A Chiral Ligand-Mediated Asymmetric Addition of a Lithium BHA Ester Enolate to an Aldehyde[1)]

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The asymmetric reaction of a lithium enolate generated from a BHA (2,6-di-*tert*-buty-4-methoxyphenyl) propanoate was allowed to react with benzaldehyde in the presence of a diether-type chiral ligand affording the corresponding *anti*-aldol product in a moderate enantioselectivity. A tetradentate ligand induced better enantioselectivity albeit relative loss of *anti*-selectivity. A variation of lithiating amide agent affected the selectivity, indicating involvement of an amine as a component of the mixed aggregate. Absolute configuration of some of the aldol products was determined by standard transformations.

Key words aldol reaction; asymmetric reaction; lithium enolate; ligand; propanoate

An asymmetric addition reaction of an ester enolate with a carbonyl compound is one of the important and fundamental carbon–carbon bond forming reactions.[2—4)] We have been involved in the chiral ligand-mediated asymmetric reactions of highly reactive metalated nucleophiles.[5—8)] Particularly, the reaction of a lithium ester enolate with an imine represents a successful entry to a carbon–carbon bond forming asymmetric reaction, which is mediated by a chiral diether **1** and a chiral aminoether affording the corresponding β-lactam in a satisfactorily high enantioselectivity and high chemical yield.[9—13)] Straightforward extension of the imine condensation to an aldol-type reaction with an aldehyde as a reaction partner provides a formidable challenge, because the reactivity of an aldehyde itself is high enough to an extent that does not need any activation for the reaction with a lithium enolate (Fig. 1).[14,15)] We describe herein that the reaction of a lithium BHA ester enolate with an aldehyde is mediated by a chiral ligand giving a moderate enantioselectivity.[16)]

Asymmetric Reaction of Propanoate We began our studies with the reaction of *tert*-butyl propanoate **4** with benzaldehyde **7** (Fig. 2). Treatment of **4** with LDA in the presence of a chiral diether ligand **1** in toluene and then with **7** gave the target **10** as a 27 : 73 mixture of *syn*- and *anti*-aldol products (Table 1, Entry 1). However, the enantioselectivity of the acetate **11** was poor. It has been reported by Heathcock that a lithium enolate generated from BHA (2,6-di-*tert*-buty-4-methoxyphenyl) propanoate **5** in THF reacted with **7** to give stereoselectively *anti*-aldol product **12**.[17)] Since a BHA ester methodology has been our favourite,[18)] we applied the Heathcock procedure in our asymmetric aldol-type reaction in toluene, instead of a THF solvent.

Generation of a lithium enolate from BHA ester **5** was possible by butyllithium treatment at −78 °C for 1 h in the presence of 1.3 eq of **1** in toluene, and following treatment with **7** at −78 °C for 5 min to give an almost diastereomerically pure *anti*-**12**. The aldol product was immediately subjected to acetylation with acetic anhydride–triethylamine–DMAP in methylene chloride to afford the corresponding acetate *anti*-**13** as a major product of a 7 : 93 mixture (Entry 2). Enantioselectivity of *anti*-**13** was determined to be 32% by a chiral stationary phase HPLC analysis. Improvement of the enantioselectivity was possible by using LDA as a base affording *anti*-**13** in 80% yield and 50% ee (Entry 3). A ternary complex reagent[12)] was proved not to be beneficial providing *anti*-**13** in 40% yield and 15% ee (Entry 4). The ether ligand **2** having an ethoxy group was not a choice, giving poorer selectivity of 9% (Entry 5). The best ligand among examined was a tetradentate **3**, which mediated the reaction to afford *anti*-**13** in 61% ee. However, the *syn*/*anti* selectivity was lost to afford *syn*-**13** as a major product in 35% ee (Entry 6). The present procedure was applicable in the reaction with pivalaldehyde **8** giving the corresponding aldol product *anti*-**15** in 56% ee by **1**, in 49% ee by **3** (Entries

