

Reductive Cleavage of the Se-Se Bond by the Sm-CdCl₂-HMPA System: A New One-Pot Method for the Synthesis of Selenoesters

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Abstract: Treatment with Sm-CdCl₂-HMPA system, dibenzyl and diphenyl diselenides react with acyl halides and acid anhydrides in one-pot to give corresponding selenoesters in good yields under mild and neutral conditions.

Keywords: Samarium, cadmium chloride, diselenide, selenoester.

Organoselenium compounds have attracted considerable interest as useful synthetic reagents and intermediates in organic synthesis¹. There are many methods for the synthesis of selenoesters, which include the reduction of the diselenide with samarium diiodide², lithium aluminium hydride³, *etc.* Here, we wish to report a new method for the preparation of the active cadmium reagent *in situ* from Sm/CdCl₂/HMPA system. It reacts with diselenides to generate cadmium(II) selenolates and then cadmium(II) selenolates react with acid chlorides and acid anhydrides to give selenoesters in good yields. The results are summarized in **Table 1**.

A typical procedure is as follows: samarium powder (1.2 mmol), cadmium chloride (1.2 mmol) and diselenide (0.5 mmol) were placed in a three-necked flask and 8ml THF (0.15ml HMPA) were added in N₂. The mixture was stirred for the time indicated in **Table 1**. Then hydrochloric acid (0.1mol/L, 3ml) was added and the mixture was extracted with ether. The extracts were washed with brine and dried over anhydrous MgSO₄. The pure product was separated from the residue on preparative TLC.

Scheme 1

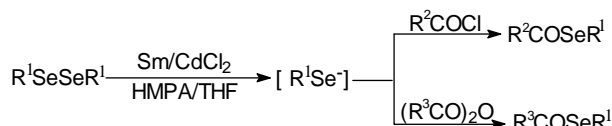


Table 1 Synthesis of Selenoesters*

Entry	R ¹	R ²	R ³	Reaction Condition		Yield(%)**
				t / h	T / °C	
a ²	Ph		CH ₃	2.5	45	86
b ⁴	Ph		CH ₃ CH ₂ CH ₂	2.5	45	82
c ²	Ph	Ph		2.5	45	90
d ⁵	Ph	CH ₃ (CH ₂) ₁₀		2.5	45	83
e ⁴	Ph		CH ₃ CH ₂	2.5	45	84
f	PhCH ₂		CH ₃	3	50	75
g	PhCH ₂		CH ₃ CH ₂	3	50	73
h	PhCH ₂		CH ₃ CH ₂ CH ₂	3	50	70
i	PhCH ₂	CH ₃ (CH ₂) ₁₀		3	50	76

* All products were characterized by ¹H NMR and IR. ** Isolated yields

References and notes

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6. Compounds **f**, **g**, **h**, **i** have not been documented up to now. Data for **f**: oil, ¹H NMR(CCl₄) δ_H 7.4-7.1(m, 5H), 3.9(s, 2H), 2.2(s, 3H); ν/cm⁻¹1740; MS, M⁺: 214, 43(100).

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