

Synthesis of α -Selenoesters and α -Thioesters via Sm/SbCl₃ System in Aqueous Media

Gen Liang LU, Yong Min ZHANG*

Department of Chemistry, Zhejiang University (Campus Xixi), Hangzhou 310028

Abstract: α -Selenoesters and α -thioesters are synthesized *via* reactions of α -bromoesters with diselenides and disulfides promoted by Sm/SbCl₃ system in aqueous media in moderate to good yields.

Keywords: α -Selenoesters, α -thioesters; samarium, antimony trichloride, aqueous media.

Since the first Barbier-type reaction in aqueous media in 1977¹, organometallic reactions have attracted considerable attention in organic synthesis². If one can perform organometallic-type reactions in aqueous media just as generally and easily as in organic solvents, such reactions may offer considerable advantages: (1) There is the practical convenience of not having to handle inflammable and anhydrous organic solvents. (2) The tedious task of protection-deprotection chemistry for certain functional groups often encountered in organic synthesis may not be required. (3) Water-soluble compounds can be reacted directly without the need of derivatization. This is a point of particular interest in carbohydrate chemistry. The most commonly used metals are zinc, tin, indium and bismuth^{2,3}.

However, the type of aqueous organometallic reaction seems to have been somewhat limited. It has been used mainly in allylation and propargylation of carbonyl compounds. We became interested in other type of the aqueous organometallic reaction⁴.

The application of metallic antimony in organic synthesis has been studied⁵. But in most cases, those reactions were carried out in nonaqueous condition. Recently, P. D. Ren and coworkers succeeded in allylation of aldehydes with SbCl₃/NaBH₄ in DMF/H₂O⁶. Here we wish to report that the reactions of α -bromoesters with diselenides and disulfides promoted by Sm/SbCl₃ system in DMF/H₂O give α -selenoester and α -thioesters under a nitrogen atmosphere. The products and the reaction conditions are shown in the **Table 1**. We examined the effects of several solvents and found that comparatively high yields are obtained from DMF/H₂O system.

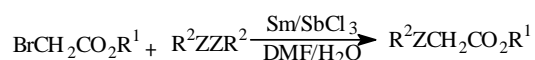


Table 1. Reaction condition and yield^{a)}

Entry	R ¹	R ²	Z	Reaction Time (h)	Yield(%) ^{b)}
1	CH ₃	Ph	Se	10	83
2	C ₂ H ₅	Ph	Se	10	90
3	CH ₃	p-ClC ₆ H ₄	Se	10	81
4	C ₂ H ₅	p-ClC ₆ H ₄	Se	10	81
5	CH ₃	p-CH ₃ C ₆ H ₄	Se	10	85
6	C ₂ H ₅	p-CH ₃ C ₆ H ₄	Se	10	82
7	CH ₃	C ₆ H ₅ CH ₂	Se	14	74
8	C ₂ H ₅	C ₆ H ₅ CH ₂	Se	14	70
9	CH ₃	Ph	S	14	76
10	C ₂ H ₅	Ph	S	14	80

a) All product were characterized by ¹H NMR and IR spectra.

b) Isolated yields based on diselenides and disulfides.

Selenides and sulfides are useful synthetic reagents as intermediates in organic synthesis⁷. We provided a novel alternative route to selenoesters and thioesters with advantage of readily available starting materials, straightforward and simple synthetic procedures, mild reaction conditions and moderate to good yield.

Acknowledgment

We thank the National Natural Science Foundation of China (Project No. 29872010 and 294938004), NSF of Zhejiang Province, China and the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences for financial support.

References

1. T. A. Killinger, N. A. Boughton and J. Wolinsky, *J. Organomet. Chem.* **1977**, *124*, 131.
2. a) T. H. Chan, C. J. Li, M. C. Lee, Z. Y. Wei, *Can. J. Chem.* **1994**, *72*, 1181;
b) C. J. Li, *Chem. Rev.* **1993**, *93*, 2023;
c) A. Lubineau, J. Auge, Y. Queneau, *Synthesis* **1994**, 741;
d) T. H. Chan, M. B. Isaac, *Pure & Appl. Chem.* **1996**, *68*, 919.
3. A. R. Katritzky, N. Shobana, P. A. Harris, *Organometallics* **1992**, *11*, 1381.
4. G. L. Lu, Y. M. Zhang, *Synth. Commun.* **1998**, *28*, 4479.
5. a) Y. Butsugan, H. Ito, S. Araki, *Tetrahedron Lett.* **1987**, *28*, 3707.
b) C. Chen, Y. C. Shen, Y. Z. Huang, *Tetrahedron Lett.* **1988**, *29*, 1395.
c) W. B. Wang, L. L. Shi, R. H. Xu, Y. Z. Huang *J. Chem. Soc. Perkin Trans. I* **1990**, 424.
6. P. D. Ren, Q. H. Jin, Z. P. Yao *Synth. Commun.* **1997**, *27*, 2761.
7. S. Patai, Z. Rappoport, (eds): *The Chemistry of Organic Selenium and Tellurium Compounds*, Vol. 1, Wiley, Chichester, **1986**.

Received 24 March 1999