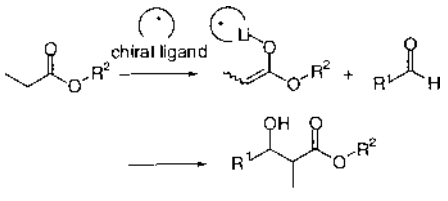
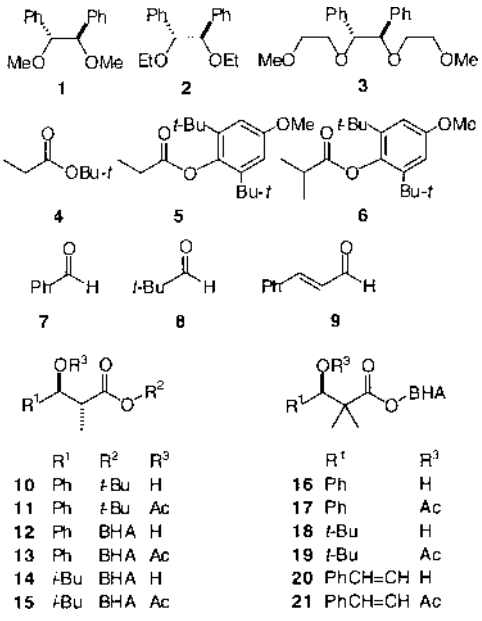


Fig. 1. Asymmetric Aldol Reaction



	R^1	R^2	R^3
10	Ph	*t*-Bu	H
11	Ph	*t*-Bu	Ac
12	Ph	BHA	H
13	Ph	BHA	Ac
14	*i*-Bu	BHA	H
15	*i*-Bu	BHA	Ac

	R^1	R^3
16	Ph	H
17	Ph	Ac
18	*t*-Bu	H
19	*t*-Bu	Ac
20	PhCH=CH	H
21	PhCH=CH	Ac

Fig. 2. Ligands, Esters, Aldehydes, and Products

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Table 1. A Chiral Ligand-Mediated Asymmetric Addition of a Lithium Enolate to an Aldehyde

Entry	Ester	Ligand	Base	eq	Aldehyde	Product	Yield %	*syn* : *anti*	*syn* ee %	*anti* ee %
1	**4**	**1**	LDA	1.2	**7**	**11**	64	27 : 73	9	11
2	**5**	**1**	BuLi	1.2	**7**	**13**	99	7 : 93		32
3	**5**	**1**	LDA	1.2	**7**	**13**	78	1 : 99		50
4	**5**	**1**	LDA	2.4	**7**	**13**	40	1 : 99		15
5	**5**	**2**	LDA	1.2	**7**	**13**	70	1 : 99		9
6	**5**	**3**	LDA	1.3	**7**	**13**	88	77 : 23	35	*ent*-61
7	**5**	**1**	LDA	1.2	**8**	**15**	76	1 : 99		56
8	**5**	**3**	LDA	1.2	**8**	**15**	60	82 : 18	35	*ent*-49

Table 2. A Chiral Ligand-Mediated Asymmetric Addition of a Lithium Enolate of **6** to an Aldehyde

Entry	Ligand	Base	eq	Aldehyde	Product	Yield %	ee %
1	**1**	BuLi	1.0	**7**	**17**	79	35
2	**1**	LDA	1.2	**7**	**17**	57	20
3	**1**	LDA	2.4	**7**	**17**	69	11
4	**1**	LICA	1.2	**7**	**17**	46	*ent*-19
5	**1**	LTMP	1.3	**7**	**17**	40	10
6	**3**	BuLi	1.0	**7**	**17**	44	*ent*-64
7	**3**	LDA	1.3	**7**	**17**	68	*ent*-69
8	**3**	LDA-LiBr	1.3	**7**	**17**	23	*ent*-44
9	**3**	LDA	2.4	**7**	**17**	79	*ent*-63
10	**1**	BuLi	1.0	**8**	**19**	56	7
11	**3**	LDA	1.0	**8**	**19**	26	16
12	**1**	BuLi	1.0	**9**	**21**	71	27
13	**3**	LDA	1.0	**9**	**21**	57	49

7, 8).

