenylthio)alkyl radical (**16**, R = cyclopropyl) bearing a cyclopropyl group can be converted quickly to the ring-opened primary radical, depressing the reverse process from **16** to the starting vinylcyclopropanes.



(11)

16

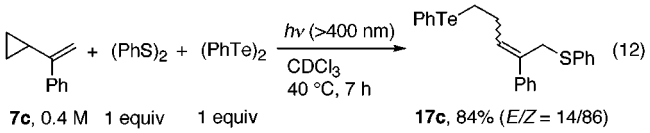
Thus, the thiotelluration of vinylic cyclopropane (**7c**) was examined with a $(PhS)_2$−$(PhTe)_2$ binary system upon irradiation with visible light (eq 12). The desired thiotelluration proceeded successfully via the selective attack of PhS• at the terminal carbon of **7c** and the selective S_H2 reaction with $(PhTe)_2$, affording the ring-opened thiotelluration product (**17c**) exclusively.

The obtained thiotelluration product (**17c**) can be converted easily to the corresponding lithium compound

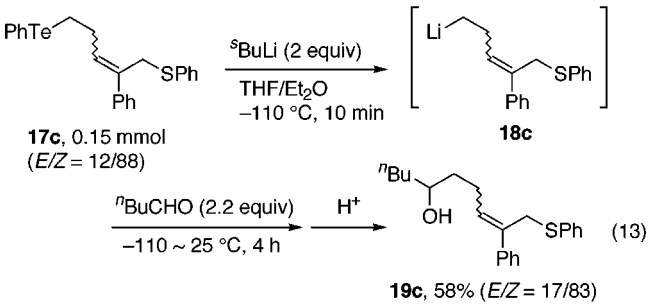
(14) (a) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5687. (b) Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5699. (c) Beckwith, A. L. J.; Bowry, V. W. *J. Am. Chem. Soc.* **1994**, *116*, 2710.

(15) The rate constant for ring-opening of 1-(cyclopropyl)ethyl radical at 25 °C is 4.0×10^7 s^{-1}, see: Newcomb, M. *Tetrahedron* **1993**, *49*, 1151.

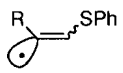
(16) For the photolysis of alkyl tellurides to generate alkyl radicals, see: (a) Han, L.-B.; Ishihara, K.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 7591. (b) Han, L.-B.; Ishihara, K.; Kambe, N.; Ogawa, A.; Sonoda, N. *Phosphorus Sulfur Silicon Relat. Elem.* **1992**, *67*, 243.



(**18c**) by treatment with *s*-butyllithium at −110 °C.[17] Accordingly, the PhTe group of **17c** can be replaced conveniently by electrophiles, as exemplified in eq 13.



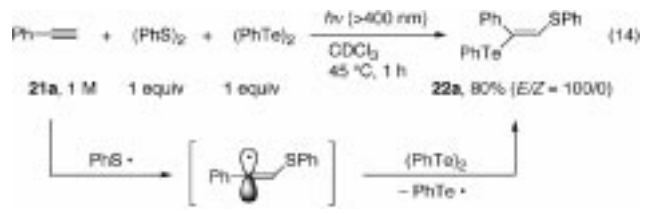
Thiotelluration of Acetylenes. Compared to the *β*-(phenylthio)alkyl radical (**16** in eq 11), the *β*-(phenylthio)vinylic radical (**20**) is kinetically more stable, so the reverse process from **20** to the starting acetylene and PhS• may be relatively suppressed. This suggests strongly



20

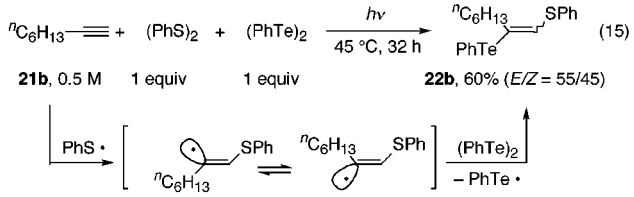
that, if the reaction of acetylenes is performed by using a disulfide−ditelluride binary system, a novel thiotelluration of acetylenes is expected to take place.

Thus, we examined the visible light-irradiated reaction of phenylacetylene (**21a**) with equimolar amounts of diphenyl disulfide and diphenyl ditelluride, which successfully gave rise to the desired thiotelluration product (**22a**) in good yield with excellent regio- and stereoselectivities (eq 14).

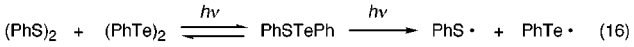


In this thiotelluration, filtering of the UV light is required ($h\nu$ > 400 nm). Irradiation with the light of wavelength over 300 nm causes the photoinduced displacement of the PhTe group of the thiotelluration product (**22a**) with a PhS group, resulting in the formation of *vic*-dithiostyrene as a byproduct.

