cis-(1*R*,2*S*)-2-ベンズアミドシクロヘキサンカルボン酸から誘導した 1,3-アミノアルコールを用いた芳香族アルデヒドへのジエチル亜鉛の不斉付加における置換基による不斉制御

Chirality control by substituents in the asymmetric addition of Et_2Zn to aromatic aldehydes catalyzed by *cis*-(1*R*,2*S*)-2-benzamidocyclohexanecarboxylic acid derived 1,3-aminoalcohols

廣瀬　卓司[1*]、王　祥波[1]、小玉　康一[1]、川村　怜[2]、小松　拓磨[2]

Takuji Hirose[1], Xiangbo Wang[1], Koichi Kodama[1], Ryo Kawamura[2], Takuma Komatsu[2]

[1] 埼玉大学　大学院理工学研究科
Graduate School of Science and Engineering, Saitama University
[2] 株式会社インテリム
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Abstract

A series of novel optically active 1,3-aminoalcohols based on *cis*-(1*R*,2*S*)-2-benzamido- cyclohexanecarboxylic acid and *trans*-(1*R*,2*R*)-2-benzamidocyclohexanecarboxylic acid were synthesized and used in the asymmetric diethylzinc addition to aromatic aldehydes. Not only the enantioselectivity but also the stereochemistry of the product were controlled by the *N*-substituents and the substituents on the vicinity carbon to hydroxyl group of the *cis*-derivatives.

Key Words: aldehyde, asymmetric addition, chirality control, 1,3-aminoalcohols, *cis*-(1*R*,2*S*)-2-benzamidocyclo-hexanecarboxylic acid

1. Introduction

Since the enantioselective addition of diethylzinc to aldehydes was first reported by Oguni and Omi in 1984,[1] various types of chiral ligands, such as aminothiols,[2] sulfonamides,[3] aminophenols,[4] amides,[5] diamines[6] and diols[7] were synthesized and applied.[8] In return, therefore, the asymmetric addition of diethylzinc to aldehydes became one of the common reactions for testing the effectiveness of new chiral ligands.

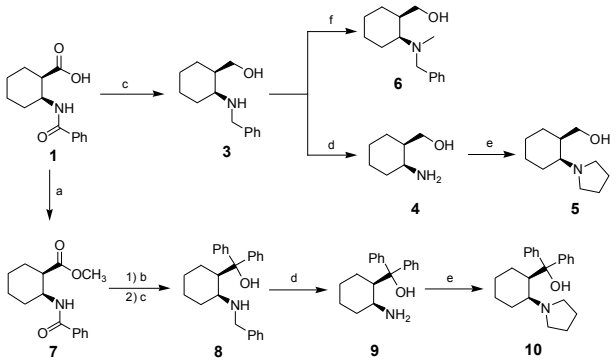
Among the chiral ligands studied, aminoalcohols are particularly attractive due to its high catalytic activity and excellent enantioselectivity. In the past twenty years, a variety of chiral 1,2-aminoalcohols have been developed and showed excellent enantioselectivity.[9] Whereas, 1,3-aminoalcohols have been rarely studied and it is interesting and challenging to examine the chiral controllability.[10] In this study, we developed some new enantiopure 1,3-aminoalcohols starting from chiral 2-benzamidocyclohexanecarboxylic acid, and studied their catalytic ability in the asymmetric addition of diethylzinc to aromatic aldehydes.

* 〒338-8570　さいたま市桜区下大久保２５５
電話：048-858-3522; FAX：048-858-3522
Email：hirose@apc.saitama-u.ac.jp