Generation of a lithium enolate from propanoate **5** involves the *E*- and *Z*-problem, which makes difficult the analysis of the reaction. Although a BHA ester produces *Z*-enolate due to its steric bulk in a THF solvent, there is no guarantee that selective formation of the fixed geometry of an enolate is possible even in a toluene solvent. Then, we turned our attention to 2-methylpropanoate **6** that does not produce such a stereochemical problem.

Asymmetric Reaction of BHA 2-Methylpropanoate Generation of an enolate from BHA 2-methylpropanoate **6** with butyllithium in the presence of **1** in toluene and following treatment with benzaldehyde **7** provided **16**, which was then converted to an acetate **17** in 79% yield and 35% ee (Table 2, Entry 1). LDA treatment and ternary complex reagent[12] did not provide any improvement to afford **17** in 20% ee and 11% ee (Entries 2, 3). The efficiency was dependent on the lithiation agent; lithium cyclohexylisopropylamide produced enantiomeric **17** in 19% ee and lithium tetramethylpiperidide afforded **17** in 10% ee (Entries 4, 5). These influences by lithiation agents apparently suggest an involvement of amine and amide moiety in an aggregate of a lithium enolate.

Improvement was realized by using a tetradentate ligand **3** as a controlling agent. The similar and relatively high enantioselectivity was observed regardless to lithiation reagents. Butyllithium and LDA treatment of **6**, and ternary complex with LDA[13] in the presence of **3** gave *ent*-**17** in the almost similar level of selectivity 63—69% ee (Entries 6, 7, 9). Presence of lithium bromide affected on chemical yield and enantioselectivity (Entry 8). However, the reaction with pivalaldehyde **8** proceeded unsatisfactorily to afford **19** in utmost 16% ee (Entries 10, 11). The reaction with cinnamaldehyde **9** gave the adduct **21** in 49% ee with an aid of **3**.

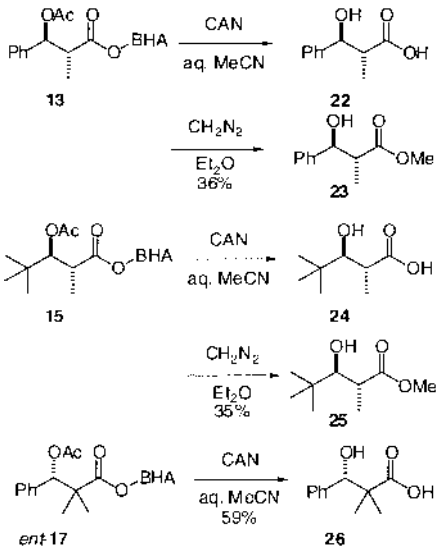

Fig. 3. Conversion to the Established Compounds

Determination of the Absolute Configuration of the Aldol Products Absolute configuration of some of the aldol products was determined as shown in Fig. 3. The acetate **13** was treated with cerium ammonium nitrate in aqueous acetonitrile to afford a carboxylic acid **22**, which was then converted to a methyl ester **23** of the established stereochemistry. The pivaloyl adduct **15** was also treated similarly to afford **25**. The 2-methylpropanoate adduct *ent*-**17** was converted to a carboxylic acid **26**.

Conclusion

The extension of an imine-enolate condensation reaction to an aldol reaction was examined using BHA propanoates. A chiral diether ligand was found to induce moderate enantioselectivity and high *anti*-selectivity. A tetradentate ligand induced better enantioselectivity albeit loss of *anti*-selectivity. These clearly indicate that more sophisticated devises are required for extension of the imine-enolate condensation technology to an aldol-type reaction with a carbonyl compound.

