Enantioselective Addition of Methallyl- and Crotyltins to Aldehydes Catalyzed by BINAP·Ag(I) Complex

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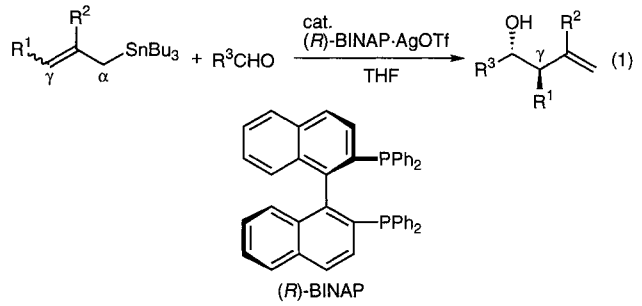
Abstract: Reaction of aldehydes with methallyltributyltin or crotyltributyltin in the presence of a catalytic amount of BINAP·silver(I) complex affords the corresponding optically active homoallylic alcohols with high enantioselectivities; γ- and antiselectivities are also obtained for crotyltributyltin.

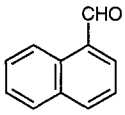
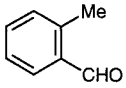
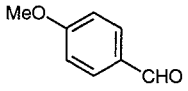
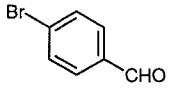
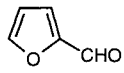
The asymmetric addition of an allyl group to carbonyl compounds to provide optically active secondary homoallylic alcohols is a valuable synthetic method since the products are readily transformed into β-hydroxy carbonyl compounds and various other chiral compounds.[1] Recently we described a catalytic enantioselective allylation reaction of aldehydes with allyltributyltin using BINAP·silver(I) complex as a catalyst.[2] Here, we wish to report further studies on this new process on methallyltributyltin (R^1 = H, R^2 = Me) or crotyltributyltin (R^1 = Me, R^2 = H) (eq 1). The highly γ-, anti-, and enantioselective allylation of an aldehyde was achieved with crotyltributyltin.



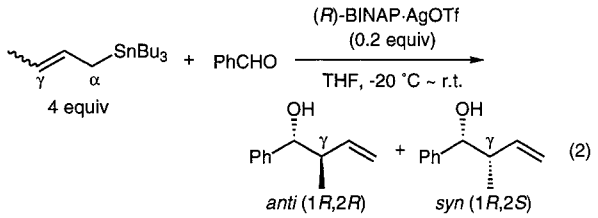
A number of important works on the enantioselective methallyl addition to carbonyl compounds employing a stoichiometric amount of chiral Lewis acids have been reported,[3] however, there are only a few methods applicable to the catalytic version of this process: e.g., chiral (acyloxy)borane (CAB) complex/methallylsilane[4] or methallylstannane[5] and binaphthol-derived chiral titanium complexes/methallylstannane.[6] Treatment of a variety of aldehydes with methallyltributyltin in THF under the influence of a catalytic amount of (*R*)-BINAP·AgOTf (5 ~ 20 mol %) at -20 °C for 8 h gave the optically active homoallylic alcohols in fair to good yields with high enantioselectivities (Table 1). Reactivity of the methallyltin compound was relatively lower than that of allyltributyltin, although use of an increased amount (up to 20 mol %) of the catalyst resulted in satisfactory yields. The other characteristic features of this process were almost identical with those of the allyl addition process.[2]

Condensation of γ-substituted allylmetals with aldehydes is an intriguing subject with respect to the regioselectivities (α/γ) and stereoselectivities (*E/Z* or *anti/syn*). Crotyltributyltin has been reported to react with aldehydes in CH_2Cl_2 with γ- and *syn* (*erythro*)-selectivities regardless of the geometry of the crotyltin in the presence of 2 equiv of $BF_3·OEt_2$.[7] When the BINAP·silver(I) complex acts as a chiral Lewis acid catalyst, optically active γ-allylated *syn*-homoallylic alcohols should be preferentially obtained in the crotyl addition. Thus, we examined the BINAP·silver(I) catalyzed reaction of (*E*)- and (*Z*)-crotyltin. Addition of (*E*)-crotyltributyltin (*E/Z* = 95/5) to benzaldehyde in the presence of 20 mol % of (*R*)-BINAP·AgOTf in THF at -20 °C ~ r.t., however, afforded the γ-adduct exclusively with an *anti/syn* ratio of 85/15, contrary to our expectation.[8] The *anti*-isomer indicated 94% ee with 1*R*,2*R* configuration (eq 2).[9] Employment of (*Z*)-crotyltributyltin (*E/Z* = 2/98) or a nearly 1:1 mixture of (*E*)- and (*Z*)-crotyltributyltin also resulted in a similar *anti/syn* ratio and enantioselectivity (eq 2).

