# Facile Formation of Ytterbium Diiodide and Its Use in the Synthesis of Allyl Selenides

SU, Wei-Ke $^a$ (苏为科) ZHANG, Yong-Min $^{*,b,c}$ (张永敏) ZHENG, Yun-Fa $^b$ (郑云法) LI, Yong-Shu $^a$ (李永曙)

Ytterbium metal reacts with iodine to generate ytterbium diiodide directly, which can react with disclenides to form ytterbium selenolates ( $RSeYbI_2$ ). These species reacted smoothly with allyl bromide to give allylselenides in moderate to good yields under neutral conditions.

**Keywords** diselenide, ytterbium diiodide, ytterbium, allylselenide

### Introduction

As a powerful and versatile single electron transfer reducing and coupling reagent, SmI2 has been widely applied in organic synthesis. 1,2 However, there are only a few reports on the utility of ytterbium diiodide in organic synthesis. 3-5 Utilization of the corresponding ytterbium diiodide has lagged behind. There are several important reasons for this. Firstly, although several rapid and convenient syntheses of samarium diiodide have been reported, the preparation of ytterbium diiodide by the reaction of ytterbium with 1, 2-diiodoethane requires a reaction time of over 2 d. In addition, although samarium diiodide is relatively soluble in solvents like THF (0.1 mol/ L), ytterbium diiodide has limiting solubility of < 0.04 mol/L in the same solvent. Finally, the redox potential of vtterbium (II) species is a borderline for the types of transformations that are of interest to synthetic organic chemists. Nevertheless, some transformations, such as reductive coupling, which nicely complement those accomplished by samarium diiodide 3-5 have been reported.

As a reductant, YbI<sub>2</sub> can not promote the intermolecular Barbier-type reactions, <sup>6</sup> but it can promote the intramolecular Barbier-type reactions smoothly. <sup>7</sup>In this paper, we wish to describe our results concerning the facile preparation of ytterbium diiodide by the reaction of ytterbium metal with iodine in THF (Scheme 1), and the synthesis of allylselenides (5) by the reaction of allyl bromide (4) with diselenides promoted by ytterbium diiodide (1) (Scheme 2). To our best knowledge, all these chemical transformations have not been reported.

### Scheme 1

$$Yb + I_2 \xrightarrow{THF} YbI_2$$

$$Yb + ICH_2CH_2I \xrightarrow{THF} YbI_2$$

#### Scheme 2

# Results and discussion

It was found that ytterbium diiodide could be easily

<sup>&</sup>lt;sup>a</sup> College of Pharmaceutical Sciences, Zhejiang University of Technology, Hangzhou, Zhejiang 310014, China

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

<sup>&</sup>lt;sup>c</sup> State Key Laboratory of Organometallic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

<sup>\*</sup> E-mail; yminzhang@mail.hz.zj.cn

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prepared by the reaction of ytterbium with iodine and can be stored for a few hours.

The experimental conditions given in Scheme 1 have been optimized from the reaction of ytterbium metal with iodine or 1,2-diiodoethane at 0  $^{\circ}$ C, 20  $^{\circ}$ C and 25

 $^{\circ}$ C. The reaction of ytterbium metal with 1, 2-diiodoethane at 0  $^{\circ}$ C completed after 50 h whereas that with iodine finished within 3.5 h at 0  $^{\circ}$ C. As already observed in Table 1, the increase of temperature speeds up the reaction.

Table 1 Preparation of YbI<sub>2</sub>

Е.	n	Reaction conditions		Conversion	7 1 16
Entry	Reactants	Temp. (℃)	Time (h)	(%) <sup>a</sup>	Product <sup>b</sup>
1	Yb, ICH <sub>2</sub> CH <sub>2</sub> I	0	50	98	$YbI_2$
2	Yb, $I_2$	0	3.5	100	$YbI_2$
3	Yb, ICH <sub>2</sub> CH <sub>2</sub> I	20	48	100	$YbI_2$
4	Yb, $I_2$	20	2.5	100	$\mathrm{YbI}_2$
5	Yb, ICH <sub>2</sub> CH <sub>2</sub> I	25	45	100	$YbI_2$
6	Yb, I <sub>2</sub>	25	2	100	YbI <sub>2</sub>

<sup>&</sup>lt;sup>a</sup>Present conversion of ytterbium metal was calculated by gravimetry; <sup>b</sup>yellow-green solution of ytterbium diiodide.

For practical and financial reasons, iodine is preferable to 1,2-diiodoethane in the above preparation of ytterbium diiodide.

Scheme 2 summarizes the cleavage of Se—Se bond in diselenides with ytterbium diiodide and the subsequent synthesis of allylselenides. It was found that under

mild conditions, ytterbium arylselenolates could be easily prepared *in situ* by the treatment of diselenides with ytterbium diiodide in THF-HMPA system, and then reacted smoothly with allyllic bromide in a one-pot manner to afford the desired allylselenides in moderate to good yields (see Table 2).

