

Michael Additions of Activated Methylene Compounds to α, β -Unsaturated Esters Promoted by Samarium (III) Iodide

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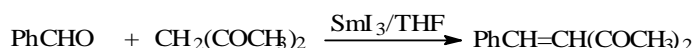
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Abstract: Promoted by SmI₃, β -diketones, β -ketoesters and α -cyano esters were added to α, β -unsaturated esters to form δ -carbonyl esters in mild conditions in moderate to good yields.

Keywords: Samarium, Michael addition, α, β -unsaturated ester, β -diketones, δ -carbonyl esters.

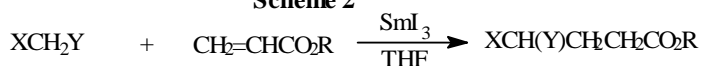
In the last decades the applications of samarium reagents in organic synthesis have been rapidly increased¹⁻⁶. Catalyzed by Sm(OTf)₃ benzyl amine can add to ethyl crotonate to form β -amino esters²; at the aid of Sm(OTf)₃ and *s*-BuLi methyl iodide has been added to carbonyl group of acetophenone³; We have reported that promoted by SmI₃ α -haloketones can react with aldehydes to give α, β -unsaturated ketones⁴. Very recently, we found that β -diketones can be synthesized *via* reaction of α -haloketones with acid chlorides or acid anhydrides at the aid of SmI₂ or SmI₃⁵. We also reported that mediated by SmI₃, β -diketones or β -ketoesters can condense with aldehydes to form benzylidene-substituted β -diketones or β -ketoesters in fair yield (**Scheme 1**)⁶.

Scheme 1



The Michael reaction is one of the most useful methods for forming carbon-carbon bond and has wide synthetic applications. These reactions are usually carried out in the presence of a strong base. Certainly many other methods have been explored in fitting with the so important reaction⁷. Our previous work⁶ on condensing aldehydes with β -diketones to form benzylidene-substituted β -diketones led us to investigate the Michael addition of activated methylene compounds such as β -diketones with α, β -unsaturated esters promoted by SmI₃ to form δ -carbonyl esters (**Scheme 2**).

Scheme 2



X = COCH₃, CO₂Et; Y = COCH₃, CN

The results were summarized in **Table 1**. We obtained δ -carbonyl esters as products in moderate to good yields. β -ketoester and ethyl α -cyano acetate were also

added to α, β -unsaturated esters in satisfactory yields. Unlike traditional base-promoted reactions this reaction was performed in neutral, mild conditions and avoided some side reaction occurred in basic condition. The mechanism should be the same with what we proposed previously⁸. The products were characterized fully by ¹H NMR and IR spectra.

Table 1 Products and the Yields

Entry	XCH ₂ Y	R	Yield(%)*
1	CH ₃ COCH ₂ COCH ₃	CH ₃	75
2	CH ₃ COCH ₂ COCH ₃	CH ₂ CH ₃	75
3	CH ₃ COCH ₂ COCH ₃	Bu- <i>n</i>	61
4	CH ₃ COCH ₂ CO ₂ Et	CH ₃	78
5	CH ₃ COCH ₂ CO ₂ Et	CH ₂ CH ₃	76
6	CH ₃ COCH ₂ CO ₂ Et	Bu- <i>n</i>	65
7	NCCH ₂ COOEt	CH ₃	72
8	NCCH ₂ COOEt	CH ₂ CH ₃	70
9	NCCH ₂ COOEt	Bu- <i>n</i>	75
10	EC	CH ₂ CH ₃	76
11	EC	Bu- <i>n</i>	68

* Isolated yields; EC=2-(ethoxycarbonyl)-cyclopentanone.

General Procedure

To a solution of SmI₃ (2mmol, in 15mL acetonitrile) were added acetylacetone (2mmol, 0.2g) and ethyl acrylate (2mmol, 0.17g) sequentially. After stirred at 30-40°C for 10-12hr, the reaction was quenched with dilute hydrochloric acid (0.1mol/L, 1ml). The crude product was isolated with usual ways and purified by preparative TLC on silica gel using cyclohexane and ethyl acetate (5:1) as eluent.

Acknowledgments

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