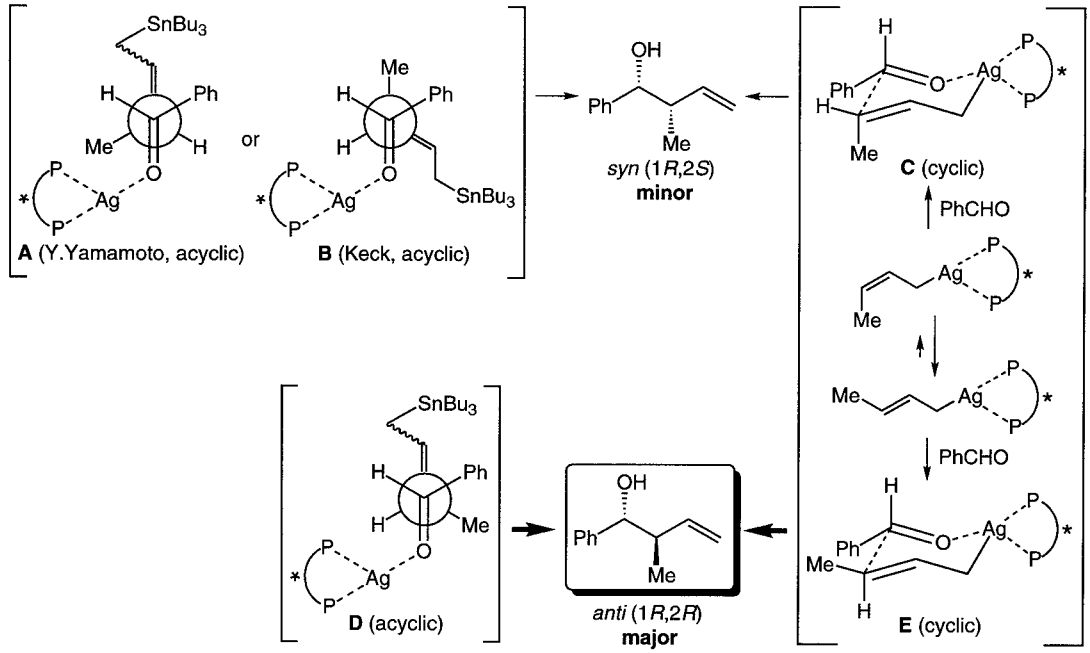
Table 1. Enantioselective addition of methallylstannane to aldehydes catalyzed by BINAP·AgOTf complex[a]

Entry	Aldehyde	Yield (%)[b]	% ee[c] (config)
1	PhCHO	75	92 (*R*)[d]
2[e]		68	88
3[f]		90	98
4[f]		96	97
5		64	89
6[f]		65	95
7[e]	(*E*)-PhCH=CHCHO	62	91
8[g]	(*E*)-*n*-C_3H_7CH=CHCHO	96	92[h]
9	$PhCH_2CH_2CHO$	22	70

[a] Unless otherwise specified, the reaction was carried out using (*R*)-BINAP·AgOTf (0.05 equiv), methallyltributyltin (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 OB-H, Daicel Chemical Industries, Ltd.). [d] The absolute configuration was determined by comparison of the $[\alpha]_D$ value with reported data; (*R*)-enriched alcohol (>98% ee): $[\alpha]^{23}_D$ +51° (*c* 1.55, C_6H_6).[3k] Observed $[\alpha]_D$ value: $[\alpha]^{23}_D$ +55.3° (*c* 1.26, C_6H_6). [e] 3 equiv of methallyltributyltin and 0.15 equiv of (*R*)-BINAP·AgOTf was used. [f] 4 equiv of methallyltributyltin and 0.2 equiv of (*R*)-BINAP·AgOTf was used. [g] The reaction was started using 2 equiv of methallyltributyltin and 0.1 equiv of (*R*)-BINAP·AgOTf, and 0.1 equiv of the catalyst was added after 4 h. [h] Determined by HPLC analysis (Chiralcel AD) of the benzoate ester of the product.