Table 2 Reaction conditions and yields of products

Entry	R	Time (h)	Temp. (℃)	Isolated yield (%)a	Product
1	$CH_3(CH_2)_3$	4	50	55	5a
2	2-ClC <sub>6</sub> H <sub>4</sub>	2.5	2025	85	5b
3	3-ClC <sub>6</sub> H <sub>4</sub>	2.5	20—25	82	5c
4	4-ClC <sub>6</sub> H <sub>4</sub>	2.5	20-25	84	5d
5	$2$ -CH $_3$ C $_6$ H $_4$	3	20—25	77	5e
6	$3-CH_3C_6H_4$	3	20—25	80	5f
7	$4$ - $CH_3C_6H_4$	2.5	20—25	78	5g
8	$C_6H_5$	2.5	20-25	81	5h

<sup>&</sup>lt;sup>a</sup> Isolated yield based on diselenide.

In order to confirm the formation of the ytterbium selenolates as an intermediate, according to Fukuzawa, 8 a transmetalatoin reaction of the intermediate with trimethylchlorosilane was performed [Eq. (1)]. Phenylselenonotrimethylsilane was isolated quantitatively by this reaction, indicating the formation of the ytterbium selenolates species as an intermediate.

$$PhSeYbI_2 + Me_3SiCl \xrightarrow{THF-HMPA} PhSeSiMe_3$$
 (1)

The yield of aryl allylselenide was better than that of alkyl allylselenide and the reason maybe that the free anion of arylselenolate is more stable than that of alkylselenolate.

# **Experimental**

Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl. Commercial HMPA was dried over calcium hydride, distilled *in vacua* and stored over 4Å molecular sieves. Allylic bromide was distilled prior to use. <sup>1</sup>H NMR spectra were recorded on a Bruker AC-80 spectrometer using TMS as internal standard. Infrared spectra were obtained on an IR-408 spectrometer in film. Mass spectra were recorded on an HP 5989B MS spectrometer. Microanalysis was carried on a Carlo-

Erba 1106 instrument.

General procedure for the preparation of YbI<sub>2</sub>

Ytterbium powder (0.086 g, 0.5 mmol), THF (12 mL) and iodine (0.125 g, 0.5 mmol) were added to a 50 mL of three-necked flask under nitrogen atmosphere. The mixture was magnetically stirred for about 2—3 h at 20—25  $^{\circ}$ C to obtain a yellow-green solution of YbI<sub>2</sub>.

# General procedure for the synthesis of allylselenides

The yellow-green solution of YbI<sub>2</sub> (0.5 mmol) in 12 mL of THF was treated with 0.5 mL of HMPA. Then 0.25 mmol of diselenides were added in one portion at 20—25 °C under nitrogen atmosphere. The mixture was stirred for 0.5 h. To the mixture was added 0.061 g (0.5 mmol) of freshly distilled allyl bromide at 20—25 °C, then stirred for 1.5—2.5 h (see Table 2) at the same temperature. The reaction mixture was extracted with ether (10 mL  $\times$  3) and dried over MgSO<sub>4</sub>. The solvent was removed by evaporation. The crude products were purified by preparative TLC on silica gel [cyclohexane and ethylacetate (20:1) as eluent]. All products were identified by IR,  $^1\text{H}$  NMR and MS spectra.

# Transmetalation reaction of diphenyl diselenide with trimethylchlorosilane mediated by ${ m YbI}_2$

To the yellow-green THF-HMPA (10—0.5 mL) solution prepared from YbI<sub>2</sub>(0.5 mmol) and diphenyl diselenide (0.085 g, 0.25 mmol) as described above, trimethylchlorosilane was added by injection through a rubber septum with a syringe at room temperature. After being stirred at ambient temperature for 1 h, the solution was diluted with dry hexane (25 mL) and the precipitate was removed by filtration. The precipitate was further washed with dry hexane (20 mL) and the filtrates were combined. The solvent was removed by a rotary evaporator under vacuum.  $^1{\rm H}$  NMR spectral measurement of the residue indicates the formation of almost pure phenylselenotrimethylsilane.  $^8$  Yield 0.113 g, 99%;  $^1{\rm H}$  NMR (CDCl<sub>3</sub>, 80 MHz)  $\delta_1$ 0.32 (s, 9H), 6.70—7.60 (m, 5H).

Allyl butylselenide (5a) Oil; 9 <sup>1</sup>H NMR

(CDCl<sub>3</sub>, 80 MHz)  $\delta$ : 5.90—5.53 (m, 1H), 4.79 (d, J = 6.2 Hz, 2H), 3.00—2.70 (m, 2H), 0.98—1.68 (m, 7H); IR (film)  $\nu$ : 2962, 2930, 2884, 1642, 1468, 1318, 992, 910 cm<sup>-1</sup>.

