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Catalytic Asymmetric Allylation of Aldehydes with BINOL-Ti(IV) Complex Accelerated by *i*-PrSSiMe$_3$

Chan-Mo Yu,* Ha-Soon Choi, Won-Hyuk Jung, and Sung-Soo Lee

Department of Chemistry, Sung Kyun Kwan University, Suwon 440-746, Korea

Abstract: Practical and efficient catalytic asymmetric allylation reaction of achiral aldehydes with allyltri-*n*-butylstannane in the presence of chiral Lewis acid catalyst has been achieved by the use of accelerator, *i*-PrSSiMe$_3$. This system exhibited not only dramatically accelerating reactivity but also significantly increasing catalytic ability. Copyright © 1996 Elsevier Science Ltd

The enantioselective allylation of carbonyl functionalities to form optically active homoallylic alcohols is very useful method for chiral building block in current organic chemistry.[1] While several chiral allylation reagents employing the chiral auxiliaries have been developed to realize high enantioselectivities,[2] chiral Lewis acids for catalytic versions have recently been introduced in the reactions of aldehydes with allylsilanes and allylstannanes.[3,4] Nonetheless, each of the known methods has included the significant problems, for instance, restriction of reagent, longer reaction time, and still inefficient catalytic ability. Within the field of catalysis implement a project with new conception has been pursued.[5] We report herein a new method based on mechanistic speculation for the catalytic asymmetric allylation by the use of accelerator, R'SSiMe$_3$. The method is successful with a variety of aldehydes in the presence of BINOL-Ti(IV) complex and affords products of high enantiomeric purity with reasonable catalytic capability.

From the mechanistic perspective, two major functions for the reactivity are immediately discernable in the catalytic process. The first is the nature of allylating reagent and catalyst itself to promote catalytic allylation, while the second point is related to general difficulties encountered in the transition state **2** as illustrated in Figure 1.

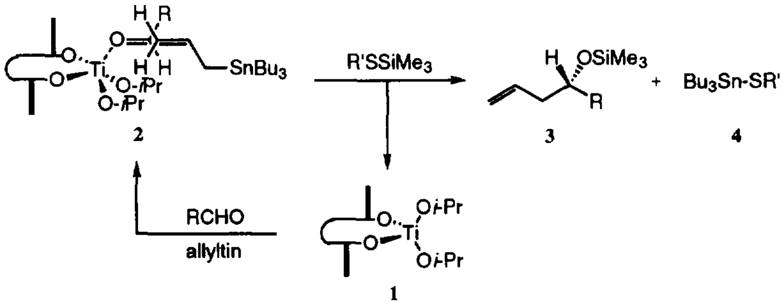
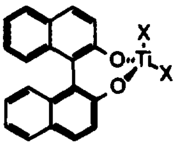


Figure 1. Mechanistic Aspect in Catalytic Allylation

For the effective catalytic process, following transformations are essential : i. breaking Sn-C bond to form double bond. ii. efficient bond formation between Sn-O to facilitate reproducing chiral catalyst as a consequence of dissociation of product from the transition state. Therefore, catalytic allylation must be accelerated by the operation of above process by the use of synergetic reagent. We reasoned that if alkylthiosilanes, R'SSiMe$_3$, could control this process through the favorable Sn-S and Si-O bonds formation to reinforce reproduction of catalyst, practical and efficient catalytic asymmetric allylation might be realized in a predictable fashion. This prediction is based on the strong affinities between Sn-S and Si-O bonds, and also relatively weaker bond between Si-S.

Several alkylthiotrimethylsilanes were prepared from the literature procedure and purified by distillation.[6] Our initial studies began with chiral catalysts (*S*)-BINOL-Ti(IV) complexes **A** and **B** and TADDOL(C)[7] due to their abilities as a catalyst in Lewis acid promoted reactions. Preliminary studies on the development of accelerator system for the catalytic allylation of aldehyde have yielded promising results as indicated in Table 1. Especially encouraging was the use of *i*-PrSSiMe$_3$ in the presence of chiral catalyst **A** (entry 4).[8] Indeed we delighted to find that this system exhibited dramatic acceleration of reaction rate in comparison with that of non-accelerator system.



