

**Synthesis of β -aminoesters and α -selenoesters
via Active Metal Bismuth Produced by Sm/BiCl₃
System in Aqueous Media**

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Abstract: Active metal bismuth is produced *in situ* via Sm/BiCl₃ system in aqueous media. Promoted by this active species, β -aminoesters and α -selenoesters are synthesized via reaction of α -bromoesters with 1-(α -aminoalkyl) benzotriazole and diselenides in moderate to good yields.

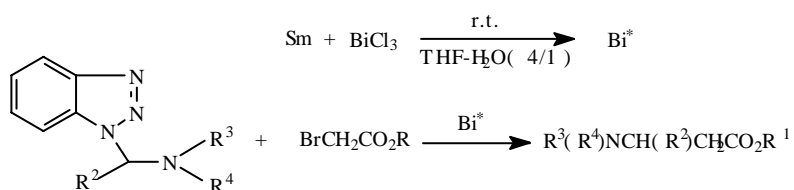
Keywords: Active metal bismuth, β -aminoesters, α -selenoesters, samarium, bismuth trichloride, aqueous media.

Since the general approach for the preparation of highly reactive metal powders was reported in 1972¹, active metals have attracted considerable attention in organic synthesis². Due to the high reactivity of active metals, reactions are typically carried out more efficiently, under milder conditions, and with a wider array of substrates than with other current methods. Up to now, active metal magnesium³, zinc⁴, indium⁵, calcium⁶, manganese⁷, samarium⁸, *etc* have been reported.

Meanwhile, metal-mediated organic reactions in aqueous media have received considerable attention in the last decade⁹. Such aqueous reactions offer a number of advantages over conventional organometallic reactions in organic solvent. They are practically convenient, environmentally friendly and do not require anhydrous organic solvents. Recently, metal Al(Hg)¹⁰, Cp₂TiCl¹¹, TiCl₃¹², Zn-ZnCl₂¹³ and Mn¹⁴ have been reported to be effective for the reductive dimerization of aldehydes or ketones under aqueous conditions. In addition, Ren and coworkers succeeded in 2-cyclohexenylation of aldehydes with BiCl₃-NaBH₄ in THF-H₂O¹⁵. Here we wish to report that active metal bismuth is easily produced *in situ* via Sm/BiCl₃ system in THF-H₂O mixture under a nitrogen atmosphere. Promoted by this active species, α -bromoesters react with 1-(α -aminoalkyl) benzotriazole to give β -aminoesters in moderate to good yields. The products and the reaction conditions are shown in **Table 1**.

In order to extend the application of active bismuth as a mediator in aqueous media, we further used it to promote the reaction of α -bromoesters with diselenides. Fortunately, the reaction results in α -selenoesters in moderate to good yields. The products and the

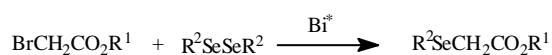
reaction conditions are shown in **Table 2**. The yields are best under a nitrogen atmosphere. The reaction can be carried out in the air. However, the yields are lower than ones obtained under a nitrogen atmosphere.

Scheme 1**Table 1** Synthesis of β -aminoesters^{a)}

Entry	R ¹	R ²	R ³	R ⁴	Time	Yield(%) ^{b)}
1	CH ₃	H	C ₆ H ₅	H	10	82
2	CH ₃	H	<i>o</i> -CH ₃ C ₆ H ₄	H	10	78
3	CH ₃	H	<i>m</i> -ClC ₆ H ₄	H	10	84
4	C ₂ H ₅	H	C ₆ H ₅	H	10	80
5	C ₂ H ₅	H	<i>p</i> -CH ₃ C ₆ H ₄	H	10	77
6	C ₂ H ₅	H	<i>o</i> -BrC ₆ H ₄	H	10	83
7	C ₂ H ₅	H	C ₆ H ₅	CH ₃	12	72

a) All products were characterized by ¹HNMR and IR spectra.

b) Isolated yields based on 1-(α -aminoalkyl) benzotriazole.

Scheme 2**Table 2** synthesis of α -selenoesters^{a)}

Entry	R ¹	R ²	Time	Atmosphere	Yield(%) ^{b)}
1	CH ₃	C ₆ H ₅	8	N ₂	80
2	CH ₃	C ₆ H ₅	8	Air	70
3	C ₂ H ₅	C ₆ H ₅	8	N ₂	81
4	C ₂ H ₅	C ₆ H ₅	8	Air	72
5	CH ₃	C ₆ H ₅ CH ₂	8	N ₂	72
6	C ₂ H ₅	C ₆ H ₅ CH ₂	8	N ₂	75
7	CH ₃	4-ClC ₆ H ₄	8	N ₂	84
8	C ₂ H ₅	4-ClC ₆ H ₄	8	N ₂	89
9	CH ₃	4-CH ₃ C ₆ H ₄	8	N ₂	82
10	C ₂ H ₅	4-CH ₃ C ₆ H ₄	8	N ₂	88

a) All products were characterized by ¹HNMR and IR spectra.

b) Isolated yields based on diselenides.

β -Aminoesters and organoselenium compounds are useful synthetic reagents as intermediates in organic synthesis¹⁶. The present procedure provides a simple, efficient and practical method for the synthesis of β -aminoesters and α -selenoesters.

Experimental

General Procedure for synthesis of β -aminoesters and α -selenoesters: In a 50 mL three-neck flask fitted with a reflux condenser, were placed BiCl₃ (1.2 mmol), THF (10 mL), Sm powder (2.0 mmol), α -bromoester (1.2 mmol), H₂O (2.5 mL) and 1-(α -aminoalkyl) benzotriazole (1.0 mmol) or diselenide (0.5mmol). The mixture was stirred at 60°C for a given hours (see **Table 1** or **Table 2**) under a nitrogen atmosphere. The inorganic by-product was filtered off and washed with ether (3×10 mL). The combined ether-THF solutions were then washed with brine (2×10 mL) and dried over magnesium sulfate. The solvent was evaporated in *vacuo* and the product was isolated by preparative TLC (silica gel) with cyclohexane and ethyl acetate (4:1 for the former and 10:1 for the latter) as eluent.

Acknowledgment

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