Tetrahedron: *Asymmetry* 20 (2009) 1150–1153

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Chiral ligand derived from (1*S*,2*R*)-norephedrine as a catalyst for enantioselective prochiral ketone reduction

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ARTICLE INFO

Article history:
Received 23 February 2009
Accepted 19 March 2009
Available online 4 May 2009

ABSTRACT

Chiral oxazaborolidines derived from (1*S*,2*R*)-(+)-norephedrine and substituted salicylaldehydes were employed in the asymmetric reduction of prochiral ketones using borane dimethyl sulfide as a reducing agent. The secondary alcohols were formed in excellent yields (45–99.8%) with enantioselectivities up to 99.8%. The effect of the substitution in the aromatic ring of the ligand was discussed with the enantioselectivity of the product.

1. Introduction

The reduction of ketones to enantiomerically enriched alcohols is a pivotal transformation in synthetic organic chemistry.[1] Since most drug effects are due to interaction with chiral biological materials, each enantiomer may have different pharmacological properties in terms of activity, potency, toxicity, transport mechanism and metabolic route.[2] Hence there is an increase in demand for the synthesis of enantiomerically pure compounds. Among them prochiral ketone reduction to secondary alcohols plays an important role as it is the intermediate for many biological transformations. Fiaud and Kagan[3] were the first to work on optically active borane complexes derived from ephedrine alkaloids as a chiral auxiliary for asymmetric reductions, resulting in very low enantioselectivity. Many chiral diols,[4] amino alcohols[5] and sulfoximines[6] have served as chiral ligands in the enantioselective borane reduction to accelerate the reaction rate and, more importantly, to provide an asymmetric environment for the reacting species. Among them, oxazoborolidines synthesized from chiral amino alcohols gave excellent ee.[7] Hirao et al.[8] reported the first effective stereoselective borane reduction, using stoichiometric amounts of in situ prepared 1,3,2-oxazaborolidines based on nonracemic chiral β-amino alcohols which was further improved by Corey et al.[9] This method (CBS reduction) has several advantages because of easy and efficient recoverability of the chiral catalyst, high yields, experimental simplicity and economy.

Among these cases, oxygen and nitrogen are used as the coordinating atoms to boron. In general, the oxygen–nitrogen-paired ligands gave a better enantioselectivity than the corresponding oxygen–oxygen-paired bidendate ligands. This phenomenon can be rationalized according to the CBS mechanism proposed by Corey,[9] in which a second molecule of borane coordinates with the more electron-rich nitrogen atom. Thus directing the borohydride to specifically approach one of the prochiral faces of the carbonyl group. However, in the diol ligands, scrambled induction may occur if both the oxygen atoms have a similar coordinating capability to the second borane and results in a significant affinity difference for coordination, possibly offering the second borane an unstable situation upon coordination with diol-type ligands. Consequently, lesser enantioselectivity could be expected compared to the oxygen nitrogen-paired ligands. The β-amino alcohol-type ligands derived from ephedra alkaloids are widely used in various asymmetric reactions such as aldol condensation,[10] diethyl zinc addition to aldehydes,[11] Michael addition[12] and reduction of prochiral ketones using borane dimethyl sulfide.[13]

Most of the oxazaborolidines used so far are formed from a β-amino alcohol moiety introduced by Corey et al.[9] and also from (1*R*,2*S*)-ephedrine.[14] Generally amino alcohols afford a suitable and relatively stable complexing site for the first boron involved in the reduction sequence,[15] although diols,[16] diamines[17] and amino acid esters[18] containing ligands have also been reported to carry out this function.[19]

Parrott II[20] et al. reported the synthesis and application of a series of mono *N*-alkylated ephedrine and norephedrine derivatives in the enantioselective addition of diethylzinc to aldehydes. In that report, a ligand derived from salicylaldehyde and norephedrine was found to give a marginal enantiomeric excess of 54:46. Herein we report the enantioselective reduction of ketones using a chiral relay amino alcohol ligand derived from norephedrine and substituted salicylaldehydes using borane dimethyl sulfide as a reducing agent. In our case, the enantioselectivity depends on the electronic effect of the substitution on the salicylaldehyde. The structure of the chiral amines is shown in Figure 1. To the best of our knowledge there are no reports on the synthesis of chiral amines **1a**–**e** derived from (1*S*,2*R*)-(+)-norephedrine and substituted salicylaldehydes and their catalytic activity on enantioselective ketone reduction.

