

CATALYTIC USE OF TIN(II) REAGENTS IN ORGANIC SYNTHESIS

Nobuharu IWASAWA, Takeshi YURA, and Teruaki MUKAIYAMA[#]

Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received in Japan 4 November 1988)

Abstracts: New carbon-carbon bond forming reactions using a catalytic amount of tin(II) reagents have been developed. Namely, an aldol type reaction of tin(II) enolate is achieved starting from α,β -unsaturated ketone, aldehyde and ethylthiotrimethylsilane in the presence of a catalytic amount of tin(II) triflate sulfide. Furthermore, the catalytic asymmetric Michael reaction of tin(II) enethiolate is realized just by using a catalytic amount of tin(II) triflate-chiral diamine complex.

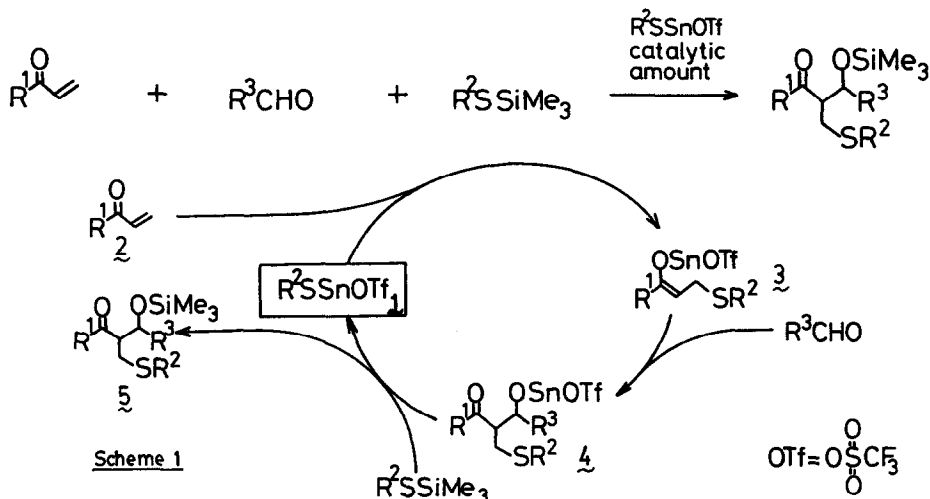
Achievement of stereoselectivity in synthetic organic reactions is one of the greatest challenges facing organic chemist today. The last decade has seen a remarkable progress in this field, where many reactions with a high degree of diastereoselectivity and enantioselectivity have been developed. A central aspect of this surge has been the utilization of various new elements such as Ti, B, Pd, Rh, etc., which were not commonly employed in synthetic reactions before. As such reactions are developed, attention is now being focussed on the development of catalytic reactions especially in the carbon-carbon bond forming reactions, in which a high degree of stereoselection, both diastereoselectivity and enantioselectivity, is achieved by using only a catalytic amount of reagents. Such reactions have not only great aesthetic value but are also of advantage in terms of both rate and economy. Thus, the development of catalytic stereoselective reactions, especially catalytic asymmetric reactions, has become a major topic of modern organic synthesis.¹⁾

During the past six years, extensive work has been carried out in our group on the utilization of tin(II) compounds in organic synthesis.²⁾ In this paper, we wish to report our efforts towards the development of organic reactions in which stereoselectivity is achieved by using a catalytic amount of the tin(II) reagents.³⁾

We first focussed our attention on the aldol reaction. The aldol reaction is a fundamental carbon-carbon bond forming reaction, and extensive research has been carried out on the stereocontrol of this reaction, utilizing various metal enolates.⁴⁾ In our group, an aldol reaction via tin(II) enolates, generated in situ from ketones and tin(II) trifluoromethanesulfonate (triflate) has been recently developed and it has been shown that the corresponding aldol product is

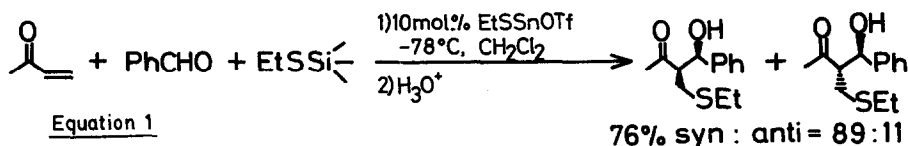
[#]Present address: Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, Shinjuku-ku, Tokyo 162.

produced in high yield with good stereoselectivity.⁵⁾ However, in all of these conventional aldol reactions employing preformed metal enolates, the starting carbonyl compound is quantitatively converted to the corresponding metal enolate and consequently a stoichiometric amount of the metal reagent is required. Therefore, we started our work on catalytic reactions with the aim of developing stereoselective aldol reactions employing a catalytic amount of the metal reagent with the expectation that such a reaction could be realized according to the catalytic cycle shown in Scheme 1.



