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Catalytic Asymmetric Allylation of Aldehydes Using a Chiral Silver(I) Complex

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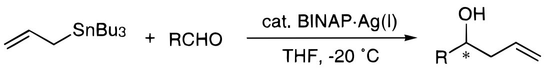
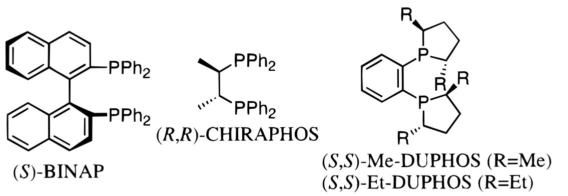
Enantioselective allylation of carbonyl compounds is a challenging problem in organic synthesis. Although numerous important works on the reaction using a stoichiometric amount of chiral Lewis acids have been reported,[1] there are only a few methods available for a catalytic process including chiral (acyloxy)borane (CAB) complex/allylic silanes[2] or allylic stannanes[3] and binaphthol-derived chiral titanium complexes/allylic stannanes.[4] Described herein is a new catalytic enantioselective allylation reaction of aldehydes with allyltributyltin using BINAP•silver(I) complex as a catalyst (eq 1).



(1)

We have recently shown that highly chemoselective allylation of carbonyl compounds occurs using tetraallyltin in acidic aqueous media.[5] Our continuing interest in selective allylation has led us to undertake an investigation of allylation of aldehydes with allyltributyltin catalyzed by various metal compounds. Among the metal catalysts examined, silver(I) compound was found to be one of the most unique. For example, treatment of benzaldehyde with allyltributyltin in the presence of 5 mol % of silver(I) trifluoroacetate in a 1:1 mixture of THF and H_2O at 20 °C for 4 h produced the homoallylic alcohol in moderate yield.[6] Noteworthy was the fact that addition of 10 mol % of triphenylphosphine improved the chemical yield significantly up to >90%. This result encouraged us to use chiral phosphine−silver(I) complex as a catalyst for asymmetric allylation of carbonyl compounds with allylstannanes.

Table 1. Allylation Reaction of Benzaldehyde with Allyltributyltin in the Presence of Various Chiral Phosphine−Silver(I) Complexes[a]



entry	complex	yield, %[b]	% ee[c] (config)
1	(*S*)-BINAP•$AgOCOCF_3$	47	40 (*S*)
2	(*S*)-BINAP•$AgClO_4$	1	26 (*S*)
3	(*S*)-BINAP•$AgNO_3$	26	53 (*S*)
4	(*S*)-BINAP•AgOTf	88	96 (*S*)
5	(*R*,*R*)-CHIRAPHOS•AgOTf	97	2 (*R*)
6	(*S*,*S*)-Me-DUPHOS•AgOTf	4	48 (*R*)
7	(*S*,*S*)-Et-DUPHOS•AgOTf	13	3 (*R*)

[a] Unless otherwise specified, the reaction was carried out using chiral phosphine•AgX (0.05 equiv), allyltributyltin (1 equiv), and benzaldehyde (1 equiv) in THF at −20 °C for 8 h. [b] Isolated yield. [c] Determined by HPLC analysis (Chiralcel OD-H, Daicel Chemical Industries, Ltd.).

The BINAP•silver(I) catalyst was prepared by stirring an equimolar mixture of (*S*)-BINAP and silver(I) triflate in THF at room temperature for 10 min. Treatment of benzaldehyde with allyltributyltin (1 equiv) in THF under the influence of this catalyst (5 mol %) at −20 °C for 8 h gave the (*S*)-enriched homoallylic alcohol in 88% yield with 96% ee (Table 1, entry 4). Using various chiral phosphine−silver(I) catalysts, we studied the enantioselectivity of this process; enantio excesses and yields of the products obtained by the reaction with 5 mol % of other chiral phosphine−silver(I) complexes in THF at −20 °C are shown in Table 1. The reaction catalyzed by the BINAP•silver(I) triflate complex at −20 °C afforded the highest yield and ee.[7]

Table 2 summarizes the results obtained for the reaction of a variety of aldehydes with 1 equiv of allyltributyltin at −20 °C in THF. The characteristic features of the results are as follows: (1) all reactions resulted in high yields and remarkable enantioselectivities not only with aromatic aldehydes but also with α,β-unsaturated aldehydes (entries 2 and 5), with the exception of aliphatic aldehyde, which gave relatively low chemical yield and enantioselectivity (entry 9); (2) in the reaction with α,β-unsaturated aldehydes, the 1,2-addition reaction proceeded exclusively (entries 2 and 5); (3) the methyl group at the *ortho*-position of benzaldehyde had no effect on the enantioselectivity (compare entries 1 and 6); (4) an electron-withdrawing substituent at the *para*-position of benzaldehyde increased the rate of the allylation (compare entries 1, 7, and 8).

