

# Synthesis of Allyl Selenides Promoted by an Sm/ZnCl<sub>2</sub> Bimetal System in the Presence of Water

ZHENG, Yun-Fa<sup>a</sup>(郑云法)    GUO, Hong-Yun<sup>b,c</sup>(郭红云)    ZHANG, Yong-Min<sup>\*,b,d</sup>(张永敏)

<sup>a</sup> Department of Chemistry, Lishui Teachers College, Lishui, Zhejiang 323000, China

<sup>b</sup> Department of Chemistry, Zhejiang University (Xixi Campus), Hangzhou, Zhejiang 310028, China

<sup>c</sup> Department of Chemistry, Zhejiang Normal University, Jinhua, Zhejiang 321004, China

<sup>d</sup> Laboratory of Organometallic Chemistry, Chinese Academy of Sciences, Shanghai, 200032, China

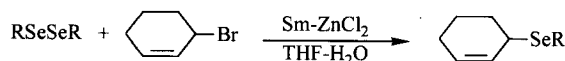
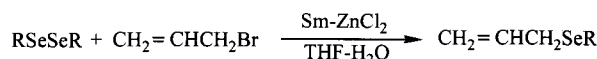
The reaction of diselenides with allylic bromides proceeded smoothly in an Sm/ZnCl<sub>2</sub> bimetal system in THF-H<sub>2</sub>O to afford allyl selenides in good yield.

**Keywords** Allyl selenide, bimetal system, diselenide

Allyl selenides are important intermediates in organic synthesis. In allylic selenides, allylic anions are stabilized by the seleno group and can be attacked by nucleophiles regioselectively.<sup>1</sup> [3, 3] sigmatropic rearrangement leads to a heterocyclic compound containing selenium.<sup>2</sup> Allyl selenides also cause reductive allyl homocoupling in the presence of a catalyst.<sup>3</sup> It is possible to carry out oxidation reaction of allyl selenides.<sup>4</sup> Allyl selenides are usually prepared by the reaction of diselenides with samarium diiodide in the presence of a palladium catalyst<sup>5</sup> or SnCl<sub>2</sub>,<sup>6</sup> or by the reaction of sodium borohydride with sodium salt of seleno phenol in absolute ethanol under nitrogen.<sup>7</sup> Recently, our group has reported the synthesis of allyl selenides by using organosamarium reagent.<sup>8</sup> But some of the methods have the disadvantage of using strong base, poisonous reagents or organometallic compounds under anhydrous conditions. To our knowledge, several bimetal systems for the allylation of aldehydes have been reported.<sup>9</sup> But no study of a bimetal system for synthesizing allyl selenides has ever been reported. Herein we wish to report our preliminary results on the preparation of allyl selenides promoted by Sm/ZnCl<sub>2</sub> bimetal system in THF-H<sub>2</sub>O mixed solvent

(Scheme 1).

Scheme 1



## Results and discussion

First, the reactions of diselenides with allyl bromides were examined in the presence of water and the results are shown in Table 1. In our experiments, it were found that the reactions could be carried out in an Sm/ZnCl<sub>2</sub> bimetal system in THF-H<sub>2</sub>O, the desired allyl selenides were obtained in 52–83% yields. Evidently no allyl selenides were formed in THF-H<sub>2</sub>O using Sm alone; and the reactions did not take place at all in the absence of Sm.


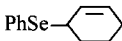

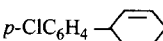

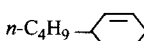
Secondly, the scope and versatility of the present reactions were investigated by using various substrates. As shown in Table 1, not only aromatic diselenides but also aliphatic diselenides reacted with allylic bromides smoothly to afford the corresponding allyl selenides, but the isolated yields of the aliphatic ones were lower than those of the aromatic ones and a longer reaction time was needed. All the products were characterized by their <sup>1</sup>H NMR and IR spectra.

\* E-mail: yminzhang@mail.hz.zj.cn

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**Table 1** Synthesis of allyl selenides in THF-H<sub>2</sub>O

Entry	Allylic bromide	RSeSeR	Reaction time (h)	Products	Yield <sup>a</sup> (%)
1	CH <sub>2</sub> = CHCH <sub>2</sub> Br	PhSeSePh	2	PhSeCH <sub>2</sub> CH = CH <sub>2</sub>	80
2	CH <sub>2</sub> = CH <sub>2</sub> CH <sub>2</sub> Br	( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Se) <sub>2</sub>	2	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SeCH <sub>2</sub> CH = CH <sub>2</sub>	76
3	CH <sub>2</sub> = CH <sub>2</sub> CH <sub>2</sub> Br	( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> Se) <sub>2</sub>	2	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> SeCH <sub>2</sub> CH = CH <sub>2</sub>	83
4	CH <sub>2</sub> = CH <sub>2</sub> CH <sub>2</sub> Br	( <i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Se) <sub>2</sub>	2	<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SeCH <sub>2</sub> CH = CH <sub>2</sub>	74
5	CH <sub>2</sub> = CHCH <sub>2</sub> Br	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> Se) <sub>2</sub>	5	C <sub>4</sub> H <sub>9</sub> SeCH <sub>2</sub> CH = CH <sub>2</sub>	52
6		(PhSe) <sub>2</sub>	2	PhSe- 	71
7		( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> Se) <sub>2</sub>	2	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> - 	74
8		( <i>n</i> -C <sub>4</sub> H <sub>9</sub> Se) <sub>2</sub>	5	<i>n</i> -C <sub>4</sub> H <sub>9</sub> - 	57

<sup>a</sup> isolated yield.

