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An Efficient Chiral Promoter in the Aldol-type Reaction. Chiral Diamine Coordinated Tin(II) Triflate-Dibutyltindiacetate Complex

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An efficient chiral promoter, chiral diamine coordinated tin(II) triflate-dibutyltindiacetate complex, promotes the asymmetric aldol type reaction between both achiral silyl enol ethers derived from thioesters and a wide variety of aldehydes in high yields with perfect stereochemical control.

In the previous papers, we have reported on the highly enantioselective aldol-type reaction of achiral silyl enol ethers derived from thioesters[1,2] or esters[3] with achiral aldehydes by the use of a chiral promoter, combined use of chiral diamine coordinated tin(II) triflate and tributyltin fluoride. In these reactions, we assumed the formation of an active complex consisting of the above three components. This assumption was supported by the observation that the mixture of three components was completely soluble in dichloromethane, while either tin(II) triflate or tributyltin fluoride was sparingly soluble under the condition. In the above aldol-type reactions, the promoter was postulated to activate both an aldehyde and a silyl enol ether (double activations); the central tin(II) atom of tin(II) triflate activates an aldehyde and the electronegative fluoride involved in the promoter would interact with a silicon atom of an approaching silyl enol ether. Then, in order to clarify the possible structure of the active species as well as the mechanism of these reactions, the effect of tin(IV) compounds other than tributyltin fluoride in the above promoter was investigated. It was postulated that the similar reaction would proceed by the use of a tin(IV) compound having oxygen atom which is also expected to show a strong affinity toward silicon atom of silyl nucleophiles.

Several tin(IV) compounds such as tin(IV) alkoxides or tin(IV) carboxylates were examined by taking the reaction of benzaldehyde with 1-trimethylsiloxy-1-ethylthiopropene as a model. As shown in Table 1, the aldol-type products were obtained by combined use of the above tin(IV) compounds and chiral diamine coordinated tin(II) triflate in good to high yields with good to excellent diastereo- and enantioselectivities. These results strongly indicate that the active key species is three components complex as expected. In particular, perfect stereochemical control was achieved by combination of tin(II) triflate, (S)-1-methyl-2-[(N-1-naphthylamino)methyl]-pyrrolidine and dibutyltindiacetate. It is noteworthy to refer that this novel chiral promoter was quite effective in the aldol-type reaction of aliphatic or α,β-unsaturated aldehydes as well as aromatic aldehydes (Table 2). The reactions proceeded smoothly to improve the yields remarkably by the use of this novel promoter system, indicating that tin(IV) diacetate involved in this promoter is superior over the other tin(IV) compounds such as tributyltin fluoride.

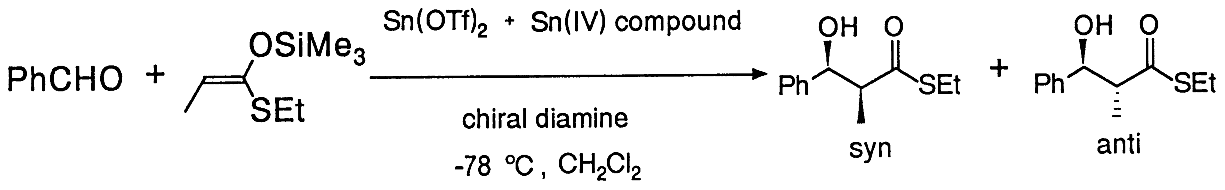
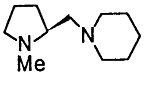


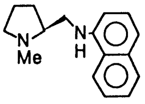
Table 1. Effect of additives, tin(IV) compounds

Tin(IV) compounds	Chiral diamine[a)]	Yield/%	syn/anti	ee/%[b)]
$^{n}Bu_3SnF$	A	80	93/ 7	80 (Ref. 2)
$^{n}Bu_3SnOAc$	A	65	63/37	55
$^{n}Bu_3SnOMe$	A	74	80/20	65
$^{n}Bu_2Sn(OMe)_2$	A	54	95/ 5	75
$^{n}Bu_3SnF$	B	86	100/ 0	>98 (Ref. 2)
$^{n}Bu_3SnOAc$	B	81	98/ 2	90
$^{n}Bu_2Sn(OAc)_2$	B	85	100/ 0	>98
$^{n}BuSn(OAc)_3$	B	93	100/ 0	75

a) Chiral diamine A:



B:



b) Optical purity given is that of the syn diastereomer.