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doi:10.1016/j.tetasy.2009.03.029

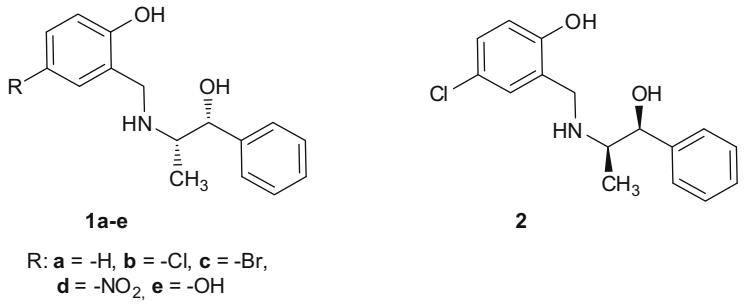


Figure 1.

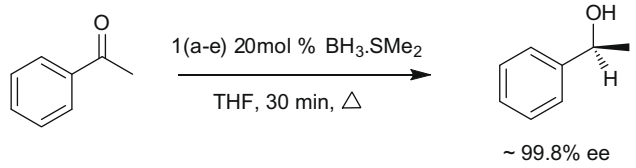
2. Results and discussion

The chiral ligands were synthesized from (1*S*,2*R*)-(+)-norephedrine and substituted salicylaldehyde by reductive amination.[20] (1*R*,2*S*)-(−)-norephedrine was also used as a chiral source in order to show the change in stereoselectivity while changing the stereoisomer of norephedrine. The synthesized ligands **1a–e** and **2** (Scheme 1) were explored for their catalytic activity in the enantioselective reduction of a prochiral ketone (Scheme 2). There are reports showing that halogen containing chiral amino alcohols shows better enantiomeric excess than the one without halogen.[21] Therefore, the reduction of acetophenone was studied in detail with ligand 1b, and the results are given in Table 1. To 5 mol % of the chiral ligand taken in dry THF, 1.2 mmol of BMS was added and refluxed for 30 min. To this 1 mmol of acetophenone was added and refluxed for another 2 h. After quenching and extraction, the (*S*)-isomer of the corresponding secondary alcohol was obtained in 95% yield and 30% ee (Table 1, entry 1).

The oxazaborolidine formation from the chiral amine and borane methyl sulfide requires 30 min under refluxing conditions in dry THF. The structure of oxazaborolidine and the mechanism of prochiral ketone reduction are shown in Scheme 3. A survey of the literature reveals that compounds with three coordination sites around a boron atom will give high ee rather than the one with two coordination sites[22] due to their rigid structure that results in excellent enantioselectivity. The chosen ligand system is also tridendate in nature which can be expected to give high ee.

The liberation of three hydrogens during the formation of the tridentate oxazaborolidine complex between the chiral amine and borane dimethyl sulfide was cross-checked with the hydrogen evolution studies. And the second borane will coordinate with the nitrogen atom from which the hydride transfer occurs.

The enantioselectivity of borane reduction may be affected by reaction conditions such as solvent, temperature and catalyst loading.[23] When the reaction was performed with toluene as a solvent, the enantiomeric excess of 1-phenyl ethanol was decreased to 20% (entry 2). From the literature survey we found that THF is better



Scheme 2. Enantioselective prochiral ketone reduction using **1a–e**.

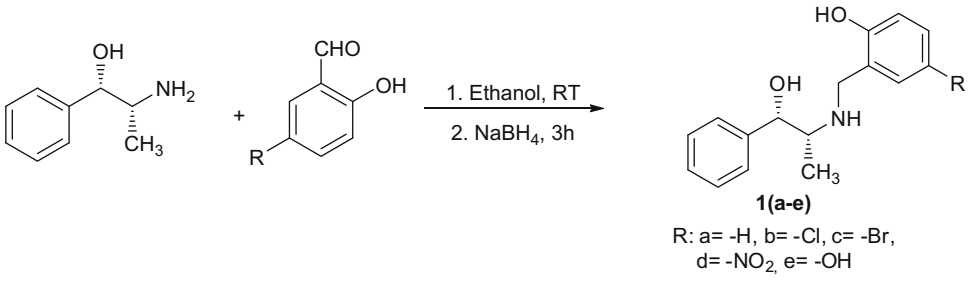
Table 1
Enantioselective ketone reduction using $BH_3{\cdot}S(CH_3)_2$ as a reducing agent with **1b** as catalyst

Entry	Catalyst amount (%)	Temperature (°C)	Yield[a] (%)	ee[b] (%)
1	5 mol	rt	95	30
2	5 mol[c]	rt	90	20
3	5 mol	−76	97	0
4	5 mol	0	74	0
5	5mol	65	87	44
6	10 mol	65	99	60
7	15	65	99	70
8	20	65	99	92
9	25	65	100	88
10	30	65	100	90
11	Stoichiometric	65	100	91