## Experimental

<sup>1</sup>H NMR spectra were recorded on a PMX-60 spectrometer using TMS as internal standard. IR spectra were determined on a PE-683 spectrometer. Diselenides were prepared by the known method.<sup>10</sup> Tetrahydrofuran, zinc dichloride, and allylic bromides are commercially available and were used without further purification.

### Synthesis of allyl selenide

To a round bottomed flask fitted with a reflux condenser were added samarium powder (0.15 g, 1 mmol), ZnCl<sub>2</sub> (0.14 g, 1 mmol), diselenide (1 mmol), allylic bromide (3 mmol), THF (9 mL), and H<sub>2</sub>O (1 mL). The mixture was stirred at 50°C for 2 h until the color of diselenide disappeared. The solution was cooled to room temperature, quenched with brine (10 mL) and extracted with ethyl ether (30 mL × 2). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated *in vacuo*. The product was separated *via* preparative TLC (silica gel) with petroleum ether/ethyl ether (10:1) as the eluent.

*Phenyl allylic selenide* (1) oil;<sup>8</sup> IR  $\nu$ : 3090, 3072, 2940, 1640, 1585, 1485, 1445, 1070, 1065, 1020, 1000, 985, 730, 685 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$ : 3.32 (d, *J* = 6.8 Hz, 2H, SeCH<sub>2</sub>), 4.65–4.90 (m, 2H, CH = CH<sub>2</sub>), 5.40–6.10 (m, 1H, CH = CH<sub>2</sub>), 7.06–7.58 (m, 5H, ArH).

*4-Methyl-phenyl allylic selenide* (2) oil;<sup>8</sup> IR  $\nu$ : 3080, 2965, 2870, 1642, 1510, 1380, 990, 830

cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$ : 2.10–2.33 (s, 3H, CH<sub>3</sub>), 3.19–3.60 (d, *J* = 6.8 Hz, 2H, SeCH<sub>2</sub>), 4.55–5.00 (d, *J* = 8.5 Hz, 2H, CH = CH<sub>2</sub>), 5.53–5.90 (m, 1H, CH = CH<sub>2</sub>), 6.75–7.55 (m, 4H, ArH).

*4-Chloro-phenyl allylic selenide* (3) oil;<sup>8</sup> IR  $\nu$ : 3100, 2950, 1650, 1180, 1090, 1005, 820, 685 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$ : 3.20–3.60 (d, *J* = 6.8 Hz, 2H, SeCH<sub>2</sub>), 4.60–5.10 (d, *J* = 8.5 Hz, 2H, CH = CH<sub>2</sub>), 5.56–5.93 (m, 1H, CH = CH<sub>2</sub>), 6.95–7.59 (m, 4H, ArH).

*2-Methyl-phenyl allylic selenide* (4) oil;<sup>8</sup> IR  $\nu$ : 3080, 2970, 1650, 1515, 1380, 995, 910, 835 cm<sup>-1</sup>; IR  $\delta$ : 2.23–2.45 (s, 3H, CH<sub>3</sub>), 3.17–3.43 (d, *J* = 6.8 Hz, 2H, SeCH<sub>2</sub>), 4.65–5.03 (d, *J* = 8.5 Hz, 2H, CH = CH<sub>2</sub>), 5.60–6.00 (m, 1H, CH = CH<sub>2</sub>), 6.75–7.60 (m, 4H, ArH).

*n-Butyl allylic selenide* (5) oil;<sup>8</sup> IR  $\nu$ : 2965, 2930, 2885, 1645, 1500, 1380, 995, 910 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$ : 0.98–1.65 (m, 7H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.30–2.75 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>Se), 3.11–3.43 (d, *J* = 6.8, 2H, SeCH<sub>2</sub>CH = CH<sub>2</sub>), 4.58–5.00 (d, *J* = 8.5, 2H, CH = CH<sub>2</sub>), 5.55–5.90 (m, 1H, CH = CH<sub>2</sub>).

*Phenyl 3-cyclohexenyl selenide* (6) oil;<sup>11</sup> IR  $\nu$ : 3090, 3080, 3050, 2950, 2880, 1650, 1585, 1480, 1445, 1020, 1000, 880, 865, 740, 690 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$ : 1.60–2.05 (m, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.82 (m, 1H, SeCH), 5.30–5.91 (m, 2H, CH = CH), 7.00–7.68 (m, 5H, ArH).

*4-Chloro-phenyl 3-cyclohexenyl selenide* (7) oil;<sup>11</sup> IR  $\nu$ : 3050, 2960, 2880, 1605, 1485, 1450, 1395, 1180, 1090, 1020, 870, 820, 730, 700, 480

$\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$ : 1.50—2.25 (m, 6H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 3.80 (m, 1H, SeCH), 5.40—5.85 (m, 2H, CH = CH), 7.00—7.56 (m, 4H, ArH).

*n*-Butyl 3-cyclohexenyl selenide (**8**) oil;<sup>11</sup> IR  $\nu$ : 3045, 2980, 2950, 2880, 1660, 1600, 1450, 1380, 1260, 1180, 1000, 985, 865, 730  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$ : 0.83 (t, 3H,  $\text{CH}_3$ ), 1.12—2.20 (m, 10H,  $\text{CH}_2 \times 5$ ), 2.45 (t,  $J = 6.4$  Hz, 2H,  $\text{CH}_2\text{Se}$ ), 3.43 (m, 1H, SeCH), 5.30—5.89 (m, 2H, CH = CH).

## Conclusion

The advantages of the method are simple operation, mild and neutral conditions as well as high-yielding.

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