A : X = O*i*Pr
B : X = Cl

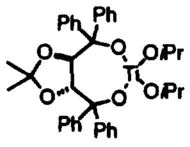


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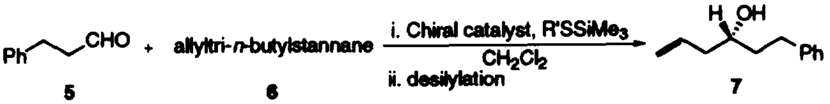
Table 1. Preliminary investigations

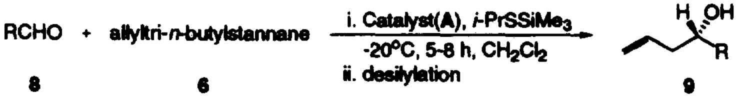


entry	R'SSiMe$_3$	catalyst (mol %)	condition	yield, %	ee, %
1	Et	A (10)	-20°C, 4 h	78	82
2	*c*-Hex	A (10)	-20°C, 5 h	77	85
3	Ph	A (10)	-20°C, 7 h	20	nd
4	*i*-Pr	A (10)	-20°C, 4 h	87	94
5	*i*-Pr	B (10)	-20°C, 7 h	68	83
6	*i*-Pr	C (10)	-20°C-rt, 30 h	38	nd
7	*t*-Bu	A (10)	-20°C, 6 h	81	94
8	control	A(10)	-20°C, 70 h	78	94

Upon optimization, the reaction was conducted by the slow addition of *i*-PrSSiMe$_3$ (1.2 eq) in CH$_2$Cl$_2$ at -20°C to the mixture of hydrocinnamaldehyde (1 eq) and allyltri-*n*-butylstannane (1.2 eq) in the presence of (*S*)-BINOL-Ti(IV) (**A**) complex (10 mol %) in CH$_2$Cl$_2$.[9] After being proceeded for 4 h at -20°C, the reaction mixture was quenched by addition of saturated aqueous NaHCO$_3$ and the unpurified product was treated with *n*-Bu$_4$NF or 10 % methanolic citric acid to effect desilylation.[10] Final purification was effected by silica gel chromatography to furnish homoallylic alcohol **7** in 87 % yield with 94 % ee.

This result prompted us to carry out more experiments with various aldehydes under reduced amounts of chiral catalyst. As shown in Table 2, various aldehydes served as substrates in the allylation reactions in high yields with reasonable enantioselectivities. The reactions are generally complete after 5-8 h at -20°C. Interesting observation was made that the reaction with less hindered aldehydes showed comparative enatiomeric excess values with very high catalytic efficacy to the stoichiometric procedures. The crucial aspect of this system is that the accelerator, *i*-PrSSiMe$_3$, dramatically increased reaction rate as well as significantly reduced dosage of catalyst.

Table 2. Enantioselective Allylation accelerated by *i*-PrSSiMe$_3$[a,b]



entry	aldehyde	catalyst (A)[c], mol %	yield, %[d]	ee, %[e]
1	PhCH$_2$CH$_2$CHO	10	87	94
2		5	82	93
3		2	78	93
4		1	70	91
5	*n*-C$_6$H$_{13}$CHO	10	83	92
6		5	78	91
7		2	73	91
8		1	56	81
9	*c*-C$_6$H$_{11}$CHO	10	75	85
10		5	60	83
11		2	47	83
12		1	41	77
13	PhCHO	10	91	97
14		5	80	95
15		2	58	91
16		1	34	61

[a] All reactions were run at -20°C in CH$_2$Cl$_2$. [b] Absolute configurations were determined by direct comparison of values of specific rotations with those of known alcohols. [c] BINOL :Ti(OiPr)$_4$ =2:1 ratio. [d] Chromatographed yields. [e] Enantiomeric excess was determined using chiral shift reagent, Eu(hfc)$_3$ and by preparation of (+)-MTPA ester derivative, analysis by ^{1}H NMR spectroscopy, and comparison with authentic sample.

The absolute sense of induction parallels with previous observation by Keck.[4] Although the role of *i*-PrSSiMe$_3$ to accelerate allyl transfer reaction must be a consequence of the dissociation of product from the transition state with regeneration of chiral catalyst, mechanistic behavior is unclear whether concerted involvement or stepwise participation in the transition state.

In summary, this paper describes a new approach for catalytic asymmetric allylation by the use of efficient accelerator system which promises to be widely useful. Studies are in progress to extend this method to more complicate system such as catalytic asymmetric crotylation and propargylation.

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9. Optimal chemical yields and enantioselectivities were observed with CH_2Cl_2 compared with other solvents such as toluene, diethyl ether, and propionitrile.
10. The O-silylated homoallylic alcohols were isolated in good yields after aqueous work up procedure.

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