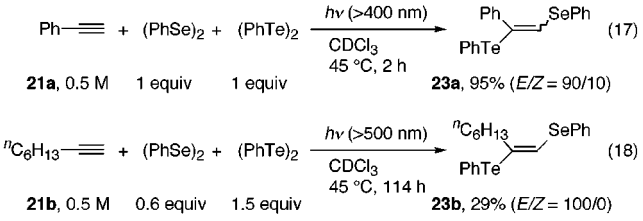
On the other hand, the thiotelluration of 1-octyne (**21b**) required prolonged photoirradiation, providing a stereoisomeric mixture of 1-(phenylthio)-2-(phenyltelluro)-1-octene (**22b**) in moderate yield (eq 15). The difference in reactivity between phenylacetylene and 1-octyne is dependent on the difference in stability between the *π*-vinylic radical (for phenylacetylene) and the *σ*-vinylic radical (for 1-octyne).[18]



A possible pathway for the generation of the thio radical is shown in eq 16. Photoinduced comproportionation takes place between $(PhS)_2$ and $(PhTe)_2$ to give phenyl phenyltelluro sulfide,[19] which undergoes homolysis upon irradiation with visible light to generate a phenylthio radical. Addition of PhS• to acetylenes and the subsequent S_H2 reaction of the thus-formed vinylic radical intermediates with $(PhTe)_2$ (or PhTeSPh) provide the thiotelluration products.



Selenotelluration of Acetylenes. Moreover, an unprecedented $(PhSe)_2$−$(PhTe)_2$ binary system is found to work well for the novel regioselective selenotelluration of aromatic acetylenes (eq 17). Surprisingly, 1,2-bis(phenylseleno)styrene was not formed at all, despite the fact that the kinetic data indicates the rate constant of $(PhTe)_2$ for capturing the carbon radical to be only four times faster than that of $(PhSe)_2$. Contrary to this, the



selenotelluration of aliphatic acetylenes such as 1-octyne (**21b**) provided a mixture of the desired selenotelluration product (**23b**, 29%) and the diselenation product (29%) upon irradiation with the light of wavelength over 500 nm (eq 18). Most probably, the prolonged photoirradiation causes the displacement of the PhTe group of **23b** with a PhSe group.

Conclusion. Highly selective and efficient introduction of two different chalcogeno groups into olefinic or acetylenic bonds has been attained by using dichalcogenide binary systems. The thioselenation with $(PhS)_2$ and $(PhSe)_2$ works well for vinylcyclopropanes to provide allylic sulfides having a phenylselenoethyl group at the *γ* position in high yields. Similarly, the $(PhS)_2$-$(PhTe)_2$ binary system can be employed for the thiotelluration of vinylcyclopropanes. Acetylenes also undergo thiotelluration successfully to afford the corresponding vicinally thiotellurated alkenes in good yields with excellent

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(19) The following two possible pathways are suggested for the comproportionation between $(PhS)_2$ and $(PhTe)_2$: (i) photoinduced homolysis of $(PhTe)_2$ to generate PhTe• and subsequent S_H2 reaction between PhTe• and $(PhS)_2$ to give PhSTePh and PhS•; (ii) photoinduced oxidative addition of $(PhTe)_2$ to $(PhS)_2$ forming "PhS−S(TePh)$_2$−Ph" and subsequent ligand-coupling reaction to give PhSTePh. We cannot specify at present which, if either, of these processes is operative.

regioselectivity. Moreover, a novel selenotelluration of acetylenes also proceeds by using a $(PhSe)_2$-$(PhTe)_2$ binary system. We believe that this study will open up a new field in radical addition chemistry of sulfur, selenium, and tellurium.

Experimental Section

General Comments. Diphenyl disulfide was purified by recrystallization from EtOH. Diphenyl diselenide[20] and diphenyl ditelluride[21] were prepared according to the literature, and were recrystallized from hexane. Vinylcyclopropanes were synthesized according to the literature.[22] Unless otherwise noted, acetylenes and olefins were used commercially and were purified by distillation or recrystallization.