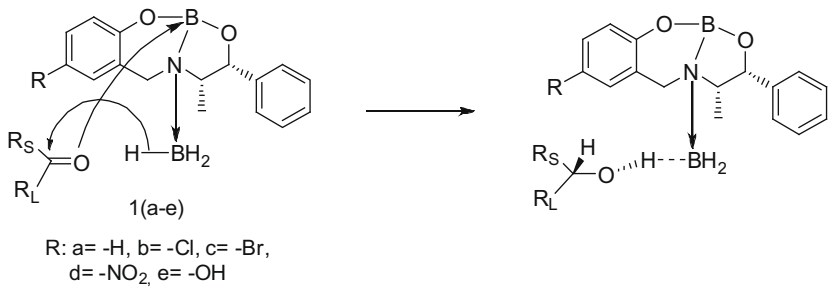
[a] Isolated yield by column chromatography.
[b] Determined by HPLC analysis using Chiralcel OD-H column.
[c] The reaction was carried out in dry toluene.

than toluene and dichloromethane.[24] So the reduction of different prochiral ketones was carried out in dry THF.

Then the effect of temperature on the enantioselectivity was studied with 5 mol % of the chiral catalyst. When the reaction was performed at lower temperatures of −76 °C and 0 °C, a racemic mixture was formed proving that some activation energy is required to form the oxazaborolidine complex. The enantioselectivity increased with an increase in temperature. At refluxing temperatures (67 °C), with 5 mol % of the catalyst the enantioselectivity was 44%. Once the reaction temperature was optimized, the



Scheme 1. Synthesis of chiral amines.



Scheme 3. Transition state for the oxazaborolidine complex during the prochiral ketone reduction.

effect of the catalytic amount on the enantioselectivity was studied and the results are shown in Table 1. (entries 3–11). Table 1 clearly explains that up to 20 mol % of the catalyst the enantioselectivity increases linearly and with 30 mol % of the catalyst, there is no further increase in enantiomeric excess. Thus the optimized reaction conditions were 20 mol % of the catalyst, reaction time of 60 min and refluxing temperature of THF.

The enantioselectivity of the chiral secondary alcohols using the chiral amines **1a–e** and **2** is given in Table 2. In the case of **1b** as a catalyst, (*S*)-enantiomer was obtained as a major product, and in the case of **2** we got the (*R*)-enantiomer as a major product (entry 7 in Table 2). Table 2 clearly shows that among the chiral amines **1a–e**, **1b** shows the best enantioselectivity. This result is in good agreement with the reported results of Zong-Xuan Shen et al., which states that the chloro-containing chiral β-amino alcohol shows better enantioselectivity than the one without chlorine atom.[21]

To explore the synthetic utility of the chiral ligand **1b**, reduction of different prochiral ketones was studied with the optimized reaction conditions. The results are presented in Table 3.

From the above results, the ketones having electron-withdrawing groups were reduced with higher ee and yield than the ketones having electron-donating groups (entries 1–6) except iodine-substituted acetophenone and *p*-methoxy acetophenone. This may be due to the strong coordination between the second boron atom and the ketones having electron-donating groups, which makes the oxazaborolidine complex more rigid than in the case of ketones having electron-withdrawing groups where the complex is flexible for the hydride transfer.

Among the ketones having halogens, iodine-substituted acetophenone were reduced with a low ee (30%) and yield (35%) compared to chlorine and bromine-substituted acetophenones which shows that as the size of the halogen increases the enantioselectivity decreases.

ortho-Substituted ketones (entries 1, 4 and 10) gave the (*R*)-isomer specifically and the *para*-substituted acetophenones gave the other isomer. This may be due to the repulsion possible between the substituents at the *ortho*-position and the second boron atom, which may change the approach of the ketones to the boron atom.

Table 2
Enantioselective ketone reduction using $BH_3{\cdot}S(CH_3)_2$ as a reducing agent with 20 mol % of the catalyst[a]

Entry	Catalyst	Yield[b] (%)	ee[c] (%)	Absolute configuration[d]
1	**1a**	99	82	(*S*)
2	**1b**	99	97	(*S*)
3	**1c**	99	81	(*S*)
5	**1d**	96	93	(*S*)
6	**1e**	70	60	(*S*)
7	**2**	97	60	(*R*)

[a] Ratio of ligand/BMS/ketone was 0.2:1.6:1.1. 30 min stirring at 65 °C.
[b] Isolated yield by column chromatography.
[c] Determined by HPLC analysis using Chiralcel OD-H column.
[d] The absolute configuration was assigned by comparison of the sign of the specific rotation with the literature data.

