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### Science Letters:

## A convenient and stereoselective synthesis of (Z)-allyl selenides via Sm/TMSCl system-promoted coupling of Baylis-Hillman adducts with diselenides\*

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**Abstract:** A simple and convenient procedure for stereoselective synthesis of (Z)-allyl selenides has been developed by a one-pot reaction of diselenides with Baylis-Hillman adducts in the presence of samarium metal-trimethylsilyl chloride under mild conditions. Presumably, the diselenides are cleaved by Sm/TMSCl system to form selenide anions, which then undergo S<sub>N</sub>2' substitution of Baylis-Hillman adducts to produce the (Z)-allyl selenides.

**Key words:** Stereoselective synthesis, (Z)-allyl selenides, Diselenides, Baylis-Hillman adducts, Sm/TMSCl system

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### INTRODUCTION

Allyl selenides have drawn much attention as a class of important intermediates in organic synthesis. For example, they are useful synthetic precursors for the [1,3]- or [2,3]-sigmatropic rearrangements (Sharpless and Lauer, 1972; Fujita *et al.*, 1998; Carter and Bourland, 2000), allylic homocoupling reactions (Masugama *et al.*, 1989), and various other chemical transformations (Shea *et al.*, 1986; Back and Moussa, 2002; 2003). Generally, allyl selenides are synthesized from allylic halides with selenide anions, which could be generated by reduction of diselenides with sodium borohydride (Hori and Sharpless, 1979), samarium diiodide (Zhang *et al.*, 1993), indium (Munbunjong *et al.*, 2005) and lithium aluminium hydride (Suzuki *et al.*, 1985), etc. Other methods include reactions of organometallic reagents with organoselenium compounds (Yu *et al.*, 1997; Huang

and Chen, 2000), conversion from  $\alpha$ -phenylseleno ketones (Nishiyama *et al.*, 1982), etc. In view of their significance in organic synthesis, it is still necessary to extend the scope of allyl selenides family and develop new synthetic routes.

The Baylis-Hillman reaction is well known as one of useful carbon-carbon bond-forming reaction in the last decades (Basavaiah *et al.*, 1996; 2003). The adducts of the reaction, 3-hydroxy-2-methylene-alkanoates (derived from acrylate esters), have been widely utilized as important precursors for stereoselective synthesis of trisubstituted alkenes (Basavaiah *et al.*, 1996; 2003). To date, a series of heteroatom-substituted allylic derivatives transferred from Baylis-Hillman adducts have been reported, among which include allyl halides (Basavaiah *et al.*, 1995; Chavan *et al.*, 1997; Yadav *et al.*, 2001), allyl sulfides (Calò *et al.*, 1988), allyl amine (Das *et al.*, 2005a), allyl ethers (Roy *et al.*, 2000), allyl phosphonates (Janecki and Bodalski, 1990), and allyl borates (Kabalka *et al.*, 2004), etc. However, to the best of our knowledge, no literature on the synthesis of Baylis-Hillman adduct-derived allyl selenides has been

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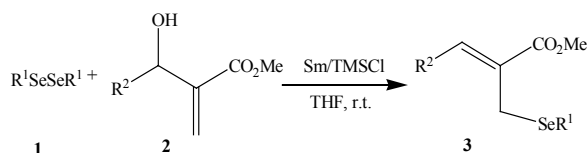
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reported. As a continuation of our interest in Baylis-Hillman reaction (Liu *et al.*, 2005; 2006) and application of samarium reagents in organic synthesis (Zhou and Zhang, 1999; Lu and Zhang, 1999), we report here a simple and convenient procedure for the stereoselective synthesis of (*Z*)-allyl selenides via one-pot reaction of diselenides with Baylis-Hillman adducts promoted by samarium-trimethylsilyl chloride system under mild conditions.

## METHODS

A typical experimental procedure is as follows: under a nitrogen atmosphere, a solution of diphenyl diselenide (0.5 mmol) in THF (10 ml) was treated with samarium (1.0 mmol) and TMSCl (0.6 ml) for 2 h at room temperature until the powdered samarium was almost consumed and the yellow solution became almost colorless. Then to the mixture was added methyl 3-hydroxy-2-methylene-3-phenylpropanoate (**2a**) with the mixture being continuously stirred at room temperature for 4 h. After usual work-up, (*Z*)-methyl 2-phenylselenomethyl-3-phenylacrylate (**3a**) was obtained in 90% yield (Fig.1). It was shown in NOESY (nuclear overhauser effect spectroscopy) experiment that there is no NOE (nuclear overhauser effect) correlation between the signals of the internal olefin proton and the allylic methylene protons. Besides, according to literature (Das *et al.*, 2005b; Basavaiah *et al.*, 1994; Larson *et al.*, 1984), in the <sup>1</sup>H NMR spectrum of a trisubstituted alkene the β-vinylic proton, *cis*- and *trans*- to the ester group are known to resonate at δ 7.5 and δ 6.5, respectively, when alkene is substituted by an aryl group; while the same proton

*cis*- and *trans*- to an ester group appears at δ 6.8 and δ 5.7, respectively, when substituted by an alkyl one. All these data suggest the products adopt *Z*-stereoconfiguration.



