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α-Amino acid-promoted asymmetric allylation of aldehydes with allylstannanes

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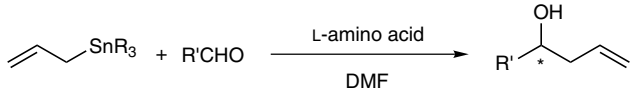
Abstract—An asymmetric allylation of aldehydes with tetraallyltin and other allylstannanes was achieved using L-aspartic acid as a chiral promoter in DMF. Various optically active homoallylic alcohols were obtained in high yields with moderate enantioselectivities up to 40% ee.

1. Introduction

Optically active α-amino acids are popular and readily available organic molecules,[1] which have so far been utilized as chiral auxiliaries, chiral ligands, and chiral synthons for natural products and drugs; however, such versatile compounds have not been hitherto used as chiral promoters for the allylation of carbonyl compounds. We herein report the first example of α-amino acid-promoted asymmetric allylation of aldehydes with allylstannanes (Scheme 1).

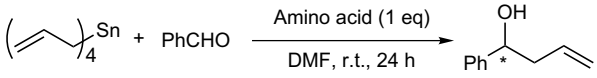
2. Results and discussion

Catalytic asymmetric addition of allylic stannanes or silanes to aldehydes or ketones is an efficient route to optically active homoallylic alcohols with numerous excellent methods having been developed; however, most of these use chiral Lewis acid catalysts or chiral Lewis base catalysts[2,3] while there are only a few reports employing chiral Brønsted acid, for example, binaphthol or its derivatives as a chiral catalyst.[4] α-Amino acids are bifunctional compounds, which have both acid and base parts, and therefore we envisioned that this Brønsted acid should function as a chiral catalyst in the allylation of aldehydes. Initially we tested the catalytic ability of various α-amino acids in the reaction of benzaldehyde with tetraallyltin[5] in DMF and found that distinct asymmetric induction occurred in the cases of L-proline and L-aspartic acid (entries 1 and 2, Table 1). In



Scheme 1.

Table 1. Asymmetric allylation of benzaldehyde with tetraallyltin promoted by various amino acids[a]



Entry	Amino acid	Yield (%)[b]	% Ee[c]
1[d]	L-Proline	54	20
2	L-Aspartic acid	88	33
3	L-Glutamic acid	74	<1
4	L-Arginine	36	<1
5	L-Histidine	40	1
6	L-Tryptophan	56	2
7[e]	L-Threonine	72	<1
8[e]	L-Serine	34	1
9[e]	L-Tyrosine	84	2

[a] Unless otherwise noted, the reaction was carried out using tetraallyltin (2 equiv), benzaldehyde (1 equiv), and amino acid (1 equiv) in dry DMF at room temperature for 24 h.
[b] Isolated yield.
[c] The enantioselectivity of the product was determined by HPLC analysis using a chiral column (OD-H).
[d] The reaction was performed for 76 h.
[e] The reaction was carried out using tetraallyltin (1 equiv), benzaldehyde (1 equiv), and amino acid (1 equiv).

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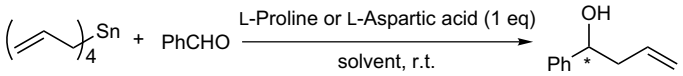
Table 2. Asymmetric allylation of benzaldehyde with tetraallyltin promoted by L-proline or L-aspartic acid in various solvents[a]



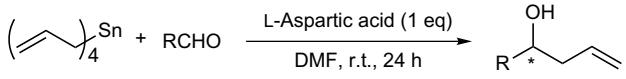
Entry	Amino acid	Solvent	Time (h)	Yield (%)[b]	% Ee[c]
1	L-Proline	THF	20	75	5
2		CH_2Cl_2	24	57	4
3		CH_3CN	24	36	4
4		CH_3NO_2	24	39	3
5		DMSO	24	67	12
6		DMF	76	54	20
7		DMA	47	62	12
8		DMI	24	21	6
9	L-Aspartic acid	DMF	24	88	33
10		DMA	24	64	25
11		DMI	24	47	19

[a] The reaction was carried out using tetraallyltin (2 equiv), benzaldehyde (1 equiv), and L-proline or L-aspartic acid (1 equiv) in dry solvent at room temperature for a specified time.
[b] Isolated yield.
[c] The enantioselectivity of the product was determined by HPLC analysis using chiral column (OD-H).

particular, L-aspartic acid showed the highest ee of 33% (entry 2).

