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cis-1-Amino-1,2,3,4-tetrahydro-2-naphthalenol: resolution and application to the catalytic enantioselective reduction of ketones

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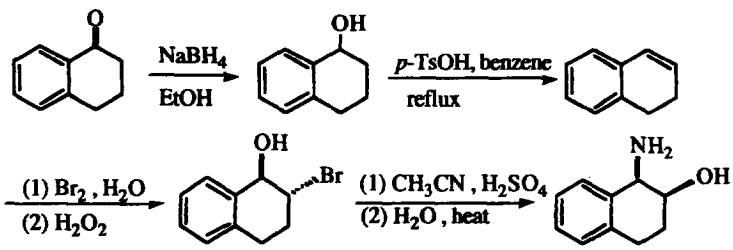
Abstract: *cis*-1-Amino-1,2,3,4-tetrahydro-2-naphthalenol was synthesized and resolved via its diastereomeric salts. Asymmetric reduction of prochiral ketones was examined using this amino alcohol at various temperatures. © 1997 Elsevier Science Ltd

The highly enantioselective borane reduction of prochiral ketones has been reported using amino alcohols as chiral auxiliaries, most of which are derived from natural homochiral compounds.[1] In recent years, many artificial chiral auxiliaries such as *cis*-2-amino-1-acenaphthenol and *cis*-1-amino-2-indanol have been developed and shown to exhibit a high enantioselectivity.[2] In our study the artificial chiral compound, optically active *cis*-1-amino-1,2,3,4-tetrahydro-2-naphthalenol **1** was prepared and several ketones were asymmetrically reduced with borane using this catalyst.[3] Racemic **1** was prepared and resolved as shown in Scheme 1. 1,2-Dihydronaphthalene, which was obtained by the $NaBH_4$ reduction of 1-tetralone followed by dehydration, was converted to the *trans* bromohydrin with bromine and hydrogen peroxide in water.[4] The Ritter reaction of the *trans* bromohydrin gave **1** in a 58% yield.



1

Scheme 1. Preparation of **1**.

At first, we examined the resolution of racemic **1** via diastereomeric salts with several kinds of chiral acids, such as tartaric acid, malic acid, camphoric acid, di-*O*-benzoyltartaric acid and mandelic acid. Successful resolution has been achieved using (−)-mandelic acid. The examination of several conditions for recrystallization indicated the optimum conditions for resolution were the preparation of the diastereomeric salt in isopropyl alcohol followed by recrystallization in ethanol; three repeated recrystallizations gave the enantiomerically pure salt of (−)-**1** in a 55.8% yield (Table 1). The absolute configuration of the obtained (−)-**1** was determined by the following method. As the chirality of the 2-position of *cis*-1,2-tetralindiol is retained in the Ritter reaction, the commercially available chiral (1*R*,2*S*)-diol was converted to (1*R*,2*S*)-**1** by this reaction.[5] Comparison of the retention time of (−)-**1** with the authentic sample from (1*R*,2*S*)-*cis*-1,2-tetralindiol using chiral HPLC indicated its configuration to be (1*R*,2*S*).

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Table 1. Optimization of resolution conditions

resolving agent	solvent	recryst. solvent	Yield % [a]	% ee [b]
tartaric acid	MeOH	MeOH×2	16.6	0
malic acid	MeOH	i-PrOH×1	75.2	5.2
camphoric acid	MeOH	—	20.2	8.2
di-*O*-benzoyl tartaric acid	MeOH	—	31.1	51.6
mandelic acid	MeOH	MeOH×1	43.3	76.8
	AcOEt	—	100	0
	i-PrOH	—	61.8	97.4
		MeOH×2	28.5	100
		EtOH×3	55.8	100

a) Based on half of racemic **1**
b) Determined by a chiral HPLC analysis (CROWNPAK CR(-))

We then used homochiral **1** in the catalytic asymmetric reduction. Three model ketones such as acetophenone, 1-indanone and 1-tetralone were chosen for our studies. The reaction mode usually used for these reactions was applied, that is, dropwise addition of the ketone over 10 minutes into a THF solution of the catalyst and BH_3–THF complex at −13, 20 and 40°C. The results of the enantioselectivity are summarized in Table 2. For comparison, the asymmetric reduction using the chiral oxazaborolidine from (1*S*,2*R*)-*cis*-1-amino-2-indanol **2** are also tabulated.