Namely, in the first step, the conjugate addition of the tin(II) species **1** to vinyl ketone **2** produces the tin(II) enolate **3** which in turn reacts with aldehyde to give the corresponding aldol product **4** as its tin(II) alkoxide.⁶⁾ In the next step, this tin(II) alkoxide reacts with alkylthiotrimethylsilane to regenerate the tin(II) species along with the aldol product as its trimethylsilyl ether **5**. The affinity of tin to sulfur, and the weakness of the silicon-sulfur bond is the main driving force of this reaction step.⁷⁾ Thus, it was assumed that the aldol reaction via tin(II) enolate would proceed by employing only a catalytic amount of the tin(II) species **1**.

We first tried this reaction according to the following procedure. A catalytic amount of tin(II) triflate sulfide, prepared in situ from tin(II) triflate and the lithium salt of ethanethiol, was treated with methyl vinyl ketone in dichloromethane, followed by addition of benzaldehyde and ethylthiotrimethylsilane. The reaction proceeded smoothly to afford the desired aldol product in 76% yield with a diastereomer ratio of 89:11. (Equation 1)



At this stage, we considered the alternative possibility that the reaction would proceed via the silyl enol ether of the ketone, promoted by the tin(II) species, a Lewis acid catalysis, as shown in Scheme 2.⁸⁾ However, when a mixture of

benzaldehyde, methyl vinyl ketone, ethylthiotrimethylsilane was treated with several Lewis acids, such as $\text{BF}_3 \cdot \text{OEt}_2$ and SnCl_4 , as shown in Table 1, both yields and stereoselectivity of the aldol products obtained were poor in all cases.

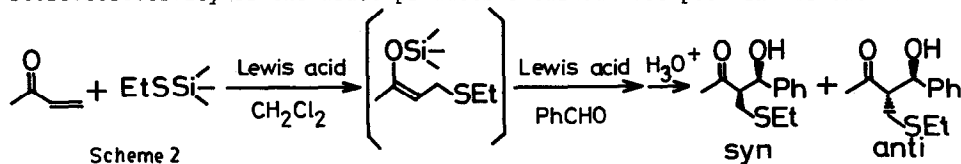


Table 1.

Lewis acid	Yield/% ^{a)}	Syn:Anti ^{b)}
$\text{BF}_3 \cdot \text{OEt}_2$ ^{c)}	36	31:69
SnCl_4 ^{c)}	24	34:66
$\text{Sn}(\text{OTf})_2$ ^{d)}	36	63:37

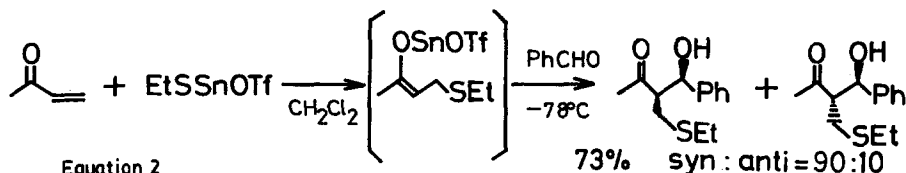
a) Isolated yield.

b) Diastereomers were separated by silica-gel column chromatography. The stereochemistry of the diastereomers was determined by the ^1H and ^{13}C NMR spectra.⁹⁾

c) The Lewis acid was employed in a catalytic amount (10 mol%).

d) Stoichiometric amount of $\text{Sn}(\text{OTf})_2$ was employed.

In contrast, when methyl vinyl ketone was treated with an equimolar amount of tin(II) triflate sulfide, followed by the addition of benzaldehyde, the reaction proceeded smoothly to afford the aldol product in 73 % yield with a syn:anti ratio of 90:10. (Equation 2) The result is similar to that obtained when a catalytic amount of tin(II) triflate sulfide is used. These observations strongly suggest that the present reaction is indeed proceeding via the tin(II) enolate by the use of tin(II) triflate sulfide as a catalyst.



Subsequent screening of solvents showed that tetrahydrofuran is the solvent of choice. Furthermore, it was found that the yield was improved to 68 % without loss of stereoselectivity when the reaction was carried out at -45°C . (Table 2)

Having attained the best reaction conditions, the reaction of methyl vinyl ketone and phenyl vinyl ketone with benzaldehyde and 3-phenylpropanal was tried and in all cases the corresponding aldol products were obtained in good yields with high stereoselectivity. (Table 3)

Thus, tin(II) enolate mediated aldol reaction of vinyl ketones, ethylthiotrimethylsilane and aldehydes was realized by using only a catalytic amount of the tin(II) species. The corresponding aldol products are obtained in good yields with high stereoselectivity.

