

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-C₆H₄Se)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)}

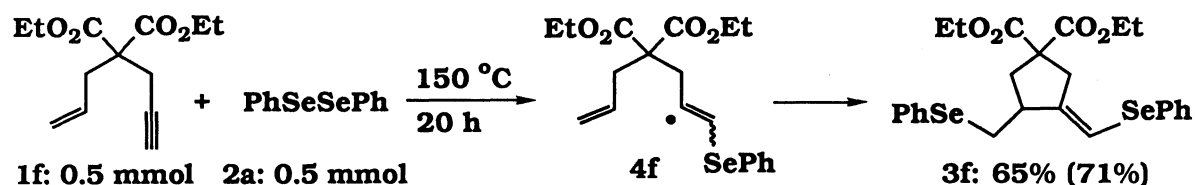
$\text{R} \equiv \text{R}' + \text{PhSeSePh} \xrightarrow{\Delta} \text{PhSe} \begin{array}{c} \diagup \text{R}' \\ \diagdown \text{R} \end{array} \text{SePh}$					
1: 0.5 mmol	2a: 0.5 mmol				
R	R'	Temp/°C	Time/h	Yield/%^{b)}	E/Z
a <i>n</i> -C ₆ H ₁₃	H	150	10	74 (81)	92/8
b HOCH ₂	H	150	10	62 (71)	80/20
c Ph	H	150	5	74 (80)	>95/5
d Ph	<i>n</i> -C ₃ H ₇	170	20	59 (69)	>95/5
e <i>n</i> -C ₃ H ₇	<i>n</i> -C ₃ H 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 ($(p\text{-R-C}_6\text{H}_4\text{Se})_2$, R = H, Me, CF₃) 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 = CF₃) 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.



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- 8) **3b**: ¹H NMR (270 MHz, CDCl₃) [*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); ¹³C NMR (68 MHz, CDCl₃) [*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: ¹H NMR (270 MHz, CDCl₃) [*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); ⁷⁷Se NMR (51.5 MHz, CDCl₃, Me₂Se) [*E*-isomer]: δ 436.15 ($J_{\text{Se-Se}} = 19$ Hz), 480.75 ($J_{\text{Se-Se}} = 19$ Hz). [*Z*-isomer]: δ 411.50 ($J_{\text{Se-Se}} = 101$ Hz), 508.40 ($J_{\text{Se-Se}} = 101$ Hz).

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