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The Stereoselective Michael Reaction of α,β-Unsaturated Thioesters with Silyl Enol Ethers Promoted by Combined Use of Antimony(V) Chloride and Tin(II) Triflate

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α,β-Unsaturated thioesters react with silyl enol ethers to afford the corresponding Michael adducts stereoselectively in high yields by the use of a new catalyst, combined use of antimony(V) chloride and tin(II) triflate.

The acid-catalyzed Michael reaction of α,β-unsaturated esters with enolate components is a useful method for the preparation of 5-oxocarboxylic acid esters or glutarate derivatives. However, there still remain several problems in the acid promoted reaction because of the low reactivities of α,β-unsaturated esters and the occurance of competitive polymerization reaction.[1)]

In the previous paper,[2)] we have demonstrated that, in the presence of a catalytic amount of trityl salts, α,β-unsaturated orthoesters react with silyl enol ethers to afford the corresponding Michael adducts in good yields. In the course of our investigations to search for effective α,β-unsaturated ester equivalents, which are more reactive than α,β-unsaturated esters, it was found that α,β-unsaturated thioesters behave as excellent Michael acceptors. In this communication, we would like to describe the Michael reaction of α,β-unsaturated thioesters with silyl enol ethers. We also report here a new catalyst system, combined use of antimony(V) chloride and tin(II) trifluoromethanesulfonate (triflate), which effectively activates α,β-unsaturated thioesters.

In the first place, the reaction of S-ethyl 2-butenethioate[3)] with silyl enol ether of propiophenone was chosen as a model reaction and several reaction conditions were examined. From the viewpoint of economy and mildness of reaction conditions, we searched for catalysts which promote the reaction by a catalytic use. In the presence of a catalytic amount of trityl salts, which is an excellent catalyst in the glycosidation reaction, aldol reaction, and the Michael reaction with α,β-unsaturated ketones,[4)] however, the desired Michael adduct was obtained in rather low yields in the present reaction of using an α,β-unsaturated thioester. Similarly, the use of catalytic amounts of several Lewis acids were not effective. On the other hand, it was recently made clear that the combined use of trimethylsilyl chloride and tin(II) chloride[5)] or trityl chloride and tin(II) chloride[6)] is an excellent catalyst system in aldol and the Michael reactions. So next, we screened the combination of several Lewis acids and tin(II) chloride in this reaction (Table 1). It was found that the desired Michael adduct was obtained in 70% yield by the combined use of antimony(V) chloride and tin(II) triflate (5 mol%) with high ul[7](anti) selectivities. It is noteworthy to point out that neither antimony(V) chloride nor tin(II) triflate is not effective in this reaction, so a new active species is formed by the combined use of the above two compounds.

Several examples are demonstrated in Table 2. In every case, the Michael adducts are obtained in good yields. Concerning the stereochemistry of the carbon-carbon bond forming process, the ul(anti) adducts are predominantly produced regardless of geometry of silyl enol ethers (Table 2, entries 2,3). The reaction of silyl enol ethers derived from ketones, which is unprecedented in the conventional methods, can be easily carried out to afford the corresponding Michael adducts in good yields. In the reaction of S-ethyl 2-propenethioate[8] (acrylic acid ethyl thioester), the adduct was obtained in rather low yield along with polymerization products. However, yield was improved by employing t-butyl thioester[8] instead of the above mentioned ethyl thioester (entries 6,7). Furthermore, S-ethyl 3-methyl-2-butenethioate, an example of α,β-disubstituted α,β-unsaturated thioester, can be successfully employed as an acceptor and the adduct with successive quarternary carbons is formed in moderate yield (entry 13).

