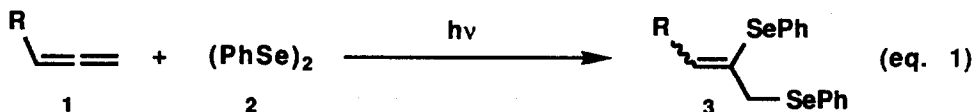


PHOTO-INITIATED ADDITION OF DIPHENYL DISELENIDE TO ALLENES

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
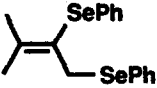

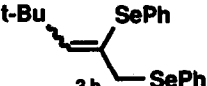

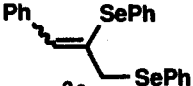

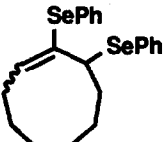

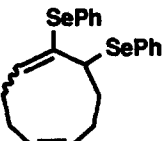

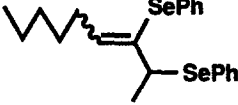
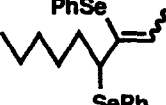
Summary: Free-radical addition of diphenyl diselenide **2** to allenes **1** took place under irradiation through Pyrex with tungsten lamp to provide 1-(phenylselenomethyl)vinyl selenides **3** in excellent yields.

Free-radical additions of heteroatom centered radicals to allenes have excited interest of synthetic organic chemists, because the reactions can be regarded as one of the most straightforward access to allylic and/or vinylic heteroatom compounds.¹ As to chalcogen-centered radicals, it is well-documented that thiols² and selenols³ add to allenes *via* a radical chain mechanism involving thio and seleno radicals as the key species.⁴ The photolysis of disulfides and diselenides has proved to be a clean source of thio and seleno radicals,⁵ but strange to say is that there exists no report up to date concerning the radical addition of disulfides and diselenides to allenes.⁶ The rate constants for the S_H2 and hydrogen abstraction reactions of primary alkyl radicals with diphenyl disulfide and benzenethiol are estimated to be 7.6×10^4 and 8×10^7 L·mol⁻¹·s⁻¹ (in benzene at 80°C), respectively, by using 5-hexenyl radical "clock".⁷ Presumably, this lower capturing ability of disulfides may affect the inefficiency of the desired addition to allenes. Contrary to this, diphenyl diselenide exhibits reactivity comparable to that of benzenethiol, toward carbon radicals (1.2×10^7 L·mol⁻¹·s⁻¹),⁷ which means that the addition of diselenides to allenes may proceed by a radical mechanism. As expected, the radical addition of diselenides to allenes has really been attained upon irradiation with visible light (eq. 1).



A CDCl_3 solution of allenes **1** (0.5 mmol) and diphenyl diselenide **2** (0.5 mmol) in a sealed tube (Pyrex), was irradiated with tungsten lamp (500 W) at 15°C for 1 h. Purification by preparative TLC (silica gel, n-hexane) provided 1-(phenylselenomethyl)vinyl selenides **3** in excellent yields. Representative results are shown in Table 1. The addition to terminal allenes (**1a**, **1b**, and **1c**) was quite regioselective, resulting

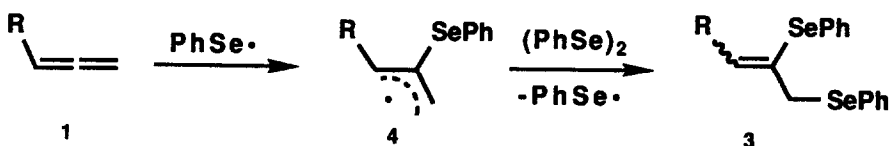
Table 1. Photo-Initiated Addition of Diphenyl Diselenide to Allenes^a

entry	substrate	product	yield, % ^{b, c}	mp., $^\circ\text{C}$
1	 1a	 3a	86 (98)	oil
2	 1b	 3b	82 (90) E/Z = 28/72	oil
3	 1c	 3c	(78) E/Z = 33/67	oil
4	 1d	 3d	84 (100) E/Z = 91/9	87-87.5
5	 1e	 3e	96 (100) ^d E/Z = 100/0	127-127.5
6	 1f	 3f (42) E/Z = 11/89	 3f' (51) E/Z = 15/85	oil

