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A Novel Thermal Addition of Diaryl Diselenides to Acetylenes

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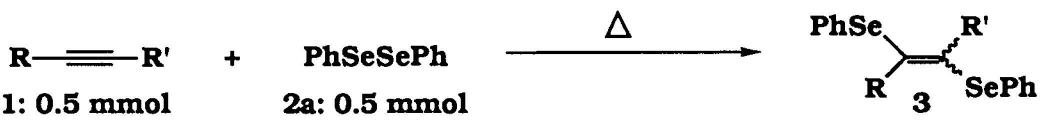
When diphenyl diselenide is heated at 150-180 °C in the presence of acetylenes, an acetylene insertion reaction into the Se-Se bond of the diselenide takes place to provide *vic*-bis(phenylseleno)alkenes in moderate to high yields.

The thermolysis of organic diselenides is generally discussed in terms of two competing radical type scissions, i.e., the C-Se bond fission and the Se-Se bond fission.[1] The former fission to give carbon-centered radicals requires the higher activation energy, and is of importance for the carbon-carbon bond formation by radical coupling reaction.[1d,2] In contrast, the latter fission to give selenium-centered radicals takes place with the lower activation energy, but the synthetic application of this thermolysis *via* the Se-Se bond fission remains undeveloped, probably due to the low reactivity of seleno radicals and the recombination reaction to re-form the starting diselenides.[3] Herein we report that the thermolysis of diaryl diselenides in the presence of acetylenes leads to a novel thermal addition of diaryl diselenides to acetylenes.[4,5]

When a mixture of diphenyl diselenide **2a** (0.5 mmol) and 1-octyne **1a** (0.5 mmol) was heated at 150 °C for 10 h in the dark, the addition of **2a** to **1a** took place to give 1,2-bis(phenylseleno)-1-octene **3a** in 81% yield. Similar conditions could be employed with propargyl alcohol **1b** and phenylacetylene **1c**, whereas the reaction of inner acetylenes required the heating at 170-180 °C. This insertion reaction was generally sluggish below 120 °C, and hardly proceeded below 100 °C (e.g., 140 °C, 5 h: 42% of **3a**; 120 °C, 5 h: 11%; 100 °C, 5 h: 3%). Exceptionally, the reaction with phenylacetylene **1c** occurred upon heating at 80 °C: the reaction of **1c** with (p-Me-$C_6H_4Se)_2$ in the refluxing benzene for 13 h produced the corresponding adduct in 76% yield. The high

Table 1. Thermal Addition of Diphenyl Diselenide to Acetylenes[a]

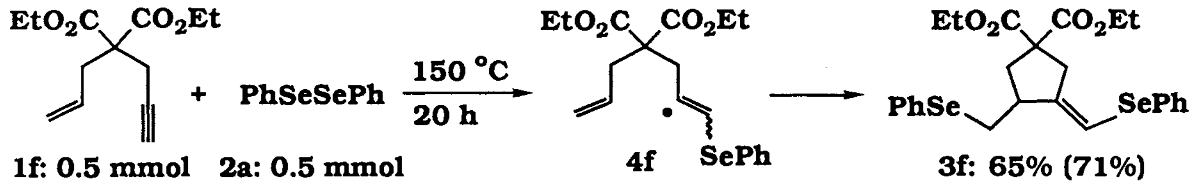


	R	R'	Temp/°C	Time/h	Yield/%[b]	E/Z
a	n-C_6H_{13}	H	150	10	74 (81)	92/8
b	$HOCH_2$	H	150	10	62 (71)	80/20
c	Ph	H	150	5	74 (80)	>95/5
d	Ph	n-C_3H_7	170	20	59 (69)	>95/5
e	n-C_3H_7	n-C_3H_7	180	24	19 (23)	>95/5

a) Representative spectral data for some adducts are shown in Ref. 8.
b) Isolated yield (NMR yield).

reactivity of **1c** is probably because vinyl radicals bearing phenyl group at the α position of the radical center, which may form π-radicals,[6a)] are much stable than usual vinyl radicals as σ-radicals.[6b,7)]

Next, the thermal reaction of 1-octyne **1a** with some diaryl diselenides ($(p\text{-R-}C_6H_4Se)_2$, R = H, Me, CF_3) at 150 °C for 5 h was examined, which resulted in the formation of corresponding adducts in 57% (R = H), 48% (R = Me), and 76% (R = CF_3) yields, respectively. These results indicate that electron-attracting substituents accelerate the reaction, and are consistent with the electrophilic nature of arylseleno radicals.[3)] Finally, the radical cyclization of enyne **1f** by thermolysis of diselenide **2a** was demonstrated to provide the five-membered cyclic product **3f** successfully.