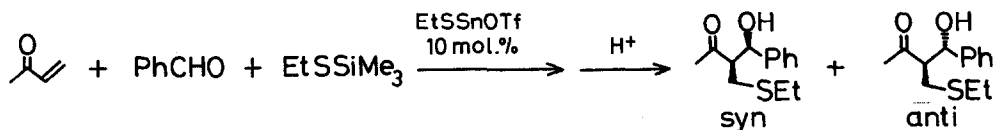


Table 2.

Solvent	Yield/% ^{a)}	Syn:Anti ^{b)}
CH ₂ Cl ₂	76	89:11
THF	54	95: 5
Et ₂ O	57	89:11
toluene	48	68:32
THF	68 ^{c)}	95: 5

a) Isolated yield.

b) Diastereomer ratio was determined by the same procedure described in Table 1.

c) The reaction was carried out at -45 °C.

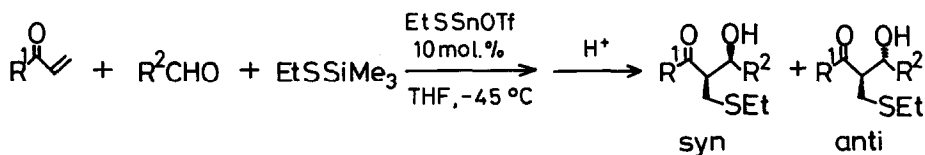


Table 3.

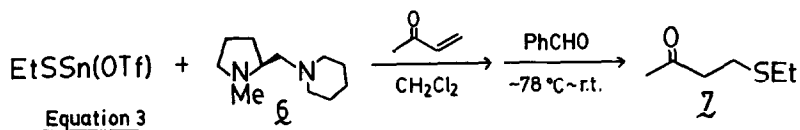
	R ¹	R ²	Yield/% ^{a)}	Syn:Anti ^{b)}
1.	CH ₃	Ph	68	95: 5
2.	CH ₃	PhCH ₂ CH ₂	75	90:10
3.	Ph	PhCH ₂ CH ₂	73	84:16

a) Isolated yield.

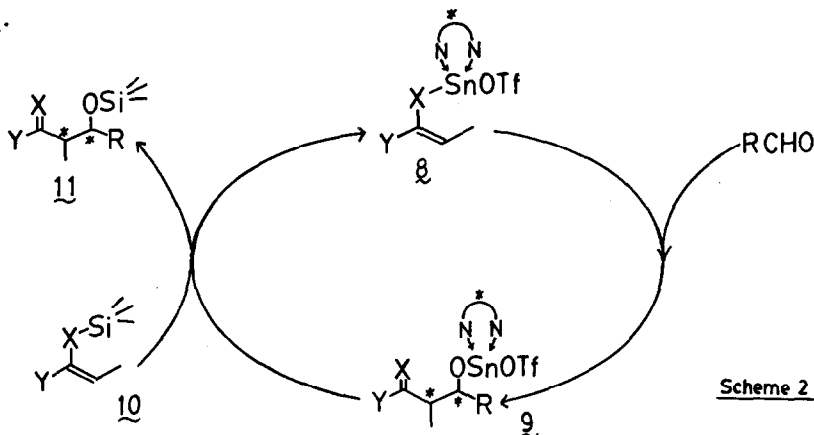
b) Diastereomers were separated by silica-gel column chromatography. The stereochemistry of the diastereomers was determined by the ¹H and ¹³C NMR spectra.⁹⁾

We have already established excellent enantioselective aldol reaction of tin(II) enolates by utilizing characteristic property of strong coordination of chiral diamines to tin(II) enolate.¹⁰⁾ Having realized a catalytic aldol reaction of tin(II) enolates, we next attempted this reaction in the presence of a chiral diamine, hoping that a catalytic asymmetric aldol reaction would become possible.¹¹⁾ Firstly, the reaction was tried with a stoichiometric amount of

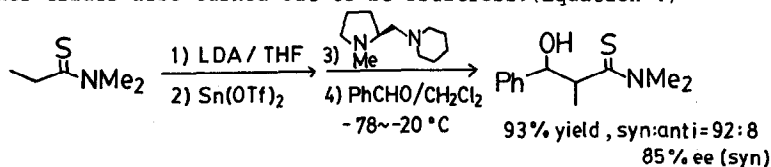
tin(II) triflate sulfide and the chiral diamine 6. That is, to the mixture of tin(II) triflate sulfide and the chiral diamine 6, equimolar amounts of methyl vinyl ketone and then benzaldehyde was added. Contrary to our expectation, only the Michael addition product 7 was obtained and no trace of the aldol product was detected. (Equation 3) This lack of reactivity is probably due to the fact that the Lewis acidity of tin(II) is diminished due to the coordination of the chiral diamine and the sulfur atom. Further examinations of reaction conditions such as solvents, sulfides, and so on gave no fruitful results.