E:Z ratio of crotyltin	Yield (%)	*anti* (% ee) : *syn* (% ee)
95 : 5	56	85 (94) : 15 (64)
2 : 98	72	85 (91) : 15 (50)
53 : 47	45	85 (94) : 15 (57)



Scheme 1. Plausible acyclic and cyclic transition-state structures

The reason is not yet clear why the *anti* selectivity is obtained irrespective of the geometry of the starting material, although some transition-state models can be considered (Scheme 1). For the *syn*-selective reaction of crotylstannane with aldehydes promoted by $BF_3 \cdot OEt_2$, Y. Yamamoto proposed an acyclic antiperiplanar transition-state structure A.[7] Recently, Keck suggested a *syn*-synclinal alternative B to explain the higher *syn*-selectivity obtained with the *E*-stannane.[10] If the BINAP·Ag(I) complex plays the role of Lewis acid in the *anti*-selective allylation, the reaction should proceed via an antiperiplanar D which seems to have the least steric interaction between BINAP·Ag(I) and the stannyl methylene carbon and/or the methyl group of the crotylstannane. However, a cyclic transition-state structure E is also a probable model leading to the *anti*-product when a transmetallation[11] to a crotylsilver occurs and an *E/Z* isomerization of crotylsilver is rapid enough. From the (*Z*)-crotylsilver, the corresponding *syn*-homoallylic alcohol should be obtained via a cyclic transition-state model C.

A representative experimental procedure is given by the BINAP·Ag(I) catalyzed reaction of benzaldehyde with crotyltributyltin (eq 2): A mixture of AgOTf (26 mg, 0.10 mmol) and (*R*)-BINAP (62 mg, 0.10 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 (53 mg, 0.50 mmol) and then (*E*)-crotyltributyltin (*E/Z* = 95/5, 690 mg, 2.0 mmol) was added dropwise at -20 °C. The mixture was stirred for 8 h at this temperature and then for 16 h at 20 °C, and treated with a mixture of 1 N HCl (10 mL) and solid KF (ca. 1 g) at ambient temperature for 30 min. After the resulting precipitate was filtered off, the organic layer was separated, washed with a saturated aqueous $NaHCO_3$ solution and brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo* after filtration. The residual crude product was purified by column chromatography on silica gel to afford a mixture of homoallylic alcohols (46 mg, 56% yield as a colorless oil): the α/γ and *anti/syn* ratios were determined to be <1/99 and 85/15, respectively, by GLC analysis. The enantioselectivities of the *anti*- and *syn*-isomers were determined to be 94% ee and 64% ee, respectively, by HPLC analysis using chiral column (Chiralcel OD-H, Daicel Chemical Industries, Ltd.). The absolute configuration of the *anti*-isomer was determined to be 1*R*,2*R* by comparison of the $[\alpha]_D$ value with reported data. (1*S*,2*S*)-enriched alcohol (66% ee): $[\alpha]^{25}_D$ -73.4° (*c* 2.0, $CHCl_3$).[12] (1*S*,2*R*)-isomer (55% ee): $[\alpha]^{25}_D$ -15.0° (*c* 0.93, $CHCl_3$).[12] Observed $[\alpha]_D$ value of the product: $[\alpha]^{30}_D$ +77.5° (*c* 0.8, $CHCl_3$; data obtained on a 85:15 mixture of *anti*- and *syn*-isomers).

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(11) It is ambiguous whether the BINAP·Ag(I) catalyzed allylation proceeds by the Lewis acid mechanism or the transmetallation mechanism. The fact that almost no transmetallation occurred at all prior to addition of aldehyde supports the Lewis acid mechanism.[2] However, the transmetallation pathway cannot be excluded entirely since the recovered crotyltributyltin was found to be slightly isomerized: for example, reaction of 1 equiv of (*Z*)-crotyltributyltin (*E*/*Z* = 7/93) with benzaldehyde (1 equiv) in the presence of 20 mol % of (*R*)-BINAP·AgOTf in THF at -20 ~ 20 °C for 24 h afforded a mixture of homoallylic alcohols in 30% combined yield with an *anti*/*syn* ratio of 86/14 and a 14:86 mixture of (*E*)- and (*Z*)-crotyltin was recovered in 47% yield. The enantioselectivities of the *anti*- and *syn*-isomers were 94% ee and 65% ee, respectively.

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