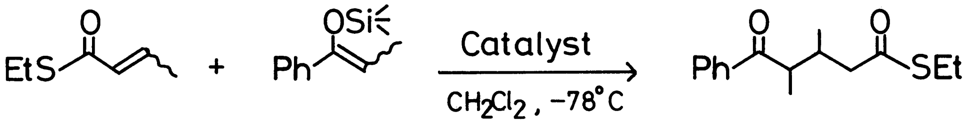


Table 1. An Effect of Catalysts

Entry	Catalyst	Yield/%
1	$TiCl_4$	0
2	BF_3 OEt_2	0
3	$SnCl_4$	32
4	$TiCl_4$-$SnCl_2$	8
5	$SnCl_4$-$SnCl_2$	41
6	$SbCl_5$-$SnCl_2$	49
7	$SbCl_5$-$Sn(OTf)_2$	70
8	$SbCl_5$	23
9	$Sn(OTf)_2$	0

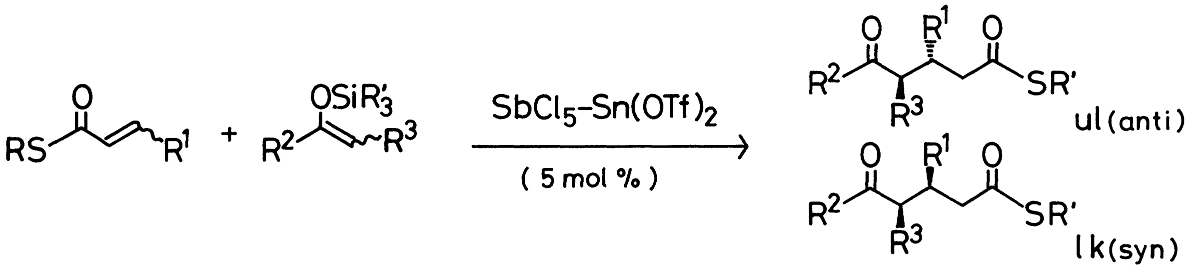
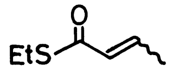
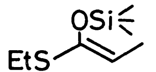
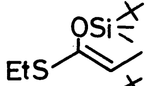
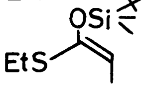
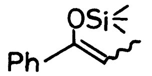
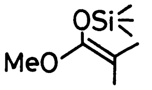
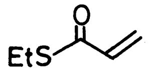
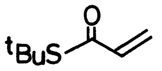
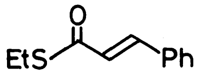
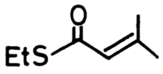


Table 2. The Reaction of α,β-Unsaturated Thioesters with Silyl Enol Ethers[a)]

Entry	α,β-Unsaturated thioester	Silyl enol ether	Yield/%	(ul / lk)[b)]
1	 1	 5	75	(87 / 13)
2	1	 6	78	(88 / 12)
3	1		84	(81 / 19)
4	1	 7	70	(94 / 6)
5	1	 8	81	
6		6	49	
7	 2	6	80	
8	2	7	48 c)	
9	2	8	73	
10	 3	5	65	(85 / 15)
11	3	6	70	(84 / 16)
12	3	8	93	
13		8	45 c)	

a) All the products gave satisfactory NMR and IR spectral data.

b) Determined by ^{13}C NMR and/or HPLC.

c) $SnCl_2$ was used insted of $Sn(OTf)_2$.

A typical procedure is described for the reaction of S-ethyl 2-butenethioate with silyl enol ether of propiophenone; antimony(V) chloride (0.025 mmol) and tin(II) triflate (0.025 mmol) was stirred in dichloromethane (1 ml) at room temperature for 30 min, and the mixture was cooled to -78 °C. S-Ethyl 2-butenethioate (0.4 mmol) and silyl enol ether of propiophenone (0.44 mmol) in dichloromethane (2 ml) was added and the mixture was allowed to stand for 4 h, then pH 7 phosphate buffer was added. After separation of the organic layer, the aqueous layer was extracted with dichloromethane. The organic layer was dried and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel to yield S-ethyl 3,4-dimethyl-5-oxo-5-phenyl-pentanethioate (70%, ul(anti)/lk(syn) = 94/6).

Thus, the reaction of α,β-unsaturated thioesters with silyl enol ethers is carried out in the presence of a catalytic amount of a new catalyst, combined use of antimony(V) chloride and tin(II) triflate, to afford the corresponding Michael adducts, synthetically valuable 5-oxocarboxylic acid ester of glutarate derivatives, stereoselectively in good yields. Further progress towards clarification of the active species of this new catalyst as well as other synthetic reactions by the use of this catalyst is now in progress.

References

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