

## Bismuth Mediated Organic Reaction: A Convenient Method for the Synthesis of Allylic (Benzylic) Selenides and $\alpha$ -Organylselenocarbonyl Compounds in Aqueous Media

Pei Pei SUN\*, Ya Ping XIAO, Bao Chuan SHI

Department of Chemistry, Nanjing Normal University, Nanjing 210097

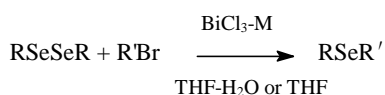
**Abstract:** In the presence of BiCl<sub>3</sub>/Al or BiCl<sub>3</sub>/Fe, in THF-H<sub>2</sub>O, allylic (benzylic) bromides or  $\alpha$ -bromoketones react with diorganyl diselenides to give allylic (benzylic) selenides or  $\alpha$ -organylselenocarbonyl compounds respectively in moderate to good yields.

**Keywords:** Bismuth, allylic (benzylic) selenides,  $\alpha$ -organylselenocarbonyl compounds, synthesis.

Organic reactions promoted by active metals have aroused much interest in recent years. Active bismuth has been used in Barbier-type reaction of allylic halides with aldehydes<sup>1</sup> and aldimines<sup>2</sup> as well as Reformatsky type reaction<sup>3</sup>. Other publications referred to the cross coupling between aldehydes and  $\alpha$ -diketones<sup>4</sup>, the substitution to benzotriazole derivatives<sup>5</sup> and the reductive coupling reaction of nitro compounds<sup>6</sup>. These reactions generally promoted by elemental bismuth generated *in situ* from a combination of BiCl<sub>3</sub>-Zn, BiCl<sub>3</sub>-Fe or BiCl<sub>3</sub>-Al. It was noteworthy that some reactions can undergo in aqueous media. It offers a number of advantages over conventional organometallic reactions. As a cheap and less toxic metal, it is showed that metallic bismuth has a great potential utility in organic synthesis, and it is essential to develop the new application of this metal.

We interested in applying bismuth to modern organic synthesis especially to synthesis of seleno compounds. These interests led us to investigate the carbon-selenium bond forming reaction mediated by bismuth. Allylic or benzylic selenides are important synthetic intermediates. For example, the allylic anions stabilized by the seleno group can be attacked by nucleophiles regioselectively<sup>7</sup>.  $\alpha$ -Organylselenocarbonyl compounds also have a wide range of synthetic utilities. They have been used for regioselective introduction of various functional groups, especially for that of unsaturation *via* well established syn-elimination<sup>8</sup>. There have been a variety of reports for the preparation of these seleno compounds<sup>9-12</sup>, but some of the methods have to suffer from disadvantages, *e. g.* have to use strong bases or acids and poisonous starting materials, or strictly anhydrous solvent. Here we report a very simple and convenient procedure for the synthesis of these seleno compounds mediated by bismuth (**Scheme**

1).

**Scheme 1**

R' =allyl, benzyl; M=Al, Fe

The reaction conditions and the results are showed in **Table 1**. Elemental bismuth is generated *in situ* from a combination of BiCl<sub>3</sub>-M(Al, Fe) system. In BiCl<sub>3</sub>-Al system the reaction proceeds faster with a higher yield than in BiCl<sub>3</sub>-Fe system. A catalytic amount (40 mol%) of BiCl<sub>3</sub> can be employed to the reaction, however the yield of the reaction would be lower if the amount of BiCl<sub>3</sub> is less than 20 mol%. The reaction can undergo in THF or THF-H<sub>2</sub>O. In the presence of water, it proceeds more fast than in anhydrous organic solvent. To most of the reactants we employed, the reaction gives good yields under the described reaction conditions (**Table 1**).

**Table 1** The synthesis of allylic or benzylic selenides <sup>a)</sup>

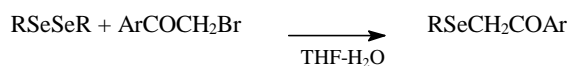
Entry	R	R'	M	Solv. <sup>b)</sup>	Time/hr	t °C	Yield/%
a	Ph	CH <sub>2</sub> =CHCH <sub>2</sub>	Al	A	8	50	86
				B	5	50	92
			Fe	A	8	60	64
				B	5	60	70
b	Ph	PhCH <sub>2</sub>	Al	B	6	60	90
			Fe	B	8	60	65
c	PhCH <sub>2</sub>	CH <sub>2</sub> =CHCH <sub>2</sub>	Al	A	6	60	85
				B	4	60	86
d	PhCH <sub>2</sub>	PhCH <sub>2</sub>	Al	B	4	50	80
e	Ph	PhCH=CHCH <sub>2</sub>	Al	B	10	65	74
f	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> =CHCH <sub>2</sub>	Al	B	5	60	82
g	n-C <sub>4</sub> H <sub>9</sub>	PhCH <sub>2</sub>	Al	B	6	60	75
h	n-C <sub>4</sub> H <sub>9</sub>	PhCH=CHCH <sub>2</sub>	Al	B	8	60	72

a) All products were confirmed by <sup>1</sup>H NMR and IR.b) Solvent A is THF; solvent B is THF-H<sub>2</sub>O (10/1,v/v).

α -Organylselenocarbonyl compounds are synthesized under the similar conditions. In THF-H<sub>2</sub>O (10/1,v/v) media, active bismuth mediated reaction of α -bromoketones with diorganyl diselenides produces α -organylselenocarbonyl compounds (**Scheme 2**).

**Scheme 2**BiCl<sub>3</sub>-Al

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and  $\alpha$ -Organylselenocarbonyl Compounds**



The reaction conditions and results are listed in **Table 2**.

**Table 2** The synthesis of  $\alpha$ -organylselenocarbonyl compounds<sup>a)</sup>

Entry	R	Ar	Temp/hr	t °C	Yield/%
a	Ph	Ph	8	55	78
b	Ph	p-BrC <sub>6</sub> H <sub>4</sub>	10	65	70
c	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Ph	6	65	65
d	n-C <sub>4</sub> H <sub>9</sub>	Ph	6	60	72

a) All products were confirmed by <sup>1</sup>H NMR and IR.

In the experiment we also found that diselenide alone is not easy to be reduced to selenolate in above reaction conditions. The reaction may be undergoes through an organobismuth intermediate<sup>1-3</sup>, which leads to the cleavage of Se-Se bond. More detailed study is in progress in our laboratory.

#### Typical procedure

To a suspension of 0.4 mmol BiCl<sub>3</sub> and 2.5 mmol aluminum in 10 ml THF-H<sub>2</sub>O (10:1) under nitrogen atmosphere, 0.5 mmol diselenide and 1.2 mmol allylic (benzylic) bromide or  $\alpha$ -bromoketone were added. The mixture was stirred at appropriate temperature for a given time (**Table 1** and **2**). After the completion of the reaction, the mixture was extracted with diethyl ether. The extracts were combined and washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The pure product was obtained by PLC.

In summary, the present work is a new application of active bismuth in organic synthesis. The notable advantages of this method are mild conditions, simple operation and higher yields. It is a useful method for the synthesis of organic seleno compounds.

#### Acknowledgments

We are grateful to the Natural Science Foundation of the Education Commission of Jiangsu Province for the financial support.

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Received 1 June 2000