Thioselenation of Vinylcyclopropane. In a Pyrex glass tube were placed vinylcyclopropane (**7a**, 0.5 mmol, 34.1 mg, 1 M), diphenyl disulfide (0.5 mmol, 109.2 mg, 1 M), diphenyl diselenide (0.5 mmol, 156.1 mg, 1 M), and $CDCl_3$ (0.5 mL). The tube was filled with Ar, and the mixture was irradiated at 25 °C for 5 h with a tungsten lamp (500 W). After the reaction was complete, the solvent was evaporated in vacuo, and purification was performed on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model LC-908), equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent, yielding 63 mg (42%) of {1-(phenylseleno)-2-(phenylthio)ethyl}cyclopropane (**8a**) and 60 mg (40%) of 1-(phenylthio)-5-(phenylseleno)-2-pentene (**9a**) as a stereoisomeric mixture (*E*/*Z* = 76/24). For **8a**: a yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.24 (sextet, J = 5.1 Hz, 1 H), 0.48 (sextet, J = 4.8 Hz, 1 H), 0.52−0.60 (m, 1 H), 0.68−0.73 (m, 1 H), 0.87−0.96 (m, 1 H), 2.70 (td, J = 5.1, 8.8 Hz, 1 H), 3.28 (dd, J = 8.8, 13.5 Hz, 1 H), 3.36 (dd, J = 5.1, 13.5 Hz, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 5.57, 8.52, 16.19, 40.91, 49.57, 125.85, 127.90, 128.39, 128.81, 128.94, 129.04, 135.86, 136.53; IR (NaCl) 3072, 1579, 738, 691 cm^{-1}; MS (EI) m/z = 334 (M^+, 6.6); HRMS calcd for $C_{17}H_{18}SSe$ 334.0294, found 334.0302. For **9a**: a yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) [*Z* isomer] δ 2.35 (q, J = 6.5 Hz, 2 H), 2.76 (t, J = 7.5 Hz, 2 H), 3.47 (d, J = 3.4 Hz, 2 H), 5.51−5.60 (m, 2 H), 7.14−7.34 (m, 10 H), 7.43−7.47 (m, 2 H); [*E* isomer] δ 2.35 (q, J = 6.5 Hz, 2 H), 2.81 (t, J = 7.6 Hz, 2 H), 3.48 (d, J = 2.2 Hz, 2 H), 5.51−5.60 (m, 2 H), 7.14−7.34 (m, 10 H), 7.43−7.47 (m, 2 H) {the stereochemistry of **9a** was determined by NOE experiments}; ^{13}C NMR (68 MHz, $CDCl_3$) [*Z* isomer] δ 26.85, 27.78, 31.48, 126.19, 126.46, 126.81, 128.78, 129.03, 130.11, 130.48, 131.44, 132.71, 132.88; [*E* isomer] δ 26.94, 32.81, 36.39, 126.23, 126.74, 126.81, 128.74, 129.00, 130.11, 131.44, 132.42, 132.68, 135.92; IR (NaCl) 1579, 736, 690 cm^{-1}; MS (EI) m/z = 334 (M^+, 55.1); HRMS calcd for $C_{17}H_{18}SSe$ 334.0294, found 334.0286.

2-Methyl-1-(phenylthio)-5-(phenylseleno)-2-pentene (9b). The thioselenation of 2-propenylcyclopropane (**7b**, 0.25 mmol, 20.5 mg, 0.5 M) with diphenyl disulfide (0.25 mmol, 54.6 mg, 0.5 M) and diphenyl diselenide (0.25 mmol, 78.0 mg, 0.5 M) in $CDCl_3$ (0.5 mL) was performed by irradiation at 40 °C for 17 h with a tungsten lamp (500 W) through Pyrex. The residual mixture was purified by a recycling preparative HPLC to provide 78 mg (86%, *E*/*Z* = 67/33) of 2-methyl-1-(phenylthio)-5-(phenylseleno)-2-pentene (**9b**) as a stereoisomeric mixture. Owing to the similar polarities of (*E*)-**9b** and (*Z*)-**9b**, the isolation of each isomers did not meet success, and therefore, the following spectral and analytical data were obtained using the *E*,*Z* mixture. For **9b**: a yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) [*Z* isomer] δ 1.82 (s, 3 H), 2.20 (q, J = 7.5 Hz, 2 H), 2.70 (t, 2 H), 3.45 (s, J = 7.6 Hz, 2 H), 5.28 (t, J = 7.1 Hz, 1 H), 7.14−7.35 (m, 8 H), 7.43−7.46 (m, 2 H). [*E*-isomer] δ 1.69 (s, 3 H), 2.33 (q, J = 7.3 Hz, 2 H), 2.75 (t, J = 7.6 Hz, 2 H), 3.47 (s, 2 H), 5.23 (t, J = 7.3 Hz, 1 H), 7.14−7.35 (m, 8 H), 7.43−7.46 (m, 2 H) {the stereochemistry of **9b** was determined by NOE experiments}; ^{13}C NMR (68 MHz, $CDCl_3$) [*Z* isomer] δ 22.77, 27.16, 28.67, 36.63, 126.64, 126.75, 127.67, 128.75, 128.98, 130.28, 131.09, 132.19, 132.60, 136.35; [*E* isomer] δ 15.30, 26.99, 28.72, 44.18, 126.34, 126.74, 127.26, 128.64, 128.97, 130.25, 130.76, 132.11, 132.59, 136.23; IR (NaCl) 2929, 1578, 736, 690 cm^{-1}; MS (EI) m/z = 348 (M^+, 23); HRMS calcd for $C_{18}H_{20}SSe$ 348.0451, found 348.0453.