Experimental

BHA Propanoate 5 A THF (60 ml) solution of 2,6-di-*tert*-butyl-4-methoxyphenol (18.9 g, 80 mmol) was added to a suspension of NaH (88 mmol) in THF (120 ml) at 0 °C over 5 min. After 1 h stirring at room temperature (rt), propionyl chloride (10.4 ml, 120 mmol) was added, and the mixture was stirred at rt for 2 h before addition of 15% NaOH (100 ml). The mixture was stirred at rt for 0.5 h and then diluted with water (100 ml). The mixture was extracted with AcOEt. The organic layer was washed with brine, and then dried over magnesium sulfate. Concentration and silica gel column chromatography (benzene/hexane=1/4) gave **5** (19.7 g, 84%) as colorless prisms (hexane) of mp 53 °C. ^{1}H-NMR ($CDCl_3$): 1.00 (18H, s), 1.33 (3H, t, J=8 Hz), 2.60 (2H, q, J=8 Hz), 3.83 (3H, s), 7.77 (2H, s). IR (nujol): 1770, 1600 cm^{-1}. MS *m/z*: 292 (M^+). *Anal.* Calcd for $C_{18}H_{28}O_3$: C 73.93, H 9.65. Found: C 73.86, H 9.80.

BHA 2-Methylpropanoate 6 Prepared by the same procedure for **5** in 90% yield as colorless prisms (hexane) of mp 44 °C. ^{1}H-NMR ($CDCl_3$): 1.31 (18H, s), 1.35 (6H, d, J=8 Hz), 2.82 (1H, q, J=8 Hz), 3.75 (3H, s), 6.84 (2H, s). IR (nujol): 1750, 1590 cm^{-1}. MS *m/z*: 306 (M^+). *Anal.* Calcd for $C_{19}H_{30}O_3$: C 74.47, H 9.87. Found: C 74.45, H 10.15.

Typical Procedure for Asymmetric Aldol Reaction (Table 1, Entry 3) A hexane solution of *n*-BuLi (1.2 mmol, 0.85 ml) was added to a solution of diisopropylamine (1.2 mmol, 0.17 ml) in toluene (10 ml) at −78 °C. After stirring for 10 min, a solution of a chiral diether **1** (440 mg, 1.8 mmol) and BHA propanoate **5** (292 mg, 1 mmol) in toluene (10 ml) was added. The mixture was stirred at −78 °C for 1 h, and then was added by benzaldehyde (0.11 ml, 1 mmol). After 5 min, the mixture was treated with satd ammonium chloride and extracted with AcOEt. The organic layer was washed with 10% HCl, water, satd sodium bicarbonate, and brine, and then dried over magnesium sulfate. Concentration gave **12** as a yellow oil, which was diluted with methylene chloride (5 ml). Acetic anhydride (0.22 ml, 2.4 mmol) and triethylamine (0.42 ml, 3 mmol) was added at −20 °C. After addition of 4-dimethylaminopyridine (DMAP) (70 mg, 0.6 mmol), the whole was stirred at rt for 20 min. The mixture was then diluted with methylene chloride and washed with 10% HCl, satd sodium bicarbonate, and brine, and then dried over sodium sulfate. Concentration and silica gel column chromatography (benzene/ether=20/1) gave **13** (0.34 g, 78%) as a solid of mp 100—126 °C (mp of racemic **13**: 133—135 °C) and $[\alpha]_{365}^{25}$ −11.5° (c=0.996, $CHCl_3$). 50% ee (Optipak TC, hexane/2-propanol=100/1, 254 nm, 1 ml/min, minor 8.7 min, major 10.8 min). ^{1}H-NMR ($CDCl_3$): 1.31 (18H, s), 1.86 (3H, s), 3.22 (1H, dq, J=8, 9 Hz), 3.69 (3H, s), 5.98 (1H, d, J=9 Hz), 6.76, 6.80 (2H, s), 7.28 (5H, m). IR (nujol): 1760 cm^{-1}. MS *m/z*: 440 (M^+). *Anal.* Calcd for $C_{27}H_{36}O_5$: C 73.61, H 8.24. Found: C 73.67, H 8.37.

