

## Zn/ ZrCl<sub>4</sub> System Induced Reductive Cleavage of Se-Se Bond in Diaryl Diselenides: A Novel Method for the Synthesis of Selenoesters

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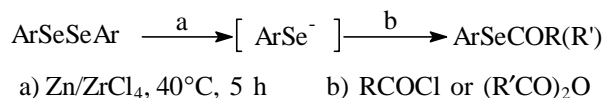
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**Abstract:** The Se-Se bond in diaryl diselenides was reduced by Zn/ZrCl<sub>4</sub> system to produce selenide anions, which react with acyl chlorides or acid anhydrides to afford selenoesters in THF under mild and neutral conditions.

**Keywords:** Diselenides, zinc, zirconium (IV) chloride, selenoesters.

In recent years, organoselenium compounds have been extensively used as important synthetic reagents and intermediates in organic synthesis<sup>1-3</sup>. Among them, selenoesters are very useful intermediates in the synthesis of natural compounds<sup>4</sup>. While there are many methods for the synthesis of selenoesters, the most common approach is the use of selenide anions reacting with acylation reagents. Selenide anions can be obtained by cleavage of diselenides with sodium in liquid ammonia<sup>5</sup> or in THF/HMPA<sup>6</sup>, with lithium aluminum hydride<sup>7</sup>, with sodium borohydride in THF/EtOH<sup>8</sup> or using resin bound borohydride<sup>9</sup>. Moreover, Grignard reagents react with selenium also to give selenide anions<sup>10</sup>. Especially, the use of samarium diiodide in THF/HMPA for cleavage of Se-Se bond have been reported to give selenide anion<sup>11,12</sup>, there also appeared some similar methods such as Sm/TiCl<sub>4</sub><sup>13</sup>, Sm/BiCl<sub>3</sub><sup>14</sup> and Sm/CoCl<sub>2</sub><sup>15</sup> to give selenide anions. These methods have been applied to the synthesis of selenoesters. Unfortunately, most of them suffer from significant defects, which include strong base and expensive starting material. Therefore, we strive to look for other reagents to overcome these defects.

As an efficient, inexpensive high reactivity reagents, metal zinc has been employed in Barbier type reactions<sup>16</sup>, reductive coupling reactions<sup>17</sup> and Reformatsky reactions<sup>18</sup>. To the best of our knowledge, there has been few report on the application of zinc in the preparation of selenoesters. Herein we wish to report that Zn/ZrCl<sub>4</sub> system reduces diselenides to give selenide anions, which react with acyl chlorides or acid anhydrides to afford selenoesters in THF under mild and neutral conditions. This is the first report that Zn/ZrCl<sub>4</sub> system was used to obtain selenoesters.

**Scheme 1****Table 1** Yields of the products

Entry	Ar	R	R'	Yield (%) <sup>a</sup>
1 <sup>4</sup>	Ph	CH <sub>3</sub>		74
2 <sup>4</sup>	Ph	Ph		68
3 <sup>4</sup>	Ph	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>		70
4 <sup>19</sup>	Ph	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>		75
5 <sup>4</sup>	Ph		CH <sub>3</sub>	60
6 <sup>19</sup>	Ph		CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	63
7 <sup>19</sup>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>		67
8 <sup>20</sup>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Ph		71
9 <sup>21</sup>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>		61
10 <sup>22</sup>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>		66
11 <sup>19</sup>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>		CH <sub>3</sub>	55
12 <sup>22</sup>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>		CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	58

a: Isolated yields.

We investigated the reactions between zinc (1.5 eq) and diselenides (0.5 eq) in the presence of zirconium(IV) chloride in THF at 40°C. After reacting for about 5 h, the color of the solution was changed from green to grey-white, which indicates the cleavage of Se-Se bond and the generation of selenoate anions. Some control experiments revealed that Se-Se bond could not be cleaved by Zn or ZrCl<sub>4</sub> alone. The exact mechanism is not clarified and a more detailed study is in progress in our laboratory.

**Experimental**

The thermometer was uncorrected. IR spectra were obtained on a FTS-40 infrared spectrophotometer. <sup>1</sup>H NMR Spectra were recorded on a PMX-60 MHz instrument. All NMR samples were measured in CCl<sub>4</sub> using TMS as internal standard. Metallic Zinc was activated before use. The THF was freshly distilled from Na/PhCOPh prior to use.

**General procedure**

Under an inert atmosphere of nitrogen, zinc powder (1.5 mmol), zirconium (IV) chloride (0.3 mmol) and diselenides (0.5 mmol) was placed in a well-dried two neck round bottom flask. Freshly distilled dry THF (10 mL) was added through a syringe. The

resulting mixture was stirred in THF at 40°C for about 5 h, the green solution was changed from green to grey-white, acyl chlorides (1.5 mmol) or anhydrides (1.5 mmol) in THF (2 mL) was then added by a syringe to the mixture and stirred for 1~2 h, then the resulting solution was poured into dilute HCl (1.2 mol/L, 20 mL) and the mixture was extracted with ether (15 mL×3). The organic layer was washed with saturated brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure, the residue was then purified by preparative TLC on silica gel (light petroleum: acetic anhydride=100:1 as eluent) to give pure product. The analytical data of products are identical with those in references.

In conclusion, we have demonstrated a novel method for the synthesis of selenoesters from diselenides by Zn/ZrCl<sub>4</sub> system. The advantages of the present method are easily available and cheap starting material, single product, simple manipulation, mild and neutral conditions.

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