Allyl 2-chlorophenylselenide (**5b**) Light yellow oil;  ${}^{1}$ H NMR (CDCl<sub>3</sub>, 80 MHz)  $\delta$ : 3.46 (d, J = 6.0 Hz, 2H), 5.0 (d, J = 6.2 Hz, 2H), 5.6—5.95 (m, 1H), 6.9—7.4 (m, 4H); IR (film)  $\nu$ : 3050, 2930, 1630, 1575, 1450, 1430, 1250, 1190, 1130, 915, 740 cm<sup>-1</sup>; MS m/z (%): 234 (M<sup>+</sup> + 2, 21), 233 (M<sup>+</sup> + 1, 11), 230 (M<sup>+</sup> - 2, 26); Anal. calcd for C<sub>9</sub>H<sub>9</sub>ClSe: C 46.68, H 3.92; found C 46.56, H 3.80.

Allyl 3-chlorophenylselenide (5c) Red oil;  $^{1}$ H NMR (CDCl<sub>3</sub>, 80 MHz)  $\delta$ : 3.54 (d, J = 6.2 Hz, 2H), 5.91—5.98 (m, 1H), 7.18—7.49 (m, 4H); IR (film)  $\nu$ : 3100, 2950, 2400, 1590, 1470, 1100, 920, 775, 750, 680 cm<sup>-1</sup>; MS m/z (%): 234 (M<sup>+</sup> +2, 15), 232 (M<sup>+</sup>, 33), 191 (19), 112 (8), 111 (12), 41 (100); Anal. calcd for  $C_{9}H_{9}$ ClSe: C 46.68, H 3.92; found C 46.58, H 3.86.

Allyl 4-chlorophenylselenide (5d) Oi1;  $^{9,10}$  <sup>1</sup>H NMR (CDCl<sub>3</sub>, 80 MHz)  $\delta$ : 2.33 (s, 3H), 3.3 (d, J = 6.0 Hz, 2H), 4.82 (d, J = 6.2 Hz, 2H), 5.60—6.00 (m, 1H), 6.70—7.60 (m, 4H); IR (film)  $\nu$ : 3110, 2950, 1650, 1480, 1180, 1100, 1000, 820, 690 cm<sup>-1</sup>.

Allyl 2-methylphenylselenide (5e) Oi1;  $^9$  <sup>1</sup>H NMR (CDCl<sub>3</sub>, 80 MHz)  $\delta$ : 2.33 (s, 3H), 3.31 (d, J = 6.0 Hz, 2H), 4.60—5.05 (d, J = 6.2 Hz, 2H), 5.60—6.00 (m, 1H), 6.70—7.60 (m, 4H); IR (film)  $\nu$ : 3080, 2960, 1645, 1510, 1380, 990, 900, 830 cm<sup>-1</sup>.

Allyl 3-methylphenylselenide (5f) Red oi1;  $^{1}$ H NMR (CDCl<sub>3</sub>, 80 MHz)  $\delta$ ; 2.40 (s, 3H), 3.33 (d, J = 6.0 Hz, 2H), 4.82 (d, J = 6.2 Hz, 2H), 5.50—6.05 (m, 1H), 6.9—7.20 (m, 4H); IR (film)  $\nu$ ; 3370, 3030, 2920, 2360, 1580, 1470, 1280, 1210, 1160, 1060, 980, 910, 820, 770, 670 cm<sup>-1</sup>; MS m/z (%); 212 (M<sup>+</sup>, 21), 211 (3), 171 (13), 91 (100), 77 (6), 41 (20); Anal. calcd for  $C_{10}H_{12}Se$ ; C 56.88, H 5.73; found C 56.78, H 5.70.

Allyl 4-methylphenylselenide (**5g**) Oil;  $^{9,11}$  <sup>1</sup>H NMR (CDCl<sub>3</sub>, 80 MHz)  $\delta$ : 2.30 (s, 1H), 3.33 (d, J = 6.0 Hz, 2H), 4.75 (d, J = 6.2 Hz, 2H), 5.50—5.90 (m, 1H), 6.70—7.50 (m, 4H); IR (film)  $\nu$ : 3100, 2970, 2880, 1640, 1510, 1380,

990, 840 cm<sup>-1</sup>.

Allyl phenyl selenide (5h) Oil;  $^{9,11}$  <sup>1</sup>H NMR (CDCl<sub>3</sub>, 80 MHz)  $\delta$ : 3.30 (d, J = 6.0 Hz, 2H), 4.75 (d, J = 6.2 Hz, 2H), 5.50—5.90 (m, 1H), 7.00—7.60 (m, 5H); IR (film)  $\nu$ : 3080, 2940, 1640, 1480, 1180, 990, 910, 730, 680 cm<sup>-1</sup>.

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