2-Phenyl-1-(phenylthio)-5-(phenylseleno)-2-pentene (9c). The thioselenation of 1-styrylcyclopropane (**7c**) was performed by irradiation at 40 °C for 5 h with a tungsten lamp (500 W) through Pyrex. The residual mixture was purified by a recycling preparative HPLC to provide 93 mg (90%, *E*/*Z* = 40/60) of 2-phenyl-1-(phenylthio)-5-(phenylseleno)-2-pentene (**9c**) as a stereoisomeric mixture. For **9c**: a yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) [*Z* isomer] δ 2.48 (q, J = 7.5 Hz, 2 H), 2.87 (t, J = 7.3 Hz, 2 H), 3.90 (s, 2 H), 5.85 (t, J = 7.6 Hz, 1 H), 7.12−7.50 (m, 15 H); [*E* isomer] δ 2.29 (q, J = 7.5 Hz, 2 H), 2.72 (t, J = 7.6 Hz, 2 H), 3.79 (s, 2 H), 5.57 (t, J = 7.6 Hz, 1 H), 7.12−7.50 (m, 15 H) {NOE experiment, irradiation of the allylic protons on the C-1 carbon at δ 3.79 resulted in a 17.4% enhancement of the vinylic signal at δ 5.57}; ^{13}C NMR (68 MHz, $CDCl_3$) [*Z* isomer] δ 26.95, 29.51, 34.71, 126.29, 126.61, 127.28, 128.34, 128.72, 128.81, 129.07, 130.06, 130.75, 131.07, 131.78, 135.98, 136.40, 141.45; [*E* isomer] δ 27.06, 29.51, 43.10, 126.33, 126.61, 126.87, 127.21, 128.20, 128.53, 128.93, 129.47, 130.18, 130.58, 132.42, 136.17, 137.32, 139.14; IR (NaCl) 3055, 1579, 736, 690 cm^{-1}; MS (EI) m/z = 410 (M^+, 20); HRMS calcd for $C_{23}H_{22}SSe$ 410.0607, found 410.0608.

Thioselenation of 1-(*tert*-Butyldimethylsiloxy)vinylcyclopropane (9d). The thioselenation of 1-(*tert*-butyldimethylsiloxy)vinylcyclopropane (**7d**) proceeded smoothly by irradiation at 25 °C for 6 h with a tungsten lamp (500 W) through Pyrex. However, the desired product, 3-(*tert*-butyldimethylsiloxy)-1-(phenylthio)-5-(phenylseleno)-2-pentene (**9d**), underwent isomerization to 3-(*tert*-butyldimethylsiloxy)-1-(phenylthio)-5-(phenylseleno)-3-pentene during the purification by a recycling preparative HPLC. The following NMR data were obtained by the measurement of the crude mixture. For **9d**: ^{1}H NMR (270 MHz, $CDCl_3$) [*Z* isomer] δ 0.19 (s, 6 H), 1.00 (s, 9 H), 2.46 (t, J = 9.2 Hz, 2 H), 3.02 (t, J = 8.6 Hz, 2 H), 3.66 (d, J = 7.3 Hz, 2 H), 4.75 (t, J = 7.3 Hz, 1 H), 7.19−7.42 (m, 6 H), 7.55−7.69 (m, 4 H); [*E* isomer] δ 0.19 (s, 6 H), 1.00 (s, 9 H), 2.48 (t, J = 8.9 Hz, 2 H), 2.99 (t, J = 8.9 Hz, 2 H), 3.51 (d, J = 8.4 Hz, 2 H), 4.88 (t, J = 8.1 Hz, 1 H), 7.19−7.42 (m, 6 H), 7.55−7.69 (m, 4 H). The stereochemistry of **9d** was determined according to the literature's method; the allylic carbon of *trans*-isomer of silyl enol ethers ($R^1-CH_2C(OSiR_3)=CH-R^2$) appears at a higher field, compared to that of *cis*-isomer:[23] ^{13}C NMR (68 MHz, $CDCl_3$) [(*Z*)-**9d**] δ 24.38; [(*E*)-**9d**] δ 28.98.