(Table 1, Entry 7) **15**: An oil of $[\alpha]_D^{25}$ +15.9° (c=1.01, $CHCl_3$). 56% ee (Chiralpak AD, hexane/2-propanol=100/1, 254 nm, 0.5 ml/min, minor 9.9 min, major 24 min). ^{1}H-NMR ($CDCl_3$): 1.02 (9H, s), 1.32 and 1.36 (each 9H, s), 1.61 (3H, d, J=8 Hz), 1.97 (3H, s), 3.16 (1H, dq, J=6, 8 Hz), 3.78 (3H, s), 4.95 (1H, d, J=6 Hz), 6.85 (2H, s). IR (neat): 1750 cm^{-1}. MS *m/z*: 420 (M^+). *Anal.* Calcd for $C_{24}H_{40}O_5$: C 71.39, H 9.59. Found: C 71.11, H 9.59.

(Table 2, Entry 2) **17**: Colorless prisms (hexane) of mp 113—114 °C and $[\alpha]_{365}^{25}$ +0.9° (c=5.64, $CHCl_3$). 20% ee (Optipak TC, hexane/2-propanol=30/1, 254 nm, 0.5 ml/min, minor 12 min, major 16 min). ^{1}H-NMR ($CDCl_3$): 1.28 and 1.40 (each 9H, s), 1.30 and 1.57 (each 3H, s), 1.99 (3H, s), 3.78 (3H, s), 6.22 (1H, s), 6.87 (2H, m), 7.3 (5H, m). IR (KBr): 1750 cm^{-1}. MS *m/z*: 454 (M^+). *Anal.* Calcd for $C_{28}H_{38}O_5$: C 73.98, H 98.42. Found: C 73.89, H 8.53.

(Table 2, Entry 11) **19**: Colorless oil with 16% ee (Optipak XC, hexane/2-propanol=100/1, 254 nm, 0.5 ml/min, minor 10 min, major 14 min). ^{1}H-NMR ($CDCl_3$): 1.10 (9H, s), 1.34 (18H, s), 1.58 and 1.62 (each 3H, s), 3.5 (1H, br s), 3.72 (1H, s), 3.79 (3H, s), 6.88 (2H, s). IR (neat): 1720 cm^{-1}. MS *m/z*: 393 (M^+).

(Table 2, Entry 13) **21**: Solid of of $[\alpha]_D^{25}$ +5.2° (c=1.02, $CHCl_3$) and mp 138—146 °C (mp 147 °C (hexane) for racemic **21**). 49% ee (Optipak XC, hexane/2-propanol=60/1, 254 nm, 0.5 ml/min, minor 14 min, major 16 min). ^{1}H-NMR ($CDCl_3$): 1.34 and 1.36 (each 9H, s), 1.49 and 1.57 (each 3H, s), 2.03 (3H, s), 3.79 (3H, s), 5.74 (1H, d, J=8 Hz), 6.29 (1H, dd, J=8, 16 Hz), 6.69 (1H, d, J=16 Hz), 6.88 (2H, s), 7.3 (5H, m). IR (KBr): 1720 cm^{-1}. MS *m/z*: 480 (M^+). *Anal.* Calcd for $C_{30}H_{40}O_5$: C 74.97, H 8.39. Found: C 74.87, H 8.47.

Determination of the Absolute Configuration of 13 A mixture of (−)-**13** (18% ee, $[\alpha]_{365}^{25}$ −4.1° (c=1.00, $CHCl_3$). 0.28 g, 0.7 mmol) and cerium (IV) diammonium nitrate (984 g, 1.8 mmol) in a mixture of water (1.5 ml) and acetonitrile (1.4 ml) was stirred at rt for 1 h under sonication. Mannitol (0.33 g, 1.9 mmol) was added to a dark red solution above giving a yellow solution, which was stirred for another 0.5 h. After addition of water, the mixture was extracted with methylene chloride. The organic layer was extracted with 5% sodium hydroxide, which was extracted back with methylene chloride after acidification with c. HCl. The organic layer was washed with brine and concentrated to give the corresponding carboxylic acid **22** (0.1 g). An ether (1 ml) solution of the acid was then treated with diazomethane (prepared from nitrosomethylurea (0.29 g, 2.8 mmol)) and diluted with methylene chloride after addition of acetic acid. The organic layer was washed with satd sodium bicarbonate, brine, and then dried over magnesium sulfate. Concentration and silica gel column chromatography (hexane–ether=4/1) gave the corresponding methyl ester (2*R*,3*S*)-**23** (50 mg, 36%) as a solid of mp 48—51 °C and $[\alpha]_D^{20}$ −11.2° (c=1.41, $CHCl_3$). The absolute configuration was determined as above by comparing specific rotation with the established (2*S*,3*R*)-(+)-**23**.[19] ^{1}H-NMR ($CDCl_3$): 0.99 (3H, d, J=7 Hz), 2.79 (1H, dq, J=7, 8 Hz), 3.00 (1H, br s), 3.71 (3H, s), 4.73 (1H, d, J=8 Hz), 7.32 (5H, m). IR (neat): 1740 cm^{-1}. MS *m/z*: 194 (M^+). Ee was confirmed by HPLC (Chiralpak XC, hexane/2-propanol=9/1, 254 nm, 0.5 ml/min, major 16 min, minor 25 min).