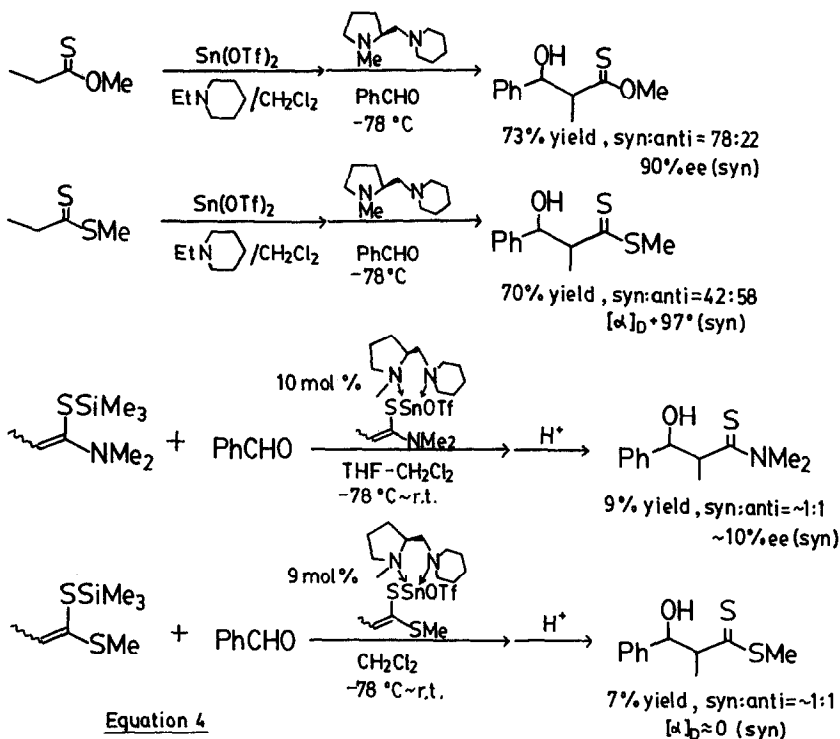


At this point, we examined another possibility of a catalytic asymmetric aldol reaction, which is schematically shown in Scheme 2. In this case, tin(II) enolate 8 coordinated by a chiral diamine is the key catalytic species, which reacts with an aldehyde to give the corresponding aldol product 9 as its tin(II) alkoxide 9. In the next step, this tin(II) alkoxide reacts with silyl enethiol ether 10 to regenerate the tin(II) enolate along with the aldol product as its TMS ether 11.



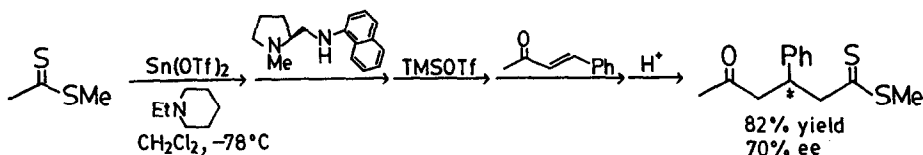
First of all, stoichiometric asymmetric aldol reactions using various propionate derivatives were examined, and as shown in Equation 4, propanethioamide and propanethioate derivatives gave very promising results. Having realized high optical purity, we next turned our attention to a catalytic reaction. Thus, to 10 mol % amount of tin(II) enolate of propanethioamide and chiral diamine 6, benzaldehyde and TMS enethiol ether of propanethioamide were added successively. However, the result was quite disappointing and the desired aldol product was obtained in only 9 % yield and the optical purity of the product was also very low. Several other trials also turned out to be fruitless. (Equation 4)