Ethyl 2-(Phenylseleno)-6-(phenylthio)-4-hexenoate (9e). The thioselenation proceeded almost quantitatively. After treatment with a recycling preparative HPLC, the isolation of *E* isomer was performed by preparative TLC (silica gel, pentane:Et_2O = 20:1 as an eluent). ^{1}H NMR (270 MHz, $CDCl_3$) [*E*-isomer] δ 1.14 (t, J = 7.1 Hz, 3 H), 2.38−2.64 (m, 2 H), 3.48 (d, J = 5.9 Hz, 2 H), 3.54 (dd, J = 6.3, 6.4 Hz, 1 H), 4.04 (q, J = 7.0 Hz, 2 H), 5.45−5.62 (m, 2 H), 7.20−7.37 (m, 8 H), 7.53−7.60 (m, 2 H) {the stereochemistry of (*E*)-**9e** was determined based on the coupling constant between vinylic protons by irradiation of allylic protons at δ 3.40−3.59 (J = 14.6 Hz)}; ^{13}C NMR (68 MHz, $CDCl_3$) [*E* isomer] δ 13.96, 34.42, 36.13, 42.47, 60.90, 126.13, 128.46, 128.46, 128.72, 128.92, 129.78, 129.78, 133.35, 135.71, 135.90, 172.21; IR (NaCl) 3056, 2979, 1728, 738, 691 cm^{-1}; MS (EI) m/z = 406 (M^+, 69); HRMS calcd for $C_{20}H_{22}O_2SSe$ 407.2494, found 406.0494.

2-(Phenylthio)-3-phenyl-6-(phenylseleno)-3-hexene (9f). The thioselenation of 1-cyclopropyl-1-phenylpropene (**7f**) proceeded very slowly upon irradiation with tungsten lamp through Pyrex (35 h) without solvent. The isolation of **9f** (35%, *E*/*Z* = 90/10) was performed by preparative TLC (silica gel, pentane:Et_2O = 100:1 as an eluent). For **9f**: ^{1}H NMR (600

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MHz, $CDCl_3$) [*E* isomer] δ 1.34 (d, J = 7.2 Hz, 3 H), 2.17 (q-like, J = 7.2 Hz, 2 H), 2.66 (t, J = 7.2 Hz, 2 H), 4.03 (q, J = 7.2 Hz, 1 H), 5.51 (t, J = 7.2 Hz, 1 H), 7.14−7.48 (m, 15 H); [*Z* isomer] δ 1.30 (d, J = 6.6 Hz, 3 H), 2.29 (q like, J = 6.6 Hz, 2 H), 2.68 (t, J = 6.8 Hz, 2 H), 4.39 (q, J = 6.6 Hz, 1 H), 5.85 (t, J = 6.6 Hz, 1 H), 7.14−7.48 (m, 15 H) {the stereochemistry of **9a** was determined by NOE experiments}; ^{13}C NMR (100 MHz, $CDCl_3$) [*E* isomer] δ 20.27, 26.90, 29.41, 51.03, 126.38, 126.88, 126.92, 127.81, 128.06, 128.59, 128.81, 129.07, 131.94, 132.44, 133.50, 135.49, 138.27, 142.16 {^{13}C NMR spectrum of (*Z*)-**9f** could not be measured due to the formation of only trace amounts of (*Z*)-**9f**}; IR (NaCl) 3055, 2970, 2923, 1578, 1477, 1439, 738, 696 cm^{-1}; MS (EI) m/z = 424 (M^+, 6.6); Anal. Calcd for $C_{24}H_{24}SSe$: C, 68.07; H, 5.71. Found: C, 68.14; H, 5.81.

Dithiolation of Vinylcyclopropane. The dithiolation of vinylcyclopropane (**7a**, 0.5 mmol, 34.1 mg, 1 M) with diphenyl disulfide (0.5 mmol, 109.2 mg, 1 M) in $CDCl_3$ (0.5 mL) was performed by irradiation at 25 °C for 6 h with a tungsten lamp (500 W) through Pyrex. The residual mixture was purified by a recycling preparative HPLC. For 1,5-bis(phenylthio)-2-pentene (**12a**): ^{1}H NMR (270 MHz, $CDCl_3$) [*E* isomer] δ 2.25−2.32 (m, 2 H), 2.83 (t, J = 7.3 Hz, 2 H), 3.48 (d, J = 5.9 Hz, 2 H), 5.51−5.78 (m, 2 H), 7.12−7.34 (m, 10 H); ^{13}C NMR (68 MHz, $CDCl_3$) [*E*-isomer] δ 31.82, 33.13, 36.31, 125.85, 126.14, 126.92, 128.66, 128.77, 129.18, 130.05, 131.49, 135.84, 136.27; IR (NaCl) 1584, 738, 690 cm^{-1}; MS (EI) m/z = 286 (M^+, 10.2); HRMS calcd for $C_{17}H_{18}S_2$ 286.0850, found 286.0846.