A typical experimental procedure is described for the reaction of silyl enol ether of S-ethyl propanethioate(1) with crotonaldehyde; to a solution of tin(II) triflate (0.4 mmol) and (S)-1-methyl-2-[(N)-1-naphthylamino)methyl]-1-pyrrolidine (chiral diamine B, 0.48 mmol) in dichloromethane (1 ml) was added dibutyltin-diacetate (0.44 mmol) at room temperature. After the mixture was cooled to -78 °C, 1 (0.4 mmol) in dichloromethane (0.5 ml) and crotonaldehyde (0.36 mmol) in dichloromethane (0.5 ml) were successively added. The mixture was stirred for 3h and quenched with aqueous sodium hydrogen carbonate. S-Ethyl 2-methyl-3-hydroxy-4-hexenethioate was isolated (92%, syn aldol) after usual work up and separation by thin layer chromatography (silica gel). Anti aldol was not detected by TLC, HPLC and ^1H NMR. The enantiomeric excess was determined to be >98% by measurement of ^1H NMR spectrum of the corresponding acetyl derivative using $Eu(hfc)_3$ as a chiral shift reagent.

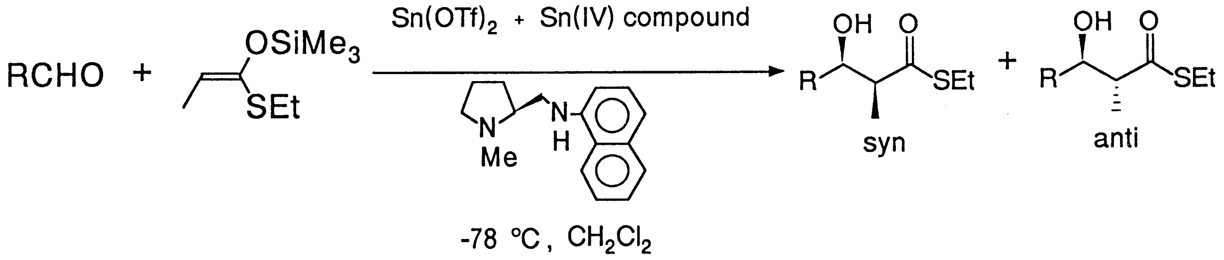


Table 2. Synthesis of syn-α-methyl-β-hydroxy thioesters

Aldehyde	Tin(IV) compound	Yield/%	syn/anti	ee/%
$CH_3(CH_2)_6CHO$	$^nBu_3SnF$	48	99/ 1	>98 (Ref. 2)
	$^nBu_2Sn(OAc)_2$	90	100/ 0	>98
$c\text{-}C_6H_{11}CHO$	$^nBu_3SnF$	54	100/ 0	>98 (Ref. 2)
	$^nBu_2Sn(OAc)_2$	90	100/ 0	>98
i-PrCHO	$^nBu_3SnF$	52	100/ 0	>98 (Ref. 2)
	$^nBu_2Sn(OAc)_2$	70	100/ 0	>98
(E)-CH_3-CH=CH-CHO	$^nBu_2Sn(OAc)_2$	92	100/ 0	>98

In order to know the structure of this chiral promoter, tin(II) triflate, (S)-1-methyl-2-[(N-1-naphthylamino)methyl]-pyrrolidine and dibutyltindiacetate, ^{119}Sn NMR spectrum was taken in dichloromethane. In this NMR spectrum, divalent tin and tetravalent tin resonated at δ -632.2 and -155.1 ppm, respectively.[4] This is the first spectral evidence of the promoter, indicating a formation of three components complex(2) without accompanying any metal exchanges.

It should be noted that three components complex, tin(II) triflate, (S)-1-methyl-2-[(N-1-naphthylamino)methyl]-pyrrolidine and dibutyltindiacetate initially accepts an aldehyde and it efficiently recognizes an enantioface of an approaching silyl enol ether to realize the asymmetric aldol reaction with perfect stereochemical control.

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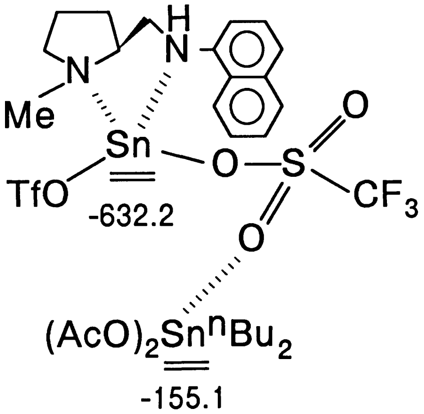

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References

1) S. Kobayashi and T. Mukaiyama, Chem. Lett., 1989, 298.

2) T. Mukaiyama, H. Uchiro, and S. Kobayashi, Chem. Lett., 1989, 1001.

3) S. Kobayashi, T. Sano, and T. Mukaiyama, Chem. Lett., 1989, 1319.

4) Tetravalent tin of dibutyltindiacetate resonated at δ -149.2 ppm in dichloromethane. All the chemical shifts were recorded relative to the signal of tetramethyltin as an external standard.

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