^aReaction conditions: $(\text{PhSe})_2$ (0.5 mmol), allene (0.5 mmol), CDCl_3 (0.5 mL), hv (tungsten lamp (500 W), Pyrex), 15°C , 1 h. ^bIsolated yield (NMR yield). ^cSpectral analyses of some representative adducts are listed in the ref. 9. ^d3 min.

in the predominant formation of 1,2-adducts to the terminal carbon-carbon double bond (3a, 3b, and 3c). The addition also proceeded well, when run with monochromatic light at 365 nm⁸ (for example, starting from 1b, 85 % of 3b [E/Z = 27/73] was obtained by irradiation for 20 h). No reaction took place in the absence of light. The reaction was not restricted to terminal allenes, but rather tolerated inner and cyclic allenes (1d, 1e, and 1f). The assignments of the stereochemistry were confirmed unambiguously by the observed NOE enhancements of vinyl singlet upon irradiation of the protons of the allylic methylene. Allene 1e having a carbon-carbon double bond underwent chemoselective addition to the allene moiety. It is of interest to note that the addition to 1e went completion within 3 minutes on account of the ring strain.

In sharp contrast to the addition of diselenide, the attempted reaction of diphenyl disulfide with allenes hardly proceeded under similar reaction conditions, as predicted. Prolonged reaction time (24 h) led to disappearance of the starting allene, but the reaction provided unidentified complex mixtures, which did not include the desired adduct. It is conceivable that the lower capturing ability of disulfide toward carbon radicals may cause complexity of the reaction of disulfide with allenes. Clearly, in the case of diselenide, other possible competing reactions such as polymerization, dimerization, or disproportionation were prevented by diphenyl diselenide. The success in the addition to allenes is most probably due to the excellent capturing ability of diselenide toward the allylic radical intermediate (4), the formation of which occurred by the attack of phenylseleno radical to the central carbon of allenes.