Additions of methallylstannanes to aldehydes were also achieved highly enantioselectively using this method.[8] For

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[1] Allylboranes: (a) Brown, H. C.; Jadhav, P. K. *J. Am. Chem. Soc.* **1983**, *105*, 2092. (b) Short, R. P.; Masamune, S. *J. Am. Chem. Soc.* **1989**, *111*, 1892. (c) Racherla, U. S.; Brown, H. C. *J. Org. Chem.* **1991**, *56*, 401. Allylboronates: (d) Herold, T.; Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 768. (e) Hoffmann, R. W.; Herold, T. *Chem. Ber.* **1981**, *114*, 375. (f) Roush, W. R.; Walts, A. E.; Hoong, L. K. *J. Am. Chem. Soc.* **1985**, *107*, 8186. (g) Roush, W. R.; Banfi, L. *J. Am. Chem. Soc.* **1988**, *110*, 3979. (h) Roush, W. R.; Hoong, L. K.; Palmer, M. A. J.; Park, J. C. *J. Org. Chem.* **1990**, *55*, 4109. See also: (i) Reetz, M. T.; Zierke, T. *Chem. Ind.* **1988**, 663. Allylboradiazolidines: (j) Corey, E. J.; Yu, C.-M.; Kim, S. S. *J. Am. Chem. Soc.* **1989**, *111*, 5495. Allyltitanates: (k) Riediker, M.; Duthaler, R. O. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 494. (l) Schmidt, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 99. (m) Hafner, A.; Duthaler, R. O.; Marti, R.; Rihs, G.; Rothe-Streit, P.; Schwarzenbach, F. *J. Am. Chem. Soc.* **1992**, *114*, 2321. Allylaluminum derivatives: (n) Minowa, N.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3697. Allylstannanes: (o) Otera, J.; Kawasaki, Y.; Mizuno, H.; Shimizu, Y. *Chem. Lett.* **1983**, 1529. (p) Otera, J.; Yoshinaga, Y.; Yamaji, T.; Yoshioka, T.; Kawasaki, Y. *Organometallics* **1985**, *4*, 1213. (q) Boldrini, G. P.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Chem. Soc., Chem. Commun.* **1986**, 685. (r) Boldrini, G. P.; Lodi, L.; Tagliavini, E.; Tarasco, C.; Trombini, C.; Umani-Ronchi, A. *J. Org. Chem.* **1987**, *52*, 5447. (s) Boga, C.; Savoia, D.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Organomet. Chem.* **1988**, *353*, 177.

[2] (a) Furuta, K.; Mouri, M.; Yamamoto, H. *Synlett* **1991**, 561. (b) Ishihara, K.; Mouri, M.; Gao, Q.; Maruyama, T.; Furuta, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 11490.

[3] Marshall, J. A.; Tang, Y. *Synlett* **1992**, 653.

[4] (a) Aoki, S.; Mikami, K.; Terada, M.; Nakai, T. *Tetrahedron* **1993**, *49*, 1783. (b) Costa, A. L.; Piazza, M. G.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Am. Chem. Soc.* **1993**, *115*, 7001. (c) Keck, G. E.; Tarbet, K. H.; Geraci, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 8467. (d) Keck, G. E.; Geraci, L. S. *Tetrahedron Lett.* **1993**, *34*, 7827. (e) Keck, G. E.; Krishnamurthy, D.; Grier, M. C. *J. Org. Chem.* **1993**, *58*, 6543. See also: (f) Keck, G. E.; Krishnamurthy, D.; Chen, X. *Tetrahedron Lett.* **1994**, *35*, 8323.

[5] Yanagisawa, A.; Inoue, H.; Morodome, M.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 10356.

[6] Results of the catalytic reaction using various metal compounds (range of yields, metal catalysts): 54−44% yields, $AgOCOCF_3$, AgOTf, $AgNO_3$, $PdCl_2$, and $PtCl_2$; 22−11% yields, $SnCl_4$, VCl_3, $ReCl_5$, $BiCl_3$, and $InCl_3$; 4−0% yields, $Sc(OTf)_3$, $FeCl_3$, BF_3•OEt_2, $TiCl_4$, $AlCl_3$, and $MgCl_2$.

[7] Results of the reaction carried out at various temperatures (temperature, yield, enantioselectivity): 20 °C, 16% yield, 79% ee; 0 °C, 16% yield, 86% ee; −20 °C, 88% yield, 96% ee; −45 °C, 54% yield, 94% ee; −78 °C, <1% yield. The catalyst was deactivated for prolonged periods above 0 °C.