Table 3
Enantioselective reduction of different ketones using chiral ligand **1b** and $BH_3{\cdot}S(CH_3)_2$ as a reducing agent[a]

Entry	Ketone	Yield[b] (%)	ee[c] (%)	Absolute configuration[d]
1	*o*-Cl Acetophenone	100	99.8	(*R*)
2	*p*-OCH_3 Acetophenone	100	99.8	(*S*)
3	*p*-Br Acetophenone	99	99	(*S*)
4	*o*-Br Acetophenone	90	94	(*R*)
5	*p*-NH_2 Acetophenone	50	60	(*S*)
6	*p*-CH_3 Actophenone	30	40	(*S*)
7	Ethyl methyl ketone	76	34	(*S*)
8	Isobutyl methyl ketone	62	30	(*S*)
9	*p*-I Acetophenone	35	30	(*S*)
10	2-Aceto naphthone	60	18	(*R*)

[a] Ratio of ligand/BMS/ketone was 0.2:1.6:1.1.
[b] Isolated yield by column chromatography.
[c] Determined by HPLC analysis using Chiralcel OD-H column.
[d] The absolute configuration was assigned by comparison of the sign of the specific rotation with the literature data.

Table 3 also shows that the aromatic ketones were reduced with better enantioselectivity than the aliphatic ketones (entries 7 and 8).

3. Conclusion

In conclusion, we have developed (1*S*,2*R*)-(+)-norephedrine-derived chiral amines that are readily synthesized in good yield and purity, for enantioselective ketone reduction with borane dimethyl sulfide as a reducing agent. Different prochiral ketones were reduced with excellent enantioselectivities of up to 99.8% and in good yield. By choosing the appropriate stereoisomer of norephedrine, corresponding optically active alcohols can be synthesized with good yield and enantioselectivity.

4. Experimental

4.1. General remarks

^1H NMR and ^{13}C spectra were recorded in $CDCl_3$ with a BRUKER AMX-300 MHz instrument using TMS as an internal standard. Specific rotation was recorded with a Rudolph Autopol IV polarimeter (589 nm and $CHCl_3$). Enantiomeric excess was determined with a Shimadzu2010A HPLC instrument (Chiral column: Chiral Cel OD-H, Mobile Phase: solvent system 98:2 hexane/*i*-PrOH) with the flow rate of 0.5 ml/min at 254 nm. FTIR spectra were recorded with a Perkin Elmer—DXB spectrometer. Melting points were determined with a Kherea digital melting point apparatus and are uncorrected.

4.2. General procedure for the synthesis of chiral amines

To an oven-dried, nitrogen-purged flask (1*R*,2*S*)-norephedrine (1.05 g, 6.94 mmol) was added and dissolved in anhydrous ethanol. To this an equal amount of substituted salicylaldehyde was added

as an ethanolic solution. The reaction mixture was allowed to stir at room temperature for 18 h, and then cooled to 0 °C. After cooling, sodium borohydride, (0.53 g, 13.9 mmol) was added and allowed to stir for 2 h. After the completion of the reaction monitored by TLC, ethanol was removed, and the reaction mixture was poured into crushed ice. Then the amine was extracted from aqueous phase using diethyl ether and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the product was recrystallized from diethyl ether and hexane (1:2). All the other chiral amines **1a**–**e** were synthesized using the similar procedure.

4.2.1. Synthesis of 4-chloro-2-(((1*S*,2*R*)-1-hydroxy-1-phenylpropan-2-ylamino)methyl)phenol 1b

(1*S*,2*R*)-Norephedrine and 5-chloro salicylaldehyde were reacted to yield compound **1b** as a yellow solid in 90% yield. Melting point: 52–54 °C. $[\alpha]_{30}^{589} = +11.1$ (*c* 0.2, $CHCl_3$). FTIR (cm^{-1}): 3630 (–OH), 3340 (–NH), 3098 (Ar-CH), 1283(C–O). ^1H NMR, $CDCl_3$ δ (ppm): 1.01 (d, 3H), 2.9 (q, 1H), 3.15 (s, 1H), 4.0 (dd, 2H), 4.8 (d, 1H), 6.7–7.4 (Ar-H, 8H). ^{13}C NMR, $CDCl_3$ δ (ppm): 14, 49, 57, 75, 117.8, 123.5, 124.2, 126.2, 127.8, 127.9, 128.4, 128.5, 141.2, 157. Elemental Anal. Calcd: C, 65.86; H, 6.22; N, 4.8. Found: C, 64.38; H, 6.63; N, 4.79.