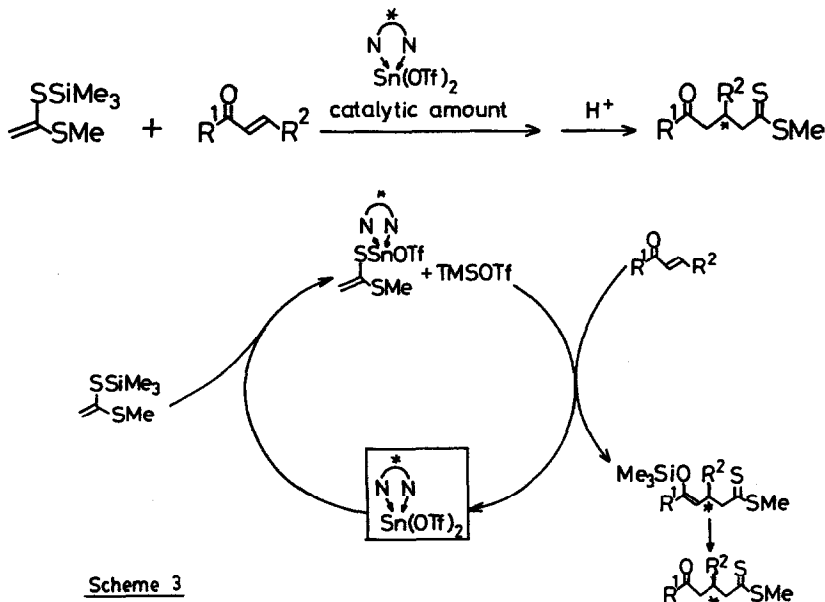
Although successful results were not obtained in the catalytic aldol reaction, it is pointed out that this is the first successful results concerning the tin(II) enolate mediated asymmetric aldol reaction of propionate derivatives utilizing the coordination of chiral diamine ligands.

While the possibilities of catalytic asymmetric aldol type reactions were being extensively examined, it was found that tin(II) enolates add in a 1,4-manner to α,β -unsaturated ketones in the presence of trimethylsilyl chloride.¹²⁾ Furthermore, the asymmetric Michael addition reaction of tin(II) enolate is achieved in moderate to high optical purity by the utilization of the coordination of chiral diamine ligands to the intermediate tin(II) enolate.¹³⁾ For example, tin(II) enolate of dithioacetic acid methyl ester reacts with benzalacetone in the presence of chiral diamine and trimethylsilyl trifluoromethanesulfonate (TMSOTf) to give the corresponding Michael adduct in 82% yield in 70% optical purity.

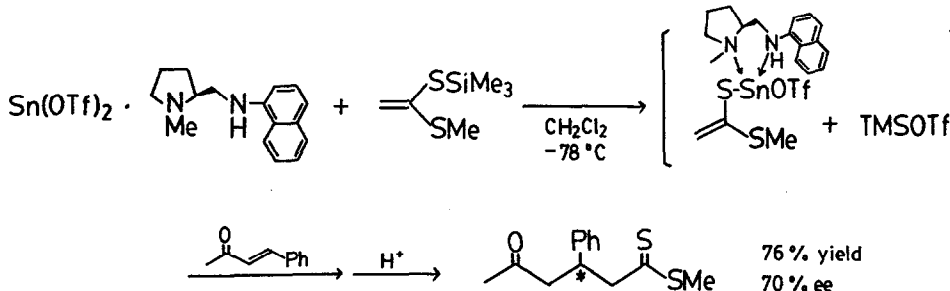


The result suggests that the Michael reaction of trimethylsilyl enethiolate and α,β -unsaturated ketones could be catalyzed by the tin(II) triflate-chiral diamine complex as shown in the Scheme 3. Based on the consideration that tin exhibits affinity towards sulfur atoms and that the silicon-sulfur bond is a

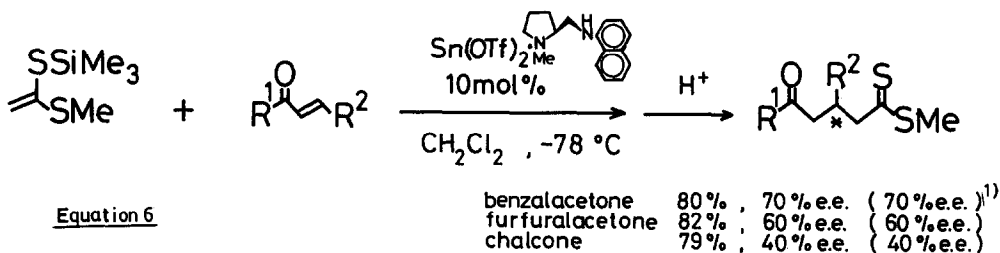
rather weak bond, we expected that the addition of trimethylsilyl enethiolate to the tin(II) triflate-chiral diamine complex would result in the metal exchange between tin and silicon to generate the tin(II) enethiolate and TMSOTf. Activation of the α,β -unsaturated ketone by the TMSOTf thus generated would lead to the Michael reaction to give the silyl enol ether of the Michael adduct along with regeneration of the tin(II) triflate-chiral diamine complex. Thus, it was expected that the asymmetric Michael addition would proceed by employing only a catalytic amount of tin(II) triflate-chiral diamine complex.¹⁴⁾