Thiotelluration of Norbornene. In a Pyrex glass tube were placed norbornene (**14**, 0.5 mmol, 47.1 mg, 10 M), diphenyl disulfide (0.5 mmol, 109.2 mg, 10 M), diphenyl ditelluride (0.5 mmol, 204.7 mg, 10 M), and $CDCl_3$ (0.05 mL). The tube was filled with Ar, and the mixture was irradiated at 45 °C for 26 h with a tungsten lamp (200 W) through a filter ($h\nu$ > 400 nm). The solvent was evaporated in vacuo. Purification by preparative TLC on silica gel (hexane) yielded 74% of the thiotelluration product (**15**, exo/endo = 51/49). Isolation of each isomers met success by flash chromatography on silica gel using hexane and then diethyl ether as eluents. For **15**: a pale yellow oil; [exo isomer] ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.13−1.20 (m, 1 H), 1.26−1.33 (m, 2 H), 1.50−1.70 (m, 2 H), 2.13 (d, J = 10.7 Hz, 1 H), 2.47 (br s, 1 H), 2.54 (br s, 1 H), 3.39 (dd, J = 1.7, 8.0 Hz, 1 H), 4.10 (dd, J = 2.2, 8.0 Hz, 1 H), 7.18−7.33 (m, 6 H), 7.45 (d, J = 7.3 Hz, 2 H), 7.77 (d, J = 6.8 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 29.08, 30.30, 34.88, 42.23, 45.82, 45.14, 57.10, 116.43, 126.37, 127.44, 128.93, 129.09, 129.73, 138.08, 138.60; IR (NaCl) 2959, 2867, 1574, 733, 690 cm^{-1}; MS (EI) m/z = 410 (M^+, 30.5); HRMS calcd for $C_{19}H_{20}STe$ 410.0348, found 410.0331; [endo isomer] ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.15−1.27 (m, 1 H), 1.38 (dd, 1 H, J = 1.5, 9.9 Hz), 1.53−1.66 (m, 2 H), 1.67−1.83 (m, 2 H), 2.28 (br s, 1 H), 2.43 (br s, 1 H), 3.10 (dd, 1 H, J = 2.0, 5.4 Hz), 3.35 (dd, 1 H, J = 2.4, 5.4), 7.16−7.28 (m, 8 H), 7.83 (d, J = 7.0 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 28.22, 28.61, 35.57, 36.77, 43.59, 43.66, 59.18, 111.79, 126.27, 127.93, 128.82, 129.11, 130.28, 136.63, 139.76; IR (NaCl) 3053, 2956, 2868, 1574, 733, 690 cm^{-1}; HRMS calcd for $C_{19}H_{20}STe$ 410.0348, found 410.0351.

Thiotelluration of 1-Styrylcyclopropane (7c). In a Pyrex glass tube were placed 1-styrylcyclopropane (**7c**, 0.2 mmol, 28.8 mg, 0.4 M), diphenyl disulfide (0.2 mmol, 43.7 mg, 0.4 M), diphenyl ditelluride (0.2 mmol, 81.9 mg, 0.4 M), and $CDCl_3$ (0.5 mL). The tube was filled with Ar, and the mixture was irradiated at 40 °C for 7 h through a filter ($h\nu$ > 400 nm) with a tungsten lamp (500 W). The solvent was evaporated in vacuo. Purification by a recycling preparative HPLC ($CDCl_3$) yielded 77 mg (84%, E/Z = 14/86) of 2-phenyl-1-(phenylthio)-5-(phenyltelluro)-2-pentene (**17c**): a pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) [*E* isomer] δ 2.40 (q, J = 7.5 Hz, 2 H), 2.71 (t, J = 7.6 Hz, 2 H), 3.78 (s, 2 H), 5.54 (t, J = 7.3 Hz, 1 H), 7.12−7.40 (m, 13 H), 7.55 (d, J = 6.8 Hz, 2 H) {NOE experiment, irradiation of the allyl singlet at δ 3.78 resulted in a 19.4% enhancement of the signal at δ 5.54 (vinyl triplet)}; [*Z* isomer] δ 2.59 (q, J = 7.5 Hz, 2 H), 2.83 (t, J = 7.6 Hz, 2 H), 3.88 (s, 2 H), 5.81 (t, J = 7.3 Hz, 1 H), 7.12−7.33 (m, 11 H), 7.38 (dd, J = 7.8, 8.8 Hz, 2 H), 7.71 (d, J = 6.8 Hz, 2 H) {NOE experiment, irradiation of the allyl singlet at δ 3.88 resulted in a 5.3% enhancement of the signal at δ 2.59 (allyl quartet)}; ^{13}C NMR (68 MHz, $CDCl_3$) [*Z* isomer] δ 7.08, 30.86, 34.61, 111.47, 126.22, 126.54, 127.21, 127.58, 128.30, 128.77, 129.15, 130.68, 132.91, 135.37, 136.36, 138.47, 141.41; IR (NaCl) 3055, 1574, 733, 691 cm^{-1}; MS (EI) m/z = 460 (M^+, 30); HRMS calcd for $C_{23}H_{22}STe$ 460.0504, found 460.0507.