We then studied solvent effects on the chemical yield and enantioselectivity. Some results using L-proline and L-aspartic acid as chiral promoters are shown in Table 2. Among the solvents tested, amides (DMF, DMA, DMI) were found to be effective in obtaining higher enantiomeric excesses with DMF being the solvent of choice (entries 6 and 9). Subsequently, using an optimized amino acid and solvent we performed the allylation of various aldehydes (Table 3). In addition to benzaldehyde, other aromatic aldehydes were smoothly allylated to give the corresponding optically active homoallylic alcohols with the highest ee being obtained when *p*-anisaldehyde was used (entry 4). Not only aromatic aldehydes but also α,β-unsaturated and aliphatic aldehydes showed remarkable reactivity though the enantioselectivity of the latter aldehyde was relatively low (entries 5 and 6). The allylation of α,β-unsaturated aldehyde proceeded in a 1,2-fashion (entry 5). No reaction occurred with a typical ketone under the standard reaction conditions (entry 7).[6] We further examined the L-aspartic acid-promoted allylation of benzaldehyde with other allylating agents (Table 4). Triallylbutyltin[4b] showed reactivity and enantioselectivity similar to those of tetraallyltin (compare entries 1 and 2). In marked

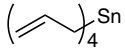
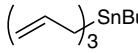
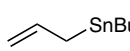
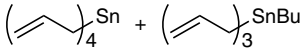
Table 3. Asymmetric allylation of various aldehydes with tetraallyltin promoted by L-aspartic acid[a]



Entry	RCHO	Yield (%)[b]	% Ee[c]	Absolute configuration[d]
1	PhCHO	88	33	*S*
2	4-BrC_6H_4CHO	95	28	—[e]
3[f]	4-$NO_2C_6H_4CHO$	99	23	—[e]
4	4-$MeOC_6H_4CHO$	79	40	*S*
5	(*E*)-PhCH=CHCHO	74	32	*S*
6	$Ph(CH_2)_2CHO$	82	20	—[e]
7	$PhCOCH_3$	<1	—	—

[a] Unless otherwise noted, the reaction was carried out using tetraallyltin (2 equiv), specified aldehyde (1 equiv), and L-aspartic acid (1 equiv) in dry DMF at room temperature for 24 h.
[b] Isolated yield.
[c] The enantioselectivity of the product was determined by HPLC analysis using a chiral column (AD, OB, OD-H, or OJ).
[d] The absolute configuration of the product was determined by comparison of the HPLC retention time with the authentic sample independently synthesized by the reported procedure.[3a]
[e] The absolute configuration of the product is unknown.
[f] The reaction was performed using tetraallyltin (1 equiv), 4-nitrobenzaldehyde (1 equiv), and L-aspartic acid (1 equiv) for 4.5 h.

Table 4. Asymmetric allylation of benzaldehydes with various allyltin reagents promoted by L-aspartic acid[a]

Entry	Allyltin reagents	Yield (%)[b]	% Ee[c]
1		88	33
2		87	32
3[d]		<1	—
4[e]	 (7:3)	41	31

[a] Unless otherwise noted, the reaction was carried out using allyltin reagent (2 equiv), benzaldehyde (1 equiv), and L-aspartic acid (1 equiv) in dry DMF at room temperature for 24 h.
[b] Isolated yield.
[c] The enantioselectivity of the product was determined by HPLC analysis using chiral column (OD-H).
[d] The reaction was performed for 6 days.
[e] The reaction was performed for 20 h.