2. Results and Discussion

2.1. Synthesis of enantiopure 1,3-aminoalcohols

In the synthetic routes, commercially available chiral ligand, *cis*-(1*R*,2*S*)-2-benzamidocyclohexanecarboxylic acid **1** and *trans*-(1*R*,2*R*)-2-benzamidocyclohexanecarboxylic acid **2** were chosen as the starting materials, which can be easily converted into appropriately substituted 1,3-aminoalcohols as follows (Scheme 1). First, *cis*-(1*R*,2*S*)-2-benzamidocyclohexanecarboxylic acid was reduced with $LiAlH_4$ in tetrahydrofuran to give aminoalcohol **3**[11] in good yield. After debenzylation of **3** by catalytic hydrogenolysis under atmospheric pressure of H_2 over 10% Pd/C,[12] primary amine **4**[13] was obtained in high yield. Cycloalkylation reaction of **4** with 1,4-dibromobutane afforded **5** in 62.9% yield. In addition, **3** was treated with iodomethane and NaOH in methanol, then reduced with $LiAlH_4$ to give tertiary amine **6** (89.3% yield). Thus, four primary alcohols with different *N*-substituents (**3**-**6**) were easily prepared.



Scheme 1. Reagents and conditions: (a) conc. H_2SO_4, MeOH, reflux; (b) 5 equiv. PhMgBr/dry THF, reflux; (c) $LiAlH_4$, dry THF, reflux; (d) 10% Pd/C, H_2, EtOH, 70 C; (e) $Br(CH_2)_4Br$, Et_3N, DMF, 60 C; (f) i) MeI, NaOH, MeOH, r.t.; ii) $LiAlH_4$, dry THF, reflux.

In order to introduce bulkiness to the vicinity of hydroxyl group, **1** was quantitatively esterified and subjected to Grignard reaction with PhMgBr, and then to reduction of amide group providing aminoalcohol **8** with two phenyl groups in high yield. Debenzylation of **8** gave the primary amine **9** as a white solid (87.5% yield) and cyclic tertiary amine **10** was obtained in 31.2% yield after cycloalkylation of **9**.[14]

2.2. Enantioselective addition of diethylzinc to benzaldehydes and enantioselecitiviy using chiral 1,3-aminoalcohols

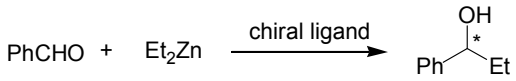
In order to examine the chiral induction abilities of chiral 1,3-aminoalcohols (**3**-**6**, **8**-**10**), we explored the enantioselective addition reaction of diethylzinc to benzaldehydes in the presence of 10 mol% of these ligands and the results were summarized in Table 1. The structural study has revealed that the enantiomeric excess changed with the number and the size of *N*-substituents; that is, secondary amines (**3** and **8**) worked as better ligands than primary amines (**4** and **9**), respectively, and **8** yielded better chemical yield than tertiary amines (**5** and **6**). However tertiary amine with a cyclic structure, **5**, showed the best chiral induction ability (71.2% *ee*) than any other ligands studied.

On the other hand, increasing the steric bulkiness at the α-position of hydroxyl group also improved the enantioselectivity, that is, when two phenyl groups were introduced to the vicinity of hydroxyl group (**3** vs. **8**, **4** vs. **9**), the enantiomeric excess increased from 33.0 to 65.5% *ee* and 9.8 to 58.9% *ee* (Table 1, Entries 1 vs. 5, 2 vs. 6).

The most interesting feature of the present system is both (*R*)- and (*S*)-1-phenyl-1-propanol were provided depending on the substituents in spite of the same chirality of the ligand, (1*R*,2*S*), derived from **1**: primary alcohols with tertiary amino groups, **5** and **6**, gave (*R*)-isomer (Table 1, Entries 3 and 4) while primary and secondary amines, **3**, **4**, and **9**, and tertiary alcohols, **8**-**10**, afforded (*S*)-isomer (Table 1, Entries 1, 2, and 5-7).