[8] Enantioselective methallyl additions to aldehydes have been achieved using methallylborane,[9] methallylboradiazolidines,[1j] CAB catalyst/methallylsilane,[2] and binaphthol-derived chiral titanium catalysts/methallylstannane.[4e]

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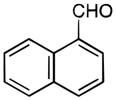
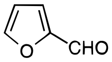
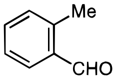
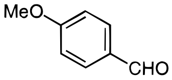
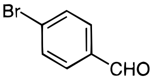
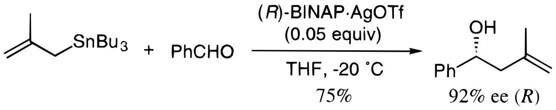
Table 2. Asymmetric Allylation Reactions of Aldehydes Catalyzed by BINAP·AgOTf Complex[a]

entry	aldehyde	yield, %[b]	% ee[c] (config)
1	PhCHO	88	96 (*S*)
2[d]	(*E*)-PhCH=CHCHO	83	88 (*S*)
3[d]		89	97
4[e]		94	93
5[f]	(*E*)-*n*-C_3H_7CH=CHCHO	72	93[g]
6		85	97
7		59	97
8		95	96
9[f]	$PhCH_2CH_2CHO$	47	88

[a] Unless otherwise specified, the reaction was carried out using (*S*)-BINAP·AgOTf (0.05 equiv), allyltributyltin (1 equiv), and aldehyde (1 equiv) in THF at −20 °C for 8 h. [b] Isolated yield. [c] Determined by HPLC analysis (Chiralcel OD-H, AD, or OJ, Daicel Chemical Industries, Ltd.). [d] 3 equiv of allyltributyltin and 0.15 equiv of (*S*)-BINAP·AgOTf was used. [e] 4 equiv of allyltributyltin and 0.2 equiv of (*S*)-BINAP·AgOTf was used. [f] The reaction was started using 2 equiv of allyltributyltin and 0.1 equiv of (*R*)-BINAP·AgOTf, and 0.1 equiv of the catalyst was added after 4 h. [g] Determined by HPLC analysis (Chiralcel AD) of the benzoate ester of the product.

example, the reaction of benzaldehyde with 5 mol % of (*R*)-BINAP·silver(I) triflate in THF at −20 °C for 8 h afforded the corresponding optically active homoallylic alcohol in 75% yield with 92% ee (eq 2).



(2)

A representative experimental procedure is given by the BINAP·Ag(I)-catalyzed reaction of benzaldehyde with allyltributyltin (entry 1 in Table 2): A mixture of AgOTf (26.4 mg, 0.103 mmol) and (*S*)-BINAP (66.5 mg, 0.107 mmol) was dissolved in dry THF (3 mL) under argon atmosphere and exclusion of direct light and stirred at 20 °C for 10 min. To the resulting solution was added a THF solution (3 mL) of benzaldehyde (200 μL, 1.96 mmol), and then allyltributyltin (620 μL, 2.00 mmol) was added dropwise at −20 °C. The mixture was stirred for 8 h at this temperature and treated with a mixture of 1 N HCl (10 mL) and solid KF (ca. 1 g) at ambient temperature for 30 min. The resulting precipitate was filtered off, and the filtrate was dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to afford the homoallylic alcohol (258 mg, 88% yield as a colorless oil): the enantioselectivity was determined to be 96% ee (*S*) by HPLC analysis.[10]

The catalytic mechanism has not yet been fully elucidated; however, the BINAP·Ag(I) complex is thought to act as a chiral Lewis acid catalyst rather than an allylsilver reagent on the basis of the following experimental result. When (*S*)-BINAP·AgOTf complex was treated with an equimolar amount of allyltributyltin in THF at 20 °C followed by quenching half of the resulting reaction mixture with brine, 98% of the allyltin compound was found to remain. Treatment of another half of the mixture with 1 equiv of benzaldehyde at −20 °C for 8 h produced the (*S*)-homoallylic alcohol in 35% yield[11] with >99% ee. This result shows that the stoichiometric allylation does not proceed via a transmetalation pathway which is, however, not completely excluded from the possible catalytic mechanism.

The reaction reported herein represents a new class of highly enantioselective allylation of aldehydes with allyltributyltin using a catalytic amount of BINAP·Ag(I) complex. Further work is now in progress on the catalytic asymmetric allylation and the precise reaction mechanism.

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Supporting Information Available: Experimental procedures and spectral data for all products in Tables 1 and 2 and eq 2 (4 pages). Ordering information is given on any current masthead page.

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(9) Jadhav, P. K.; Bhat, K. S.; Perumal, T.; Brown, H. C. *J. Org. Chem.* **1986**, *51*, 432.

(10) Chiral column (Chiralcel OD-H, Daicel Chemical Industries, Ltd.) was used. The absolute configuration was determined to be *S* by comparison of the $[\alpha]_D$ value with reported data. (*R*)-enriched alcohol (90% ee): $[\alpha]_D$ +43.7° (*c* 6.7, benzene).[1k] Observed $[\alpha]_D$ value of the product with 90% ee: $[\alpha]^{24}_D$ −42.9° (*c* 6.7, benzene).

(11) Although allyltributyltin was completely consumed, ca. 50% of benzaldehyde was recovered, probably due to the occurrence of unknown side reactions specific to this stoichiometric reaction system.