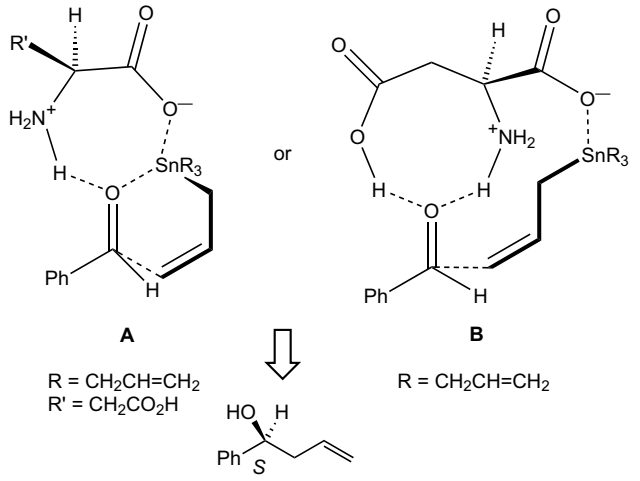


Figure 1. Possible bicyclic transition-state structures **A** and **B** for the L-aspartic acid-promoted asymmetric allylation of benzaldehyde.

contrast, the reaction using allyltributyltin did not proceed at all (entry 3). An attempt to improve the enantiomeric ratio proved unsuccessful using a 7/3 mixture of tetraallyltin and triallylbutyltin as an allyl source (entry 4).[4b]

The mechanism of the L-aspartic acid-promoted allylation of an aldehyde with tetraallyltin has not been fully elucidated, however, the reaction is considered to proceed via a bicyclic transition state **A** or **B** (Fig. 1) containing an L-aspartic acid-coordinated tin atom on the basis of the following NMR results. When tetraallyltin was treated with an equimolar amount of L-aspartic acid in DMSO-d_6 at room temperature for 5 h, new peaks assignable to triallyltin carboxylate were not observed in the ^{1}H NMR spectra though a change in the shape of peaks of L-aspartic acid was. This result implies that the reaction of tetraallyltin with L-aspartic acid is sluggish at room temperature. From the above NMR observations, the tin atom of allylstannane is proposed to act as a Lewis acid to activate an aldehyde and/or to be coordinated with the amino acid. In addition, double activation of the aldehyde owing to the simultaneous coordination of the carbonyl oxygen atom[7] to a H atom of the amino acid and a Sn atom of tetraallyltin (assembly **A**) or to two H atoms of the amino acid (assembly **B**) is suggested as a reaction mechanism to facilitate the allylation. In assembly **A**, the tin atom of allylstannane exists as a hexacoordinate structure in a six-membered cyclic transition state, which is further stabilized by the adjacent seven-membered ring formed by the amino acid and aldehyde. Assembly **B** is, however, a more plausible transition-state structure with respect to both reactivity and enantioselectivity. An eight-membered ring is formed from an aldehyde and L-aspartic acid and subsequently, its carboxylate anion coordinates to the tin atom of tetraallyltin. Thus, the allyltin reacts selectively at the *si* face of the aldehyde to give the (*S*)-enriched homoallylic alcohol. A similar favorable bicyclic transition state is not formed from amino acids other than L-aspartic acid as shown in Table 1. As a result, the structure and nature of an alkyl group of the α-amino acid are considered to be crucial for the enantioface discrimination.

3. Conclusion

In summary, we have demonstrated a novel example of the asymmetric allylation of aldehydes with allyltin reagents promoted by L-aspartic acid. This procedure can be carried out without any difficulty by using commercially available chemicals and can provide various optically active homoallylic alcohols not only from aromatic and α,β-unsaturated aldehydes but also from aliphatic aldehydes with moderate enantioselectivity (up to 40% ee). Further work is currently in progress on the asymmetric allylation with a detailed reaction mechanism.