Thiotelluration of Phenylacetylene (21a). In a Pyrex glass tube were placed phenylacetylene (**21a**, 0.25 mmol, 25.5 mg, 1 M), diphenyl disulfide (0.25 mmol, 54.6 mg, 1 M), diphenyl ditelluride (0.25 mmol, 102.4 mg, 1 M), and $CDCl_3$ (0.25 mL). The tube was filled with Ar, and the mixture was irradiated at 45 °C for 1 h through a filter ($h\nu$ > 400 nm) with a tungsten lamp (500 W). The solvent was evaporated in vacuo, and purification by preparative TLC on silica gel (hexane/Et_2O = 10/1) yielded 86 mg (80%, E/Z = 100/0) of α-(phenyltelluro)-β-(phenylthio)styrene (**22a**): a pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) [*E* isomer] δ 7.00 (s, 1 H), 7.18−7.36 (m, 12 H), 7.41−7.44 (m, 2 H), 7.72 (d-like, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) [*E* isomer] δ 114.74, 115.51, 126.90, 127.80, 128.05, 128.08, 128.21, 128.72, 129.05, 129.42, 135.04, 135.72, 138.36, 141.26; IR (NaCl) 3051, 3054, 1574, 757, 733, 706, 690 cm^{-1}; MS (EI), m/z = 418 (M^+, 35); HRMS calcd for $C_{20}H_{16}STe$ 418.0035, found 418.0023. On the other hand, prolonged irradiation led to the isomerization of (*E*)-**22a** to (*Z*)-**22a**. The NMR spectral data of (*Z*)-**22a** are listed as follows: ^{1}H NMR (270 MHz, $CDCl_3$) [*Z* isomer] δ 7.13 (s, 1 H), 7.18−7.36 (m, 12 H), 7.41−7.44 (m, 2 H), 7.55 (d, J = 7.8 Hz, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) [*Z* isomer] δ 114.94, 122.76, 127.21, 127.27, 127.54, 128.38, 129.10, 129.21, 129.47, 129.96, 135.36, 136.21, 137.70, 142.50.

1-(Phenylthio)-2-(phenyltelluro)-1-octene (22b). The reaction of 1-octyne (**21b**, 0.25 mmol, 27.5 mg, 0.5 M) with diphenyl disulfide (0.25 mmol, 54.6 mg, 0.5 M) and diphenyl ditelluride (0.25 mmol, 102.4 mg, 0.5 M) in $CDCl_3$ (0.5 mL) was performed by irradiation at 45 °C for 32 h with a tungsten lamp (500 W) through a filter ($h\nu$ > 400 nm). The residual mixture was purified by a recycling preparative HPLC ($CDCl_3$) to provide 64 mg (60%, E/Z = 55/45) of 1-(phenylthio)-2-(phenyltelluro)-1-octene (**22b**) as a mixture of stereoisomers accompanied by 9% of a disulfide adduct as a byproduct. Isolation of (*E*)-**22b** met success by preparative TLC on silica gel, whereas the isolation of (*Z*)-**22b** was failed owing to the similar polarities of (*Z*)-**22b** and $(PhTe)_2$ (the obtained (*Z*)-**22b** was contaminated by small amounts of the ditelluride. For (*E*)-**22b**: a pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.87 (t, J = 6.8 Hz, 3 H), 1.28 (m, 6 H), 1.54 (m, 2 H), 2.41 (t, J = 7.3 Hz, 2 H), 6.33 (s, 1 H), 7.20−7.42 (m, 10 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.07, 22.57, 28.16, 28.77, 31.59, 32.88, 123.86, 126.38, 127.33, 128.60, 129.05, 129.13, 134.50, 134.07, 136.13, 138.47; IR (NaCl) 3058, 2954, 2928, 2855, 1583, 737, 690 cm^{-1}; MS (EI) m/z = 426 (M^+, 46); HRMS calcd for $C_{20}H_{24}STe$ 426.0661, found 426.0647. The NMR spectral data of (*Z*)-**22b** are listed as follows: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.87 (t, J = 6.8 Hz, 3 H), 1.28 (m, 6 H), 1.54 (m, 2 H), 2.52 (t, J = 7.3 Hz, 2 H), 6.76 (s, 1 H), 7.20−7.42 (m, 10 H) {NOE experiment, irradiation of the allyl triplet at δ 2.52 resulted in a 4.9% enhancement of the signal at δ 6.76 (vinyl singlet)}; ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.07, 22.57, 28.60, 29.17, 31.65, 37.77, 121.00, 126.58, 127.97, 128.95, 129.10, 129.44, 133.00, 134.48, 135.95, 140.41.