In the first place, we examined the possibility of the exchange reaction between silicon-sulfur bond and tin(II)-OTf bond. Thus, to the tin(II) triflate-chiral diamine complex was added 0.8 equivalent of trimethylsilyl enethiolate and 0.64 equivalent of benzalacetone at -78°C . Work-up of the reaction mixture gave the Michael adduct in 76 % yield, and the optical purity of the product was shown to be the same with that obtained by the previous procedure.¹³⁾ This result indicates that the exchange reaction between tin(II) triflate and trimethylsilyl enethiolate really takes place rapidly as expected. (Equation 5)



Then, we next examined the catalytic asymmetric Michael reaction. Thus, benzalacetone was added to a dichloromethane solution of trimethylsilyl enethiolate in the presence of 20 mol % of tin(II) triflate-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. 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) 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 tin(II) triflate-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 10 % citric acid solution. Purification of the crude product gave the Michael adduct in 80 % yield based on benzalacetone (827 % based on tin(II) triflate). 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 Equation 6, the same result was obtained with both chalcone and furfuralacetone.



Equation 6

1) Optical yield obtained when stoichiometric amount of chiral diamine is employed.

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 tin(II) triflate-chiral diamine complex.

Experimental

Tin(II) triflate and chiral diamines were prepared according to the procedure described in reference 2a). Ethylthiotrimethylsilane¹⁵ and trimethylsilyl enethiolate of methyl dithioacetate¹⁶) were prepared according to the literature method.

Catalytic aldol reaction.

A typical procedure is described for the reaction of methyl vinyl ketone with

3-phenylpropanal. (Table 3, entry 2)

To a solution of ethanethiol (10 mg, 0.17 mmol) in 2 ml of tetrahydrofuran (THF) was added 0.11 ml of 1.54 M *n*-butyllithium in hexane at 0 °C under argon atmosphere. Tin(II) triflate (69 mg, 0.17 mmol) was added and, after 20 min, the mixture was cooled to -45 °C. Methyl vinyl ketone (118 mg, 1.68 mmol) in 1.5 ml THF and 3-phenylpropanal (350 mg, 2.61 mmol) in 1.5 ml of THF were successively added to the mixture. The reaction mixture was further stirred for 12 h, then quenched with 10 % aqueous solution of citric acid, and the organic materials were extracted with methylene chloride three times. To completely hydrolyze the trimethylsilyl ether group, the crude aldol product obtained after evaporation of the solvent was dissolved in methanol and to this solution was added citric acid. After stirring for 30 min, the reaction was quenched with pH 7 phosphate buffer. The organic layer was extracted three times with methylene chloride and the combined extracts were dried over anhydrous Na₂SO₄. After evaporation of the solvent, the crude product was purified by silica-gel column chromatography to afford 3-ethylthiomethyl-4-hydroxy-6-phenyl-2-hexanone (336 mg, 75 % yield, syn:anti= 90:10).

IR (neat) 3450, 1750 cm⁻¹; ¹H NMR (CCl₄) δ 1.1 (t, 3H, J=8 Hz), 1.3-1.7 (m, 2H), 1.9 (syn) 2.0 (anti) (s, 3H), 2.1-3.2 (m, 8H), 3.6 (br, 1H), 7.0 (s, 5H).

Diastereomer ratio was determined by integration of the methyl signal. Relative stereochemistry was determined by ¹³C NMR spectra.⁹⁾ ¹³C NMR (CDCl₃) 70.97 (syn) 71.73 (anti).

3-Ethylthiomethyl-4-hydroxy-4-phenyl-2-butanone. (Table 3, entry 1)

Syn isomer: IR (neat) 3450, 1750 cm⁻¹; ¹H NMR (CCl₄) δ 1.1 (t, 3H, J=7 Hz), 1.9 (s, 3H), 2.1-3.1 (m, 5H), 3.3 (br, 1H), 4.63 (d, 1H, J=5 Hz), 7.2 (s, 5H).

Anti isomer: IR (neat) 3500, 1750 cm⁻¹; ¹H NMR (CCl₄) δ 1.2 (t, 3H, J=8 Hz), 2.1 (s, 3H), 2.1-3.3 (m, 6H), 4.7 (d, 1H, J=8 Hz), 7.2 (s, 5H).