4.2.2. Synthesis of 2-(((1*S*,2*R*)-2-hydroxy-1-methyl-2-phenylethyl)amino) methyl)phenol 1a

(1*S*,2*R*)-Norephedrine and salicylaldehyde were reacted to yield compound **1a** as a yellow colour semi solid in 80% yield. $[\alpha]_{30}^{589} = +17.6$ (*c* 0.25, $CHCl_3$). FTIR (cm^{-1}): 3560, 3318, 3045, 1260. ^1H NMR, $CDCl_3$, δ (ppm): 0.9 (d, 3H), 2.85 (q, 1H), 3.82 (dd, 2H), 4.75 (d, 1H), 5.2 (s, 1H), 6.6–6.9 (Ar-H, 3H), 7.15–7.3 (Ar-H, 6H).

4.2.3. Synthesis of 4-bromo-2-(((1*S*,2*R*)-1-hydroxy-1-phenylpropan-2-ylamino)methyl)phenol 1c

(1*S*,2*R*)-Norephedrine and 5-bromo salicylaldehyde were reacted to yield compound **1c** as a brown colour solid in 86% yield. Melting Point: (65–67 °C); $[\alpha]_{30}^{589} = +14$ (*c* 0.3,$CHCl_3$). FTIR (cm^{-1}): 3613 (–OH), 3328 (–NH), 3065 (Ar-CH), 1271 (C–O). ^1H NMR, $CDCl_3$ δ (ppm): 1.08 (d, 3H), 2.98 (m, 1H), 4.03 (dd, 2H), 4.8 (d, 1H), 6.6–6.7 (Ar-H, 3), 7.2–7.3 (Ar-H, 5H).

4.2.4. Synthesis of 2-(((1*S*,2*R*)-1-hydroxy-1-phenylpropan-2-ylamino)methyl)-4-nitrophenol 1d

(1*S*,2*R*)-Norephedrine and 5-nitro salicylaldehyde were reacted to yield compound **1d** as a yellow colour solid in 90% yield. Melting Point: (153–154 °C); $[\alpha]_{30}^{589} = +53$ (*c* 0.2, $CHCl_3$). FTIR (cm^{-1}) 3633 (–OH), 3341 (–NH), 3091 (Ar-CH), 1290 (C–O). ^1H NMR, $CDCl_3$ δ (ppm): 1.25 (d, 3H), 3.0 (m, 1H), 4.1 (dd, 2H), 4.83 (d, 1H), 6.8–6.9 (Ar-H, 5H), 7.9–8.2 (Ar-H, 3H).

4.2.5. Synthesis of 4-(((1*S*,2*R*)-1-hydroxy-1-phenylpropan-2-ylamino)methyl)benzene-1,4-diol 1e

(1*S*,2*R*)-Norephedrine and 2,5-dihydroxy benzaldehyde were reacted to yield compound **1e** as a yellow colour solid in 78% yield. Melting Point: (77–79 °C); $[\alpha]_{30}^{589} = +28$ (*c* 0.2, $CHCl_3$). FTIR (cm^{-1}): 3628 (–OH), 3337 (–NH), 3070 (Ar-CH), 1260 (C–O). ^1H NMR, $CDCl_3$ δ (ppm): 1.2 (d, 3H), 2.9 (m, 1H), 3.14 (s, 1H), 3.8 (dd, 2H), 4.78 (d, 1H), 6.6–6.8 (Ar-H, 3H), 7.2–7.3 (Ar-H, 5H).

4.3. General procedure for the prochiral ketone reduction

The reaction was carried out with the molar ratio of ligand/acetophenone/BMS as 0.2:1:1.6. To the chiral ligand **1b** (53 mg, 0.2 mmol) dissolved in dry THF (3 ml) under a nitrogen atmosphere, borane dimethyl sulfide (0.15 ml, 1.6 mmol) was added dropwise and refluxed for 30 min. To this mixture acetophenone (0.12 ml, 1 mmol) was added dropwise and refluxed for 2 h. Then the reaction mixture was quenched with 2 M HCl and extracted with chloroform. The chiral alcohol was separated by column chromatography with silica gel as an adsorbent and 98:2 (hexane/ethylacetate) as an eluent.

Acknowledgements

The authors thank DST for financial assistance (SR/FTP/CS-142-2006) in the form of a Fast track sponsored project and Dr. M. Chidambaram, Director, NITT for his constant encouragement, support and research grant.

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