Selenotelluration of Phenylacetylene (21a). In a Pyrex glass tube, were placed phenylacetylene (**21a**, 0.25 mmol, 25.5 mg, 0.5 M), diphenyl diselenide (0.25 mmol, 78.0 mg, 0.5 M), diphenyl ditelluride (0.25 mmol, 102.4 mg, 0.5 M), and $CDCl_3$ (0.5 mL). The tube was filled with Ar, and the mixture was irradiated at 45 °C for 2 h through a filter ($h\nu$ > 400 nm) with a tungsten lamp (500 W). The residual mixture was purified by a recycling preparative HPLC ($CDCl_3$) to provide 110 mg (95%, E/Z = 90/10) of α-(phenyltelluro)-β-(phenylseleno)-styrene (**23a**): a pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) [*E* isomer] δ 7.00 (s, 1 H), 7.07 (d, J = 7.3 Hz, 2 H), 7.13−7.36 (m, 10 H), 7.41−7.46 (m, 2 H), 7.72 (d, J = 8.3 Hz, 1 H); [*Z* isomer] δ 7.03 (s, 1 H), 7.13−7.36 (m, 12 H), 7.41−7.46 (m, 2 H), 7.55 (d, J = 7.8 Hz, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) [*E*

isomer] δ 115.52, 127.39, 127.94, 128.24, 128.27, 128.35, 128.64, 129.18, 129.22, 129.45, 132.13, 132.22, 132.90, 138.50; [*Z* isomer] δ 115.58, 127.28, 127.56, 127.71, 128.06, 128.09, 128.12, 129.42, 131.13, 131.74, 133.10, 137.20, 137.84, 142.39; IR (NaCl) 3052, 2920, 1574, 1536, 732, 701, 690, 670, 647, 615 cm^{-1}; MS (EI) m/z = 466 (M^+, 4); HRMS calcd for $C_{20}H_{16}SeTe$ 465.9466, found 465.9452.

1-(Phenylseleno)-2-(phenyltelluro)-1-octene (23b). In a Pyrex glass tube were placed 1-octyne (**21b**, 0.25 mmol, 27.5 mg, 0.5 M), diphenyl diselenide (0.15 mmol, 46.8 mg, 0.3 M), diphenyl ditelluride (0.38 mmol, 155.6 mg, 0.76 M), and $CDCl_3$ (0.5 mL). The tube was filled with Ar, and the mixture was irradiated at 45 °C for 114 h through a filter (>500 nm) with a tungsten lamp (500 W). The residual mixture was purified by a recycling preparative HPLC ($CDCl_3$) to provide 34 mg (29%, E/Z = 100/0) of 1-(phenylseleno)-2-(phenyltelluro)-1-octene (**23b**), accompanied by 29% of a diselenide adduct as a byproduct. For **23b**: a pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) [*E* isomer] δ 0.87 (t, J = 6.8 Hz, 3 H), 1.27 (m, 4 H), 1.54 (m, 4 H), 2.45 (t, J = 7.3 Hz, 2 H), 6.97 (s, 1 H), 7.21−7.30 (m, 6 H), 7.41−7.44 (m, 2 H), 7.76 (d, J = 6.4 Hz, 2 H) {NOE experiment, irradiation of the allyl triplet at δ 2.45 resulted in no enhancement of the signal at δ 6.97 (vinyl singlet)}; ^{13}C NMR (68 MHz, $CDCl_3$) [*E* isomer] δ 14.06, 22.57, 28.58, 29.08, 31.63, 39.84, 117.77, 121.37, 127.13, 127.99, 128.95, 129.24, 129.24, 129.46, 131.96, 138.53; IR (NaCl) 2925, 2853, 1574, 732, 690 cm^{-1}; MS (EI) m/z = 474 (M^+, 15); HRMS calcd for $C_{20}H_{24}SeTe$ 474.0106, found 474.0115.

Acknowledgment. This research was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas (no. 09239102) from the Ministry of Education, Science and Culture, Japan. Thanks are due to the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for assistance in obtaining mass spectra with a JEOL JMS-DX303 instrument and elemental analyses.

Supporting Information Available: Spectral data (24 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.

JO981053Q