4. Experimental

4.1. General

Analytical TLC was done on precoated (0.25 mm) silica gel plates. Column chromatography was conducted with 70–230 mesh silica gel. ^{1}H NMR spectra were recorded on 400 and 500 MHz spectrometers. Chemical shifts of ^{1}H NMR spectra were reported relative to tetramethylsilane (δ 0) or chloroform (δ 7.26). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Analytical high-performance liquid chromatography (HPLC) was done using a chiral column (4.6 mm × 25 cm, Chiralcel OB, OD-H, OJ, or Chiralpak AD). Optical rotations were measured on a polarimeter. All experiments were carried out under an atmosphere of standard grade argon gas (oxygen <10 ppm). Triallylbutyltin was prepared by treatment of butyltin trichloride with allylmagnesium bromide (3.3 equiv) in dry ether at room temperature. Other chemicals were used as purchased.

4.2. General procedure for asymmetric allylation of aldehydes with tetraallyltin promoted by L-aspartic acid

A mixture of L-aspartic acid (67 mg, 0.5 mmol) and tetraallyltin (283 mg, 1.0 mmol) was dissolved in dry DMF (6 mL) under an argon atmosphere and stirred at room temperature. To the resulting solution was added the aldehyde (0.5 mmol) at room temperature. The mixture was stirred for 24 h at this temperature and treated with a saturated $NaHCO_3$ aqueous solution (10 mL) at ambient temperature. The aqueous layer was extracted with ether (10 mL) and the combined organic extracts washed with brine, dried over Na_2SO_4 and concentrated in vacuo after filtration. The residual crude product was purified by column chromatography on silica gel (ethyl acetate/hexane as the eluant) to afford the desired optically active homoallylic alcohol. Most of the unreacted tetraallyltin was hydrolyzed on the silica gel and readily separated from the product without any special treatment by KF or other fluoride sources.

4.2.1. (*S*)-1-Phenyl-3-buten-1-ol (entry 2 in Table 1, entry 9 in Table 2, entry 1 in Table 3, and entry 1 in Table 4).[8] TLC R_f 0.34 (1/3 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.01 (d, 1H, $J = 2.5$ Hz, OH), 2.52 (m, 2H, CH_2), 4.75 (dt, 1H, $J = 6.9$, 2.5 Hz, CH), 5.14–5.20 (m, 2H, 2 vinyls), 5.82 (m, 1H, vinyl), 7.25–7.37 (m, 5H, aromatic); $[\alpha]_D^{22} = -19.1$ (*c* 1.1, $CHCl_3$). The enantioselectivity was determined to be 33% ee by HPLC analysis using a chiral column (Chiralcel OD-H, hexane/*i*-PrOH = 20/1, flow rate = 0.5 mL/min): t_{minor} = 15.3 min (*R*), t_{major} = 18.4 min (*S*).

4.2.2. 1-(*p*-Bromophenyl)-3-buten-1-ol (entry 2 in Table 3).[9,10] TLC R_f 0.39 (1/3 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (d, 1H, $J = 3.0$ Hz, OH), 2.48 (m, 2H, CH_2), 4.71 (m, 1H, CH), 5.14–5.20 (m, 2H, 2 vinyls), 5.80 (m, 1H, vinyl), 7.24 (d, 2H, $J = 8.3$ Hz, aromatic), 7.48 (d, 2H, $J = 8.3$ Hz, aromatic); $[\alpha]_D^{22} = -10.3$ (*c* 1.7, $CHCl_3$). The enantioselectivity was determined to be 28% ee by HPLC analysis using a chiral column (Chiralcel OJ, hexane/*i*-PrOH = 9/1, flow rate = 0.5 mL/min): t_{major} = 15.2 min, t_{minor} = 17.1 min.