1f: 0.5 mmol **2a**: 0.5 mmol **4f** **3f**: 65% (71%)

References

1) a) L. Henriksen, "The Chemistry of Organic Selenium and Tellurium Compounds," ed by S. Patai, John Wiley & Sons Ltd., New York (1987), Vol. 2, Chap. 10; b) M. A. London, *Ann. N. Y. Acad. Sci.*, **192**, 132 (1972); c) T. Hirabayashi, S. Mohmand, and H. Bock, *Chem. Ber.*, **115**, 483 (1982); d) J. Y. C. Chu and J. W. Lewicki, *J. Org. Chem.*, **42**, 2491 (1977); e) L. A. Ostroukhova, N. A. Korchevin, E. N. Deryagina, and M. G. Voronkov, *Zh. Obshch. Khim.*, **58**, 2171 (1988).

2) H. Higuchi, T. Otsubo, F. Ogura, H. Yamaguchi, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **55**, 182 (1982). *Cf.* K. Kondo, N. Sonoda, K. Yoshida, M. Koishi, and S. Tsutsumi, *Chem. Lett.*, **1972**, 401.

3) O. Ito, *J. Am. Chem. Soc.*, **105**, 850 (1983) and references cited therein.

4) The reaction of diphenyl diselenide with acetylenedicarboxylate proceeded very slowly in refluxing benzene in the dark (8% for 30 h): T. G. Back and M. V. Krishna, *J. Org. Chem.*, **53**, 2533 (1988).

5) The photo-initiated radical addition of diphenyl diselenide to acetylenes, see: A. Ogawa, H. Yokoyama, K. Yokoyama, T. Masawaki, N. Kambe, and N. Sonoda, *J. Org. Chem.*, **56**, 5721 (1991).

6) a) L. A. Singer and J. Chen, *Tetrahedron Lett.*, **1969**, 4849; b) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

7) The formation of vinyl radical by the attack of PhSe• to acetylene appears to be the rate-determining step. See, G. A. Russell and H. Tashtoush, *J. Am. Chem. Soc.*, **105**, 1398 (1983) and Ref. 3.

8) **3b**: ^{1}H NMR (270 MHz, $CDCl_3$) [*E*-isomer]: δ 2.35 (t, 1H, J = 8.0 Hz), 4.34 (d, 2H, J = 8.0 Hz), 6.97 (s, 1H), 7.26-7.53 (m, 10H). [Z-isomer]: δ 1.82 (brs, 1H), 4.07 (s, 2H), 7.20-7.25 (m, 6H), 7.32 (s, 1H), 7.45-7.53 (m, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) [*E*-isomer]: δ 64.57, 126.83, 127.53, 127.69, 129.34, 129.42, 130.83, 131.73, 132.14, 132.32, 132.93. [Z-isomer]: δ 67.56, 127.54, 127.83, 128.57, 129.35, 129.41, 130.28, 132.10, 132.36, 133.18, 133.51.

3d: ^{1}H NMR (270 MHz, $CDCl_3$) [*E*-isomer]: δ 0.87 (t, 3H, J = 8.0 Hz), 1.61 (m, 2H, J = 8.0 Hz), 2.63 (t, 2H, J = 8.0 Hz), 7.09-7.47 (m, 15H). [Z-isomer]: δ 0.55 (t, 3H), 1.31-1.47 (m, 2H), 2.11 (t, 2H), 7.09-7.47 (m, 15H); ^{77}Se NMR (51.5 MHz, $CDCl_3$, Me_2Se) [*E*-isomer]: δ 436.15 ($J_{Se\text{-}Se}$ = 19 Hz), 480.75 ($J_{Se\text{-}Se}$ = 19 Hz). [Z-isomer]: δ 411.50 ($J_{Se\text{-}Se}$ = 101 Hz), 508.40 ($J_{Se\text{-}Se}$ = 101 Hz).

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