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The Catalytic Asymmetric Michael Reaction of Tin(II) Enethiolates

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The catalytic asymmetric Michael reaction of tin(II) enethiolates forming 5-oxodithioesters in high yield with moderate to good enantioselectivity is achieved by employing catalytic amounts of stannous triflate and chiral diamine.

The development of chiral catalysts for organic synthesis has attracted great interest in recent years.$^{1)}$ However, examples of chiral catalysts for basic carbon-carbon bond forming reactions such as the aldol reaction$^{2)}$ and the Michael reaction$^{3)}$ are extremely limited. In the previous paper, we reported an asymmetric Michael reaction of tin(II) enolates employing chiral diamine ligands. In this communication we wish to report the first example of the catalytic asymmetric Michael addition reaction of metal enethiolates which proceeds under kinetic control conditions to give the corresponding adducts in moderate to good optical purity.

We assumed that the Michael reaction of trimethylsilyl enethiolate$^{4)}$ and α,β-unsaturated ketones could be catalyzed by the tin(II) triflate ($Sn(OTf)_2$)-chiral diamine complex as shown in the Scheme. Based on the consideration that tin exhibits affinity towards sulfur atoms and that the silicon-sulfur bond is a rather weak bond,$^{5)}$ we expected that the addition of enethiolate 1 to the $Sn(OTf)_2$-chiral diamine complex would result in the metal exchange reaction of tin and silicon to generate the tin(II) enethiolate 2 and TMSOTf. Activation of the α,β-unsaturated ketone by the generated TMSOTf would lead to the Michael reaction to give the silyl enol ether of the Michael adduct along with regeneration of the $Sn(OTf)_2$-chiral diamine complex. Thus, it was expected that the asymmetric Michael addition would proceed by employing only a catalytic amount of $Sn(OTf)_2$-chiral diamine complex.

We first tried the reaction by adding benzalacetone to a dichloromethane solution of enethiolate 1 in the presence of 20 mol% of $Sn(OTf)_2$-chiral diamine complex. In this case, the Michael adduct was obtained in 79% yield based on benzalacetone. However, the optical purity of this product was 24% e.e., which is substantially lower than the optical purity obtained when a stoichiometric amount of the chiral diamine is used, as reported in the preceding paper. We concluded that this decrease in enantioselectivity was due to the progress of a competitive reaction, in which the nucleophilic species is not the tin(II)

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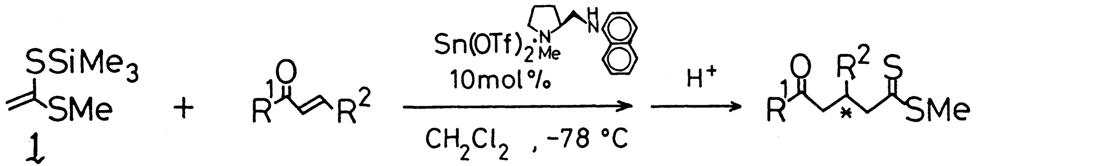
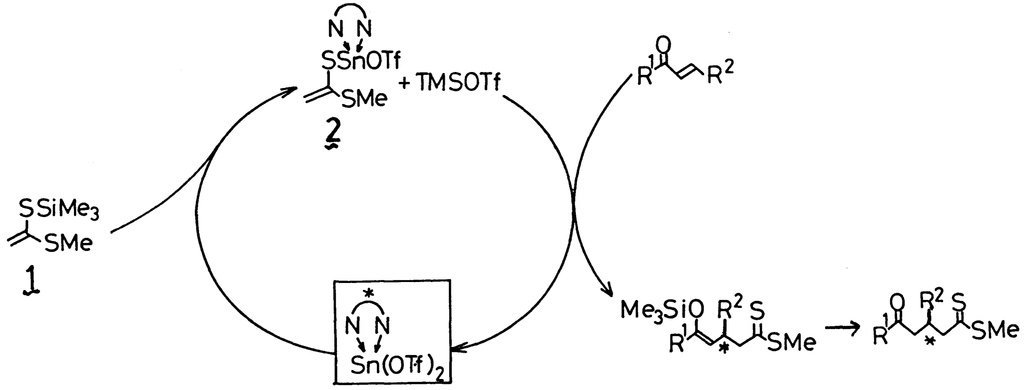


benzalacetone	80% ,	70% e.e.	(70% e.e.)[a]
furfuralacetone	82% ,	60% e.e.	(60% e.e.)
chalcone	79% ,	40% e.e.	(40% e.e.)

a) Optical purity obtained when stoichiometric amount of chiral diamine is employed.



Scheme 1.

enethiolate but trimethylsilyl enethiolate itself. With the expectation that this competitive reaction could be precluded by keeping the trimethylsilyl enethiolate in low concentration during the reaction, we attempted the slow charge of this substrate. A dichloromethane solution of benzalacetone (0.93 mmol) and 10 mol% of Sn(OTf)$_2$-diamine (0.09mmol) was cooled to -78 °C. To this mixture a dichloromethane solution of trimethylsilyl enethiolate (1.11 mmol) was added slowly over 4 hours. The solution was stirred for another hour and then the reaction was quenched with a 10% citric acid solution. Purification as described in the previous paper gave the Michael adduct in 80% yield based on benzalacetone (827% based on Sn(OTf)$_2$). Furthermore, the optical purity of this compound was 70% e.e., which is identical to the optical purity obtained when a stoichiometric amount of the chiral diamine is used. Therefore, a catalytic asymmetric reaction was realized. As shown in the equation, the same result was obtained with both chalcone and furfuralacetone.

Thus, the Michael adducts are obtained from trimethylsilyl enethiolate and α,β-unsaturated ketones in high yield with moderate to good enantioselectivity by using only a catalytic amount of Sn(OTf)$_2$-chiral diamine complex.

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