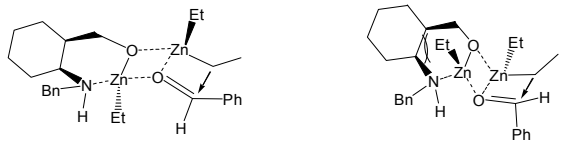
The substituent effect and chirality inversion can be explained by the transition state model proposed by some researchers for 1,3-aminoalcohols,[10b,10g,10h] which also corresponds to that by Noyori *et al.*[15] for 1,2-aminoalcohol (Figures 1-3). Supposing the *anti*-6/4/4 tricyclic transition state, the cyclohexane ring plays an important role in primary and secondary amine ligands. As an example, *anti*-(*Si*) and *anti*-(*Re*) transition states for the alkylation using **3** are compared in Figure 1. In the *anti*-(*Re*) form, large steric repulsion between the cyclohexane ring and the Et group is expected due to the 1,3-diaxial relationship in the six-membered Zn-chelate ring while the *anti*-(*Si*) form avoids such repulsion to afford (*S*)-1-phenyl-1-propanol (33.0% *ee*, Table 1, Entry 1).

Table 1. Enantioselective addition of diethylzinc to benzaldehyde catalyzed by various chiral ligands.[a]



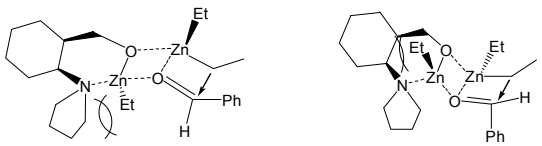
Entry	Ligand	Time/h	Yield[b]/%	*ee*[c]/%	Config.[c]
1	**3**	60	11.5	33.0	*S*
2	**4**	70	13.0	9.8	*S*
3	**5**	40	30.1	71.2	*R*
4	**6**	40	13.2	58.1	*R*
5	**8**	20	68.5	65.5	*S*
6	**9**	60	46.0	58.9	*S*
7	**10**	18	63.6	27.2	*S*

[a] All reactions were carried out in dry *n*-hexane-toluene (2:3, *V*/*V*) at 0 °C. Aldehyde/Et_2Zn/chiral ligand = 1/3/0.1; Et_2Zn (1 M solution in *n*-hexane). [b] Isolated yield. [c] See the experimental.



favored *anti* (*Si*) disfavored *anti* (*Re*)

Figure 1. Proposed transition states for the alkylation using **3**.



disfavored *anti* (*Si*) favored *anti* (*Re*)

Figure 2. Proposed transition states for the alkylation using **5**.

In addition, it was shown that secondary amines, **3** and **8**, provided better ee values than corresponding primary amines, **4** and **9**, (**3** [33.0% *ee*] vs. **4** [9.8% *ee*] and **8** [65.5% *ee*] vs. **9** [58.9% *ee*]). The result seems to suggest one *N*-substituent favours the *pseudo*-equatorial position stabilizing the *anti*-(*Si*) form.

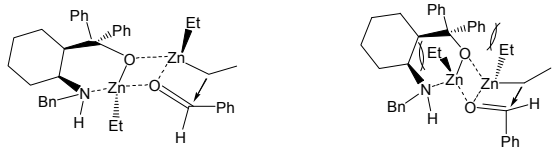
More rigid and bulky cyclic tertiary amine **5**, however, should have much larger steric repulsion with the Et group on Zn in 1,2-relationship of the *anti*-(*Si*) form than that with the cyclohexane ring in 1,3-relationship of the *anti*-(*Re*) (Figure 2). As a result, (*R*)-1-phenyl-1-propanol was obtained in a high enantiomeric excess, 71.2% *ee* (Table 1, Entry 3). Similarly another tertiary amine **6** gave the same stereoselectivity but more flexible structure (benzyl methylamine) seemed to lead to lower enantioselectivity of 58.1% *ee* (Table 1, Entry 4).

Similar and interesting chirality inversion by *N*-substituent-effect has been observed for 1,3-aminoalcohols derived from α-pinene by Szakonyi *et al*.[10i] Their primary and tertiary amines gave 1-phenyl-1-propanol of the same chirality (40 & 62% *ee*) with those obtained by **4**, **5**, and **6** (9.8-71% *ee*). On the other hand, their secondary amine gave the opposite chirality (13% *ee*) to that obtained by **3** (33% *ee*). While the cyclohexyl ring is the common structural feature, the bridging methylene might cause the difference due to its effect on the transition state geometry for the α-pinene derived ligands.[10i] On the other hand, the bulkiness of the hydroxyl group also affected the stereochemistry of alkylation.

