# A Novel Synthesis of Allyl and Prop-2-ynyl Selenides Promoted by Tin in the Presence of Water†

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**Puhong Liao, Weiliang Bao and Yongmin Zhang***

*Department of Chemistry, Hangzhou University, Hangzhou, 310028, P.R. China*

Allylic and prop-2-ynyl (propargyl) bromides react with diorganyl diselenides in the presence of water to give allylic and prop-2-ynyl selenides in moderate to good yields; the reaction rate is faster than for the same reaction in anhydrous organic media.

Metal-mediated reactions in aqueous media have recently found considerable applications in organic synthesis.[1,2] Such aqueous organometallic reactions offer a number of advantages over conventional organometallic reactions, including their simple operation through obviating the need for anhydrous organic solvents and an inert atmosphere, and there is no need to protect 'reactive' hydroxy functional groups *etc*. Although tin has been one of the most commonly used metals in aqueous organometallic reactions, tin-mediated reactions in aqueous media have only focused on the allylation reaction of carbonyl compounds, crossed aldol and Reformastasky-type reactions.[1a] It is expected that the scope of the reactions will be extended.

We report here a novel synthesis of allyl and prop-2-ynyl (propargyl) selenides *via* reactions, promoted by tin, of allyl and pro-2-ynyl bromides with diselenides in aqueous media.

$$\mathrm{R'CH{=}CHCH_2Br + RSeSeR \xrightarrow[\text{THF–H}_2\text{O}]{\text{Sn}} R'CH{=}CHCH_2SeR}$$

$$\mathrm{CH{\equiv}CCH_2Br + RSeSeR \xrightarrow[\text{THF–H}_2\text{O}]{\text{Sn}} CH{\equiv}CCH_2SeR}$$

Allylic selenides are useful intermediates in organic synthesis. In allylic selenides, the allylic anions are stabilized by the seleno group and can be attacked by nucleophiles regioselectively.[3] Allylic selenides can be prepared by several methods, *e.g.* by the displacement of allylic halide by selenide anions,[4] dehydroxysilylation of 2-hydroxy-3-trimethylsilypropylselenide catalysed by $SnCl_2$,[5] and the reaction of allylic acetates with diphenyl diselenide induced by samarium diiodide in the presence of a palladium catalyst.[3] Some of the methods suffer from disadvantages, *e.g.* a strong base (EtONa) and poisonous starting material (PhSeH) were used.[4] Here we provide a very simple and easy alternative method for the synthesis of allylic and prop-2-ynyl selenides in moderate to good yields.

As can be seen from Table 1, when the reaction takes place in the presence of water it is faster than the same reaction in anhydrous organic media (entries 1, 2 and 3). Compared with the dialkyl diselenide, diphenyl diselenide is more suitable as a substrate (entries 5 and 6).

## Experimental

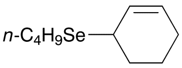
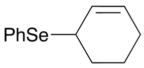
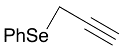
$^1H$ NMR spectra were recorded in $CCl_4$ on a JEOL PMX 60si spectrometer using TMS as internal standard. IR spectra were obtained on a Perkin Elmer 683 spectrometer.

*General Procedure*.—In a 50 ml three-necked flask fitted with a reflux condenser and a magnetic stirrer were placed 1.5 mmol metallic tin powder, 1.5 mmol diorganyl diselenide, 4 mmol allylic bromide and the solvent (as listed in Table 1). The mixture is stirred vigorously at a specified temperature for a given time, until the powdered tin is almost consumed. The mixture is extracted with diethyl ether twice (30 ml × 2). The extracts are washed with brine, dried ($Na_2SO_4$) and concentrated *in vacuo*. The product is obtained from the residue through preparative TLC (silica gel) with light petroleum (bp 30-60 °C)–diethyl ether as eluent.

*Allyl phenyl selenide* (**1**).—Oil[5]; $\nu_{max}/cm^{-1}$, 3090, 3075, 2940, 1645, 1590, 1485, 1445, 1075, 1065, 1020, 1000, 985, 730, 685; $\delta_H$ 3.32 (2 H, d, $J$ 7 Hz), 4.65–4.92 (2 H, m), 5.45–6.15 (1 H, m), 7.06–7.58 (5 H, m).

*Butyl cyclohex-2-enyl selenide* (**4**).—Oil[7]; $\nu_{max}/cm^{-1}$, 3045, 2980, 2950, 2880, 1650, 1590, 1450, 1382, 1260, 1180, 1000, 985, 862, 730;

**Table 1** Reaction conditions and yields

| Entry | Products | Solvents[a] | Temp. ($T$/°C) | Time ($t$/h) | Yield (%) |
|---|---|---|---|---|---|
| **1**[5] | $PhSeCH_2CH{=}CH_2$ | A | 50 | 24 | 75 |
| | | B | 50 | 12 | 80 |
| **2**[6] | $p\text{-}CH_3C_6H_4SeCH_2CH{=}CH_2$ | A | 50 | 30 | 73 |
| | | B | 50 | 20 | 78 |
| **3**[6] | $p\text{-}ClC_6H_4SeCH_2CH{=}CH_2$ | A | 65 | 30 | 70 |
| | | B | 50 | 24 | 74 |
| **4**[7] |  | B | 60 | 24 | 55 |
| **5**[3] |  | B | 50 | 20 | 72 |
| **6**[7] |  | B | 60 | 24 | 43 |
| **7**[7] | $CH_3(CH_2)_5SeCH_2CH{=}CH_2$ | B | 60 | 24 | 45 |

[a]Solvent A is THF (20 ml) and solvent B is THF–$H_2O$(20 ml 1 ml).

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*To receive any correspondence.

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$\delta_H$ 0.83 (3 H, t, *J* 5.4 Hz), 1.12–2.14 (10 H, m), 2.43 (2 H, t, *J* 6.4 Hz), 3.43 (1 H, m), 5.30–5.82 (2 H, m).

*Cyclohex*-2-*enyl phenyl selenide* (**5**).—Oil[3]; $\nu_{max}/cm^{-1}$, 3090, 3080, 3045, 2950, 2880, 1648, 1585, 1480, 1445, 1020, 1000, 880, 865, 735, 685; $\delta_H$ 1.59–1.93 (6 H, m), 3.82 (1 H, m), 5.30–5.91 (2 H, m), 7.00–7.60 (5 H, m).

*Phenyl prop*-2-*ynyl selenide* (**6**).—Oil[7]; $\nu_{max}/cm^{-1}$, 3320, 3090, 3080, 2940, 2870, 1700, 1590, 1485, 1445, 1070, 1025, 1000, 860, 735, 685; $\delta_H$ 1.95 (1 H, t, *J* 2.6 Hz), 3.25 (2 H, d, *J* 2.6 Hz), 7.00–7.53 (5 H, m).

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