Diastereomer ratio was determined by separation of each isomer. Relative stereochemistry was determined by ¹³C NMR spectra.⁹⁾ ¹³C NMR (CDCl₃) 74.03 (syn) 75.20 (anti).

2-Ethylthiomethyl-3-hydroxy-1,5-diphenyl-1-pentanone. (Table 3, entry 3)

Syn isomer: IR (neat) 3450, 1680 cm⁻¹; ¹H NMR (CCl₄) δ 1.1 (t, 3H, J=8 Hz), 1.4-2.0 (m, 2H), 2.1-3.3 (m, 7H), 3.4-4.1 (m, 2H), 7.1-7.5 (m, 8H), 7.7-8.0 (m, 2H).

Anti isomer: IR (neat) 3500, 1680 cm⁻¹; ¹H NMR (CCl₄) δ 1.1 (t, 3H, J=8 Hz), 1.4-1.9 (m, 2H), 2.1-3.3 (m, 7H), 3.4-4.0 (m, 2H), 7.0-7.5 (m, 8H), 7.7-8.0 (m, 2H).

Diastereomer ratio was determined by separation of each isomer.

Catalytic asymmetric Michael reaction.

A typical procedure is described for the reaction of trimethylsilyl enethiol ether derived from methyl dithioacetate and 4-phenyl-3-buten-2-one in the presence (S)-1-methyl-2-(*N*-1-naphtylamino)methylpyrrolidine.

Under argon atmosphere, to a dichloromethane suspension (2 ml) of tin(II) triflate (38 mg, 0.09 mmol) and (S)-1-methyl-2-(*N*-1-naphtylamino)methylpyrrolidine (23 mg, 0.10 mmol) was added a dichloromethane solution (1 ml) of 4-phenyl-3-buten-2-one (136 mg, 0.93 mmol) was added at -78 °C. To this mixture was slowly

added a dichloromethane solution (2 ml) of vinylthiosilane (199 mg, 1.11 mmol) over 4 h. After the addition had completed, the mixture was further stirred for 1 h at this temperature and then 10 % aqueous citric acid solution was added and organic materials were extracted with dichloromethane three times. The combined extracts were washed with 4 % aqueous NaHCO₃ solution twice and brine successively and the organic phase was dried with anhydrous MgSO₄. After evaporation of the solvent, the residue was dissolved in methanol (10 ml) and citric acid (800 mg, 4.16 mmol) was added to the solution and the mixture was stirred for 1 h at room temperature. To the mixture was added pH 7 phosphate buffer and the organic materials were extracted with dichloromethane three times, and the combined extracts were dried over anhydrous MgSO₄. After evaporation of the solvent, the crude product was purified by silica-gel thin layer chromatography to afford methyl 5-oxo-3-phenylhexanedithioate (187 mg, 80 % yield, 70 % e.e.). IR (neat) 1710 cm⁻¹; ¹H NMR (CDCl₃) δ 1.9 s, (3H), 2.5 (s, 3H), 2.7 (d, 2H, J=7 Hz), 3.2 (d, 2H, J=7 Hz), 3.6-4.1 (m, 1H), 7.1 (s, 5H).

The optical purity of the product was determined by ¹H NMR analysis of the corresponding methyl ester (Hg(OCOCH₃)₂-diisopropylethylamine/MeOH) using chiral shift reagent Eu(hfc)₃. MeO- signal separates.

Methyl 5-oxo-3-furylhexanedithioate.

IR (neat) 1680 cm⁻¹; ¹H NMR (CDCl₃) δ 1.9 (s, 3H), 2.4 (s, 3H), 2.7 (d, 2H, J=7 Hz), 3.2 (d, 2H, J=7 Hz), 3.7-4.2 (m, 1H), 5.9 (d, 1H, J=3 Hz), 6.1 (m, 1H), 7.2 (s, 1H).

Methyl 5-oxo-3,5-diphenylpentanedithioate.

IR (KBr) 1675, 1255 cm⁻¹; ¹H NMR (CDCl₃) δ 2.5 (s, 3H), 3.2-3.6 (m, 4H), 3.9-4.4 (m, 1H), 7.21 (s, 5H), 6.8-7.7 (m, 3H), 7.7-8.0 (m, 2H).