**Fig.1** Synthesis of (*Z*)-allyl selenides from Baylis-Hillman adducts and diselenides promoted by Sm/TMSCl system

## RESULTS AND DISCUSSION

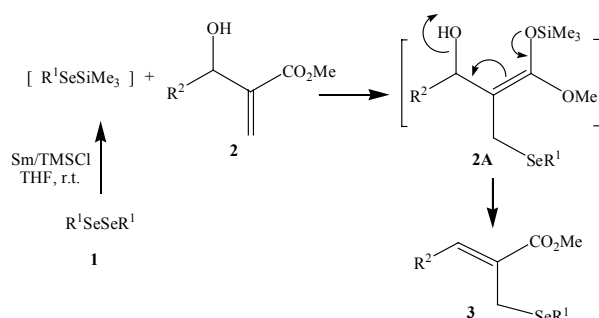
The results are summarized in Table 1. A variety of Baylis-Hillman adducts either possessing aryl groups (with donating as well as withdrawing functionalities) or alkyl ones were used in this reaction in order to establish the generality, with all reactions proceeding smoothly and giving desirable yield of products under similar conditions. As for diselenides, those dialkyl diselenides needed longer time to be cleaved by Sm/TMSCl system comprised of those diaryl diselenides. Besides good yields, the present process also exhibited excellent stereoselectivity. Only *Z*-stereoconfiguration of the products was obtained while no *E*-isomer was observed from the spectra.

Although the exact mechanism is not very clear to us at this moment, it is speculated that the reaction may involve a silyl enolate intermediate **2A**, which is a key intermediate for facilitating the S<sub>N</sub>2' substitution of selenide anions to Baylis-Hillman adducts (Fig.2) (Ranu and Das, 2005).

**Table 1** Synthesis of (*Z*)-allyl selenides from Baylis-Hillman adducts and diselenides promoted by Sm/TMSCl system<sup>a</sup>

Entry	R <sup>1</sup>	R <sup>2</sup>	Time (h)	Product <sup>b</sup>	Yield (%) <sup>c</sup>
1	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	6.0	<b>3a</b>	90
2	C <sub>6</sub> H <sub>5</sub>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	6.0	<b>3b</b>	92
3	C <sub>6</sub> H <sub>5</sub>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	6.0	<b>3c</b>	88
4	C <sub>6</sub> H <sub>5</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	6.0	<b>3d</b>	91
5	C <sub>6</sub> H <sub>5</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	8.0	<b>3e</b>	86
6	C <sub>6</sub> H <sub>5</sub>	2-furyl	6.0	<b>3f</b>	89
7	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>	6.0	<b>3g</b>	92
8	C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>7</sub> H <sub>15</sub>	6.0	<b>3h</b>	87
9	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	6.0	<b>3i</b>	89
10	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	8.0	<b>3j</b>	85

<sup>a</sup> Reagents and conditions: **1** (0.5 mmol), **2** (1.0 mmol), Sm (1.0 mmol), TMSCl (0.6 ml), THF (10 ml), r.t., 6.0–8.0 h; <sup>b</sup> All products were characterized by <sup>1</sup>H NMR, MS and IR; <sup>c</sup> Isolated yields



**Fig.2** Presumed mechanism for synthesis of (Z)-allyl selenides

## CONCLUSION AND REPRESENTATIVE ANALYTICAL DATA

In conclusion, the Sm/TMSCl system-promoted one-pot coupling of diselenides with Baylis-Hillman adducts provides an efficient methodology for synthesizing (Z)-allyl selenides. The remarkable advantages of this process are its simple operation, mild reaction conditions, high yields and excellent stereoselectivity.

Representative analytical data for (Z)-allyl selenides. (Z)-methyl 2-phenylselenomethyl-3-phenylacrylate (**3a**): oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ: 3.79 (s, 3H, OCH<sub>3</sub>), 4.05 (s, 2H, methylene-H), 7.20~7.35 (m, 8H, ArH), 7.49~7.53 (m, 2H, ArH), 7.67 (s, 1H, ArCH=); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ: 25.22, 52.50, 127.78, 128.82, 128.98, 129.24, 129.63, 129.89, 130.24, 134.43, 135.11, 140.21, 168.06; IR (film) ν<sub>max</sub>: 3057, 3025, 1715, 1625, 1577, 1266 cm<sup>-1</sup>; MS m/z (%): 332 (M<sup>+</sup>). Anal. calcd. for C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>Se: C 61.64, H 4.87; Found: C 61.92, H 4.77.

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