Table 2. Optimization of the reaction conditions [a]

Entry	**5**/mol %	Solvent	Time/h	T/ºC	Yield[c]/%	ee[d]/%	Config.[d]
1	20	*n*-Hexane	40	0	69.3	71.0	*R*
2	20	CH_2Cl_2	40	0	49.2	51.0	*R*
3	20	Et_2O	40	0	28.0	30.2	*R*
4	20	THF	40	0	19.8	26.8	*R*
5	10	*n*-Hexane	40	0	40.8	63.3	*R*
6	10	H/T[b], 2:3	60	r.t.	26.9	33.5	*R*
7	10	H/T, 2:3	40	0	30.1	71.2	*R*
8	10	H/T, 2:3	25	-18	2.5	-	-
9	30	*n*-Hexane	40	0	72.1	79.4	*R*
10	30	H/T, 2:3	20	0	45.5	76.1	*R*

[a] Aldehyde/Et_2Zn = 1:3; Et_2Zn (1 M solution in *n*-hexane). [b] The volume ratio of *n*-hexane to toluene. [c] Isolated yield. [d] See the experimental.



favored *anti* (*Si*) disfavored *anti* (*Re*)

Figure 3. Proposed transition states for the alkylation using **8**.

When tertiary alcohol **8** was used as a chiral ligand, additional repulsion between the Ph group and the Et group on Et_2Zn for alkylation further destabilizes the *anti*-(*Re*) form (Figure 3). Chirality change by the substitution on the α-carbon of hydroxyl group of 1,3-aminoalcohols has been reported by Cicchi *et al.*[10e] In their system, diphenyl methanol and 9-hydroxy fluorene moieties caused opposite chirality in the product. Although similar substitution effect on the α-carbon of hydroxyl group has been also observed for chiral 1,2-aminoalcohol ligands,[9c] there are only limited systems reported for the chirality inversion by this kind of substituent-effect. Considering the diversity of structural modification, chiral 1,3-aminoalcohols would be interesting scaffolds for asymmetric reactions.[4,10e,10f,10i]

2.3. Enantioselective addition of diethylzinc to various aldehydes

In order to optimize the reaction, the solvent, temperature and ligand loading effects were examined and the results are shown in Table 2. Apparently less-polar solvents (Entries 1 & 2) gave better chemical yield and enantiomeric excess than polar ethers (Entries 3 & 4), especially in THF (26.8% *ee*). Many studies have shown that toluene or *n*-hexane-toluene mixture is a proper solvent system to provide higher enantioselectivity[9c-e,9j,9k] so that the ratio of this mixed solvent system was changed in our study as well. Although the ratio of *n*-hexane to toluene has less effect on the chiral control, the yield was observably enhanced when only *n*-hexane was used (Entries 5 vs. 7, 9 vs. 10). At the same time, the effect of the amount of chiral ligand on the enantioselectivity was investigated by the use of **5**. Although the reaction proceeded with 10 mol% ligand loading, the enantioselectivity and the yield were gradually

improved by increasing the amount of **5** from 10 to 20 and 30 mol% (Entries 1, 5 & 9).

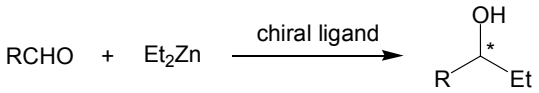
When the reaction was carried out at different temperatures, we found a large effect on the conversion and the enantioselectivity. The best result was obtained at 0 ˚C and either lower or higher

the presence of 20 mol% of 5 and 8 for not only various aromatic aldehydes having an electron donating or withdrawing group but also heteroaromatic and aliphatic aldehydes. The results were summarized in Table 3. The enantioselectivity observed in Table 1 was confirmed for all aromatic aldehydes: **5** gave

temperature decreased both the chemical yield and ee value (Table 2, Entries 6-8). Similar results on the temperature effect were observed by other researchers.[4c,5b,7c,16].