References

- 1) "Asymmetric Synthesis", ed. by J. D. Morrison, Academic Press Inc., New York (1984), Vol. 5.
- 2) a) T. Mukaiyama, N. Iwasawa, R. W. Stevens, and T. Haga, *Tetrahedron*, **40**, 1381 (1984); b) T. Mukaiyama, N. Iwasawa, T. Yura, and R. S. J. Clark, *Tetrahedron*, **43**, 5003 (1987), and references cited therein.
- 3) For preliminary communications, see; a) T. Yura, N. Iwasawa, and T. Mukaiyama, *Chem. Lett.*, **1986**, 187; b) T. Yura, N. Iwasawa, K. Narasaka, and T. Mukaiyama, *Chem. Lett.*, **1988**, 1025.
- 4) a) T. Mukaiyama, "Organic Reactions," ed by W. G. Dauben, John Wiley and Sons, Inc., New York (1982), Vol. 28, Chap. 3; b) C. H. Heathcock, "Asymmetric Synthesis," ed by J. D. Morrison, Academic Press, Inc., New York (1984), Vol 3, Chap. 3.
- 5) See reference 2a). See also; T. Mukaiyama, R. W. Stevens, and N. Iwasawa, *Chem. Lett.*, **1982**, 353.
- 6) Several examples of the generation of enolates by conjugate addition of stoichiometric amount of metal compounds to α,β-unsaturated carbonyl compounds have been reported; a) R. J. K. Taylor, *Synthesis*, **1985**, 364; b) R. Noyori and M.

- Suzuki, *Angew. Chem., Int. Ed. Engl.*, 23, 847 (1984); c) T. Mukaiyama, K. Inomata, and M. Muraki, *J. Am. Chem. Soc.*, 95, 967 (1973); d) T. Shono, Y. Matsumura, S. Kashimura, and K. Hatanaka, *J. Am. Chem. Soc.*, 101, 4752 (1979); e) A. Itoh, S. Ozawa, and H. Nozaki, *Tetrahedron Lett.*, 1980, 361; f) A. Itoh, S. Ozawa, K. Oshima, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, 54, 274 (1981); g) W. R. Leonard and T. Livinghouse, *J. Orgg. Chem.*, 50, 730 (1985).
- 7) D. A. Armitage and A. W. Sinden, *J. Organomet. Chem.*, 90, 285 (1975). See also A. G. Davies and P. J. Smith, "Comprehensive Organometallic Chemistry", ed. by G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press Ltd., Oxford (1982), Vol. 2, pp. 604-608.
- 8) Conjugate addition of phenyl silyl selenide to α,β -unsaturated ketones followed by an aldol type reaction of the silyl enol ether (both catalyzed by TMSOTf) has been reported. M. Suzuki, T. Kawagishi, and R. Noyori, *Tetrahedron Lett.*, 1981, 1809.
- 9) a) H. O. House, D. S. Crumrine, A. Y. Teranishi, and H. D. Olmstead, *J. Am. Chem. Soc.*, 95, 3310 (1973); b) C. H. Heathcock, M. C. Pirrung, and J. E. Sohn, *J. Org. Chem.*, 44, 4294 (1979).
- 10) See reference 2a). See also; a) N. Iwasawa and T. Mukaiyama, *Chem. Lett.*, 1982, 1441; b) N. Iwasawa and T. Mukaiyama, *Chem. Lett.*, 1983, 297; c) T. Mukaiyama and N. Iwasawa, *Chem. Lett.*, 1984, 753.
- 11) a) U. Eder, G. Sauer, and R. Wiechert, *Angew. Chem., Int. Ed. Engl.*, 10, 496 (1971); b) Y. Ito, M. Sawamura, and T. Hayashi, *J. Am. Chem. Soc.*, 108, 6405 (1986).
- 12) T. Yura, N. Iwasawa, and T. Mukaiyama, *Chem. Lett.*, 1987, 791.
- 13) T. Yura, N. Iwasawa, and T. Mukaiyama, *Chem. Lett.*, 1988, 1021.
- 14) For previous reports concerning the asymmetric catalytic Michael reaction, see; a) D. J. Cram and G. D. Y. Sogah, *J. Chem. Soc., Chem. Commun.* 1981, 625; b) K. Hermann and H. Wynberg, *J. Org. Chem.*, 44, 2238 (1979); c) N. Kobayashi and K. Iwai, *J. Am. Chem. Soc.*, 100, 7071 (1978); d) H. Brunner and B. Hammer, *Angew. Chem., Int. Ed. Engl.*, 23, 312 (1984). However, the carbonyl compounds in these reactions are limited to active methylene compounds.
- 15) K. A. Hooton and A. L. Allred, *Inorg. Chem.*, 4, 671 (1965).
- 16) R. S. Sukhai, L. Brandsma, *Synthesis*, 1979, 455.