Determination of the Absolute Configuration of 15 A mixture of (+)-**15** ($[\alpha]_D^{25}$ +15.9° (c=1.01, $CHCl_3$), 0.64 g, 1.5 mmol) and cerium (IV) diammonium nitrate (2.19 g, 4 mmol) in a mixture of water (3 ml) and acetonitrile (3 ml) was stirred at rt for 1 h under sonication. Mannitol (0.75 g, 4 mmol) was added to a dark red solution above giving a yellow solution, which was stirred for another 0.5 h. After addition of water, the mixture was extracted with methylene chloride. The organic layer was extracted with 5% sodium hydroxide, which was extracted back with methylene chloride after acidification with c. HCl. The organic layer was washed with brine and concentrated to give the corresponding carboxylic acid **24** (0.18 g). An ether (2 ml) solution of the acid was treated with diazomethane (prepared from nitrosomethylurea (0.46 g, 4.5 mmol)) and diluted with methylene chloride after addition of acetic acid. The organic layer was washed with satd sodium bicarbonate, brine, and then dried over magnesium sulfate. Concentration and silica gel column chromatography (hexane/ether=4/1) gave the corresponding methyl ester (2*R*,3*S*)-**25** (113 mg, 35%) as a pale yellow oil of $[\alpha]_D^{25}$ −16.5° (c=0.96, $CHCl_3$). The absolute configuration was determined as above by comparing specific rotation with the established (2*R*,3*S*)-(−)-**25**.[20] ^{1}H-NMR ($CDCl_3$): 0.89 (9H, s), 1.34 (3H, d, J=7 Hz), 2.79 (1H, dq, J=1, 8 Hz), 3.17 (1H, d, J=1 Hz), 3.68 (3H, s). IR (neat): 1740 cm^{-1}. MS *m/z*: 174 (M^+).

Determination of the Absolute Configuration of 17 A mixture of (−)-**17** (69% ee, $[\alpha]_{365}^{25}$ −1.7° (c=1.20, $CHCl_3$). 0.4 g, 0.9 mmol) and cerium (IV) diammonium nitrate (CAN) (1.88 g, 3.4 mmol) in a mixture of water (2 ml) and acetonitrile (2 ml) was stirred at rt for 2 h under sonication. Mannitol (1.07 g, 5.9 mmol) was added to a dark red solution above giving a yellow solution, which was stirred for another 0.5 h. After addition of water, the mixture was extracted with methylene chloride. The organic layer was extracted with 5% sodium hydroxide, which was extracted back with methylene chloride after acidification with c. HCl. The organic layer was washed with brine and concentrated to give an oil. Silica gel column chromatography (methylene chloride/methanol=9/1) gave the corresponding methyl ester (*S*)-**26** (102 mg, 59%) as solid of mp 140—152 °C and $[\alpha]_D^{25}$ +5.0° (c=0.88, MeOH). The absolute configuration was determined as above by comparing specific rotation with the established (*S*)-(+)-**25**.[21] ^{1}H-NMR ($CDCl_3$): 0.99 and 1.06 (each 3H, s), 4.92 (1H, s), 5.06 (2H, br s), 7.2 (5H, m). IR (nujol): 1750 cm^{-1}. MS *m/z*: 194 (M^+).

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References and Notes

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