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4. Interestingly, thiyl radicals attacked mostly at the terminal carbon to give allylic sulfides, while the attack of seleno radicals occurred predominantly at the center carbon to provide vinylic selenides.¹⁻³
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8. Diphenyl diselenide exhibits its absorption maximum in near ultraviolet ($\lambda_{\max} = 330 \text{ nm}$, $\epsilon_{\max} = 10^3$), see: Ito, O. *J. Am. Chem. Soc.* **1983**, *105*, 850.
9. Spectral data of some adducts (**3a**, **3b**, **3e**, **3f**, and **3f'**) are as follows.
- 3a:** $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 1.64 (s, 3H), 1.97 (s, 3H), 3.88 (s, 2H), 7.20~7.49 (m, 10H); $^{13}\text{C NMR}$ (68 MHz, CDCl_3) δ 20.55, 25.76, 34.64 ($\text{CH}_2\text{-SePh}$), 122.07 ($=\text{C-SePh}$), 125.97, 126.45, 128.69, 129.04, 130.11, 131.28, 131.55, 134.53, 141.86 ($\text{Me}_2\text{C}=\text{C}$); IR (NaCl) 3060, 1640, 1450, 1375, 740, 700 cm^{-1} ; MS, $m/e = 382$ (M^+ , 45). Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{Se}_2$: C, 53.72; H, 4.74. Found : C, 53.98; H, 4.89.
- 3b:** [Z-isomer], $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 1.09 (s, 9H), 3.53 (s, 2H), 5.75 (s, 1H), 7.23~7.46 (m, 10H); $^{13}\text{C NMR}$ (68 MHz, CDCl_3) δ 30.48, 33.58, 39.37 ($\text{CH}_2\text{-SePh}$), 125.97 ($=\text{C-SePh}$), 127.15, 127.50, 128.76, 129.15, 129.68, 129.88, 133.12, 135.05, 147.30 ($\text{CH}=\text{C}$); IR (NaCl) 3070, 2956, 2864, 1577, 735, 691 cm^{-1} ; MS, $m/e = 410$ (M^+ , 16). Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{Se}_2$: C, 55.89; H, 5.43. Found : C, 56.02; H, 5.59. NOE study: Irradiation of allylic singlet at δ 3.53 resulted in 9 % increase at δ 5.75 (vinyl singlet). [E-isomer], $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 1.10 (s, 9H), 3.95 (s, 2H), 6.08 (s, 1H), 7.23~7.46 (m, 10H); $^{13}\text{C NMR}$ (68 MHz, CDCl_3) δ 30.69, 32.53 ($\text{CH}_2\text{-SePh}$), 35.49, 127.01, 127.31, 127.37 ($=\text{C-SePh}$), 128.92, 129.10, 130.65, 131.03, 132.48, 133.82, 150.49 ($\text{CH}=\text{C}$).
- 3e:** [E-isomer], $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 1.80~2.13 (m, 8H), 4.45 (dd, 1H, $J = 12.5, 3.1 \text{ Hz}$), 5.47 (dt, 1H, $J = 11.0, 5.8 \text{ Hz}$), 5.78 (m, 2H), 7.22~7.28 (m, 6H), 7.52~7.62 (m, 4H); $^{13}\text{C NMR}$ (68 MHz, CDCl_3) δ 25.63, 25.87, 28.16, 35.38, 45.29 (CH-SePh), 127.07, 127.54, 128.71, 129.01, 129.52, 130.14 ($=\text{CH}$), 131.08 ($=\text{CH}$), 131.25, 133.50, 135.14, 135.18 ($=\text{C-SePh}$), 138.07 ($\text{CH}=\text{C-SePh}$); IR (KBr) 3052, 2933, 2913, 2852, 1612, 1578, 1479, 1437, 999, 907, 844, 732, 688 cm^{-1} ; MS, $m/e = 434$ (M^+ , 13). Anal. Calcd for $\text{C}_{21}\text{H}_{22}\text{Se}_2$: C, 58.34; H, 5.13. Found : C, 58.04; H, 5.46.
- 3f:** [Z-isomer], $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 0.82 (t, 3H, $J = 7.0 \text{ Hz}$), 1.07~1.36 (m, 8H), 1.56 (d, 3H, $J = 5.7 \text{ Hz}$), 2.13 (m, 2H), 4.01 (q, 1H, $J = 6.7 \text{ Hz}$), 5.80 (t, 1H, $J = 7.0 \text{ Hz}$), 7.18~7.46 (m, 10H); $^{13}\text{C NMR}$ (68 MHz, CDCl_3) δ 13.97, 21.54, 22.45, 28.52, 31.34, 31.90, 48.80 (CH-SePh), 126.18, 127.80, 128.74, 129.03, 130.90, 131.66 ($=\text{C-SePh}$), 134.31, 134.73, 135.73, 137.93 ($\text{CH}=\text{C}$); IR (NaCl) 3053, 2954, 2924, 2854, 1577, 1436, 734, 690 cm^{-1} ; MS, $m/e = 438$ (M^+ , 16). Anal. Calcd for $\text{C}_{21}\text{H}_{26}\text{Se}_2$: C, 57.80; H, 6.01. Found : C, 57.93; H, 6.13. NOE study: Irradiation of vinyl triplet at δ 5.80 resulted in 8 % increase at δ 4.01 (allylic quartet). [E-isomer]: $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 4.54 (q, 1H, $J = 7.0 \text{ Hz}$).
- 3f':** [Z-isomer], $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 0.82 (t, 3H, $J = 7.0 \text{ Hz}$), 1.07~1.36 (m, 8H), 1.66 (d, 3H, $J = 6.7 \text{ Hz}$), 1.84 (m, 2H), 3.87 (t, 1H, $J = 6.7 \text{ Hz}$), 5.73 (q, 1H, $J = 7.0 \text{ Hz}$), 7.18~7.46 (m, 10H); $^{13}\text{C NMR}$ (68 MHz, CDCl_3) δ 13.97, 17.71, 22.47, 27.85, 31.37, 34.69, 55.65 (CH-SePh), 126.18, 127.69, 128.65, 128.97, 129.62, 129.80, 131.05, 131.27 ($=\text{C-SePh}$), 132.35 ($\text{CH}=\text{C}$), 135.67. NOE study: Irradiation of vinyl quartet at δ 5.73 resulted in 5 % increase at δ 3.87 (allylic triplet). [E-isomer]: $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 4.40 (dd, 1H, $J = 9.3, 5.6 \text{ Hz}$).