4.2.3. 1-(*p*-Nitrophenyl)-3-buten-1-ol (entry 3 in Table 3).[8b,11] TLC R_f 0.26 (1/3 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 1H, OH), 2.40–2.60 (m, 2H, CH_2), 4.84–4.90 (m, 1H, CH), 5.14–5.20 (m, 2H, 2 vinyls), 5.72–5.86 (m, 1H, vinyl), 7.52 (d, 2H, $J = 8.9$ Hz, aromatic), 8.30 (d, 2H, $J = 8.9$ Hz, aromatic); $[\alpha]_D^{21} = -11.5$ (*c* 0.10, $CHCl_3$). The enantioselectivity was determined to be 23% ee by HPLC analysis using a chiral column (Chiralpak AD, hexane/*i*-PrOH = 20/1, flow rate = 0.4 mL/min): t_{minor} = 45.2 min, t_{major} = 48.4 min.

4.2.4. (*S*)-1-(*p*-Methoxyphenyl)-3-buten-1-ol (entry 4 in Table 3).[8b,9,12] TLC R_f 0.27 (1/3 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.94 (d, 1H, $J = 0.9$ Hz, OH), 2.50 (d, 2H, $J = 6.6$ Hz, CH_2), 3.81 (s, 3H, CH_3), 4.69 (t, 1H, $J = 6.3$ Hz, CH), 5.11–5.18 (m, 2H, 2 vinyls), 5.80 (m, 1H, vinyl), 6.89 (d, 2H, $J = 8.8$ Hz, aromatic), 7.29 (d, 2H, $J = 8.8$ Hz, aromatic); $[\alpha]_D^{21} = -24.4$ (*c* 0.52, $CHCl_3$). The enantioselectivity was determined to be 40% ee by HPLC analysis using a chiral column (Chiralcel OD-H, hexane/*i*-PrOH = 20/1, flow rate = 1.0 mL/min): t_{minor} = 9.4 min (*R*), t_{major} = 10.9 min (*S*).

4.2.5. (*S*),(*E*)-1-Phenyl-1,5-hexadien-3-ol (entry 5 in Table 3).[8a,b,9,11,12b] TLC R_f 0.28 (1/3 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.78 (br, 1H, OH), 2.39 (m, 2H, CH_2), 4.37 (dd, 1H, $J = 12.3$, 6.1 Hz, CH_2), 5.16–5.22 (m, 2H, 2 vinyls), 5.87 (m, 1H, vinyl), 6.25 (dd, 1H, $J = 15.9$, 6.3 Hz, vinyl), 6.62 (d, 1H, $J = 15.7$ Hz, vinyl), 7.22–7.40 (m, 5H, aromatic); $[\alpha]_D^{22} = -6.4$ (*c* 1.0, $CHCl_3$). The enantioselectivity was determined to be 32% ee by HPLC analysis using a chiral column (Chiralcel OD-H, hexane/*i*-PrOH = 20/1, flow rate = 0.5 mL/min): t_{minor} = 24.0 min (*R*), t_{major} = 42.7 min (*S*).

4.2.6. 1-Phenyl-5-hexen-3-ol (entry 6 in Table 3).[9,12a,13] TLC R_f 0.33 (1/3 ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60 (d, 1H, $J = 1.9$ Hz, OH), 1.80 (m, 2H, CH_2), 2.16–2.23 (m, 1H, one proton of CH_2), 2.29–2.36 (m, 1H, one proton of CH_2), 2.64–2.84 (m, 2H, CH_2), 3.68 (m, 1H, CH), 5.15 (d, 2H, $J = 11.8$ Hz, 2 vinyls), 5.75–5.86 (s, 1H, vinyl), 7.16–7.31 (m, 5H, aromatic); $[\alpha]_D^{22} = +1.8$ (*c* 1.4, $CHCl_3$). The enantioselectivity was determined to be 20% ee by HPLC analysis using a chiral column (Chiralcel OB, hexane/*i*-PrOH = 99/1, flow rate = 0.5 mL/min): t_{minor} = 19.7 min, t_{major} = 23.5 min.

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