Considering the results shown in Table 2, we investigated the ligand effect on the chiral induction in (*R*)-1-aryl-1-propanol while **8** afforded (*S*)-enantiomer in good yields. In addition, little substituent effect was observed for the *meta*- or *para*-substituted benzaldehydes on both chemical yield and enantioselectivity. However, the *ortho*-substituent, especially an *ortho*-bromo substituent,

Table 3. Asymmetric addition of diethylzinc to aldehydes in the presence of **5** or **8** [a]



Entry	Ligand	Aldehyde	Yield[b]/%	ee[c]%	Config.[c]
1	**5**	*p*-ClC_6H_4CHO	62.0	65.6	*R*
2	**5**	*p*-MeC_6H_4CHO	56.0	63.6	*R*
3	**5**	*m*-ClC_6H_4CHO	72.5	75.4	*R*
4	**5**	*m*-MeC_6H_4CHO	68.8	75.0	*R*
5	**5**	*o*-BrC_6H_4CHO	58.6	32.6	*R*
6	**5**	*o*-ClC_6H_4CHO	51.1	38.1	*R*
7	**5**	*o*-MeC_6H_4CHO	64.8	53.4	*R*
8	**5**	Furan-2-carboxaldehyde	70.4	52.0	*R*
9	**5**	Thiophene-2-carboxaldehyde	57.1	47.5	*R*
10	**5**	Isobutyraldehyde	trace	—	—
11	**5**	Hexanal	trace	—	—
12	**5**	Cyclohexanecarboxyaldehyde	trace	—	—
13	**8**	*p*-ClC_6H_4CHO	77.3	60.1	*S*
14	**8**	*p*-MeC_6H_4CHO	81.0	55.8	*S*
15	**8**	*m*-ClC_6H_4CHO	78.3	66.0	*S*
16	**8**	*m*-MeC_6H_4CHO	82.5	61.1	*S*
17	**8**	Thiophene-2-carboxaldehyde	60.6	27.3	*S*

[a] All reactions were carried out in dry *n*-hexane at 0 ºC for 72 h. Aldehyde/Et_2Zn/chiral ligand = 1/3/0.2; Et_2Zn (1 M solution in *n*-hexane). [b] Isolated yield. [c] See the experimental.

decreased the enantioselectivity. The substituent effect on the substrate needs to be further investigated since the present result is in accordance with the results reported by Yang *et al*.,[4a,4b] Sun *et al*.,[17a] Jaworska *et al*.,[17b] but was opposite to the results reported by Joshi *et al*.[9i]

Among the heteroaromatic aldehydes, a similar result was obtained for furan-2-carboxaldehyde (Entry 8) but lower enantioselectivity was obtained for thiophene-2-carboxaldehyde (Entries 9 and 17). The heteroatom might be the cause as commented by Noyori *et al*.[15a] On the other hand, the present system was not effective for aliphatic aldehydes as complex product mixtures were obtained for three aliphatic aldehydes examined (Entries 10-12). Comparing 1,2-aminoalcohol ligands, a more flexible 6/4/4 tricyclic transition state might be the cause of this limitation. Further control of molecular design needs to the present ligand structure.

3. Conclusion

We have synthesized a series of novel optically active 1,3-aminoalcohols from *cis*-(1*R*,2*S*)-2-benzamidocyclohexanecarboxylic acid **1**. The structural characteristics of the chiral ligands were explored in asymmetric diethylzinc addition to various aldehydes. The results demonstrated that the cyclohexane ring, *N*-substituents and the substituents to the vicinity of hydroxyl group have crucial effect on chirality control. Providing the rigid and bulky cyclic tertiary amine **5** showed the best promoting ability to aromatic aldehydes with (*R*)-selectivity (79.4% *ee*) in the ligands studied in this article. With two phenyl groups to provide the proper steric bulkiness, the tertiary alcohol **8** showed the opposite (*S*)-selectivity (66.0% *ee*). Further studies on chiral control and versatility are currently underway by 1,3-aminoalcohol ligands derived from **1**.

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