No significant difference was observed in the enantioselectivity depending on the catalyst used. However, an appreciable temperature dependence on the selectivity was realized; there was an increase in selectivity with increasing temperature over the temperature range used in this study. This supports the postulate by Douglas *et al.* in which the rate of catalyst recycle from the reaction intermediate **A** is accelerated at higher temperature (Scheme 2).[6]

Experimental section

General

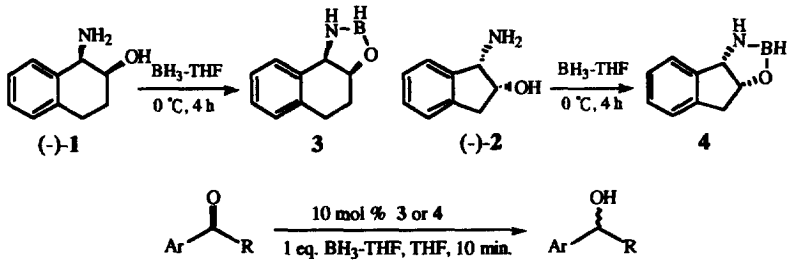
^{1}H-NMR spectra were taken at 400 MHz for solutions in deuterated solvents. Chemical shifts are given in δ units with respect to TMS and coupling constants (J) are in Hz. ^{13}C-NMR spectra were run at 100 MHz for solutions in deuterated solvents, by using uncoupled techniques. IR spectra were taken on a HITACHI 270-50 instrument. Analytical TLC analyses were performed by using precoated silica gel 60 F_{254} plates supplied by Merck; visualization was accomplished under ultraviolet light. The removal of solvents under reduced pressure refers to the evaporation of the solvent at ca. 25 mmHg on a rotary evaporator. All solvents and reagents were commercially available (reagent grade) and were used without further purification.

Preparation of cis-*1-amino-1,2,3,4-tetrahydro-2-naphthalenol*

trans-*1,2,3,4-Tetrahydro-2-bromo-1-naphthalenol* **5**

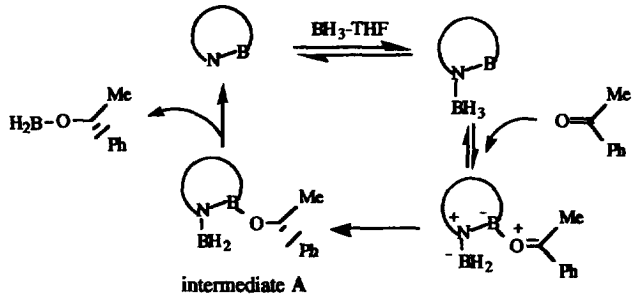
A solution of 1,2-dihydronaphthalene (65.0 g, 0.50 mol), triton X (1.2 g), water (150 cm^3) and chlorobenzene (80 cm^3) was stirred at 65°C, and then bromine (40.0 g, 0.25 mol) was added dropwise over 2 hours. After stirring for 4 hours, 30% hydrogen peroxide (29.2 g, 0.25 mol) was added dropwise over 2 hours, then the mixture was stirred for 5 hours at 65°C. The reaction mixture was cooled, and the precipitates were filtered to give **5** as a colorless solid (94.3 g, 83.5%): mp 109–112°C; IR (KBr)

Table 2. Catalytic enantioselective reduction of ketones



Ketone	Cat.	% ee[a](Config.)[b]		
		-13 °C	20 °C	45 °C
$PhCOCH_3$	3	23.9 (S)	85.2 (S)	85.7 (S)
	4	36.5 (R)	79.8 (R)	80.7 (R)
	3	19.3 (S)	65.4 (S)	81.0 (S)
	4	13.3 (R)	56.8 (R)	84.8 (R)
	3	22.9 (S)	80.5 (S)	80.2 (S)
	4	27.7 (R)	73.4 (R)	87.4 (R)

a) Determined by a chiral HPLC analysis (Daicel chiralcel OB)
b) The absolute configlation was determined by the comparison of the retention time with commercial chiral alcohol (HPLC analysis)



Scheme 2.

3226, 2904; ^{1}H-NMR ($CDCl_3$) 2.27 (1H, m), 2.50 (1H, m), 2.58 (1H, br s), 2.95 (2H, m), 4.35 (1H, dt, *J*=6.83, 3.17), 4.89 (1H, d, *J*=6.83), 7.2–7.4 (4H, m); ^{13}C-NMR 28.1, 29.7, 56.2, 74.1, 126.7, 128.0, 128.2, 128.5, 135.0, 135.5.

cis-*1-Amino-1,2,3,4-tetrahydro-2-naphthalenol 1*

To a stirred solution of **5** (68.0 g, 0.30 mol) in acetonitrile (24.8 g, 0.60 mol) and CH_2Cl_2 (100 cm^3) was added sulfuric acid (45.0 g, 0.45 mol) at room temperature. After stirring for 2 hours, water (250 cm^3) was added. The reaction mixture was concentrated until the internal temperature reached 65°C by atmospheric distillation and the residue was then stirred for 20 hours at 65°C. After cooling off,

the mixture was washed with CH_2Cl_2 (250 cm^3) and the aqueous layer was basified to about pH 12 with 25% aqueous NaOH solution. The precipitate was collected by filtration and washed with water to give racemic **1** as a colorless solid (24.8 g, 73.2%): mp 104–106°C; ^{1}H-NMR ($CDCl_3$) 1.79 (1H, m), 1.93 (1H, m), 2.31 (3H, br s), 2.78 (1H, m), 2.91 (1H, m), 3.89 (1H, ddd, J=10.49, 4.88, 3.42), 3.92 (1H, d, J=4.88), 7.09–7.32 (4H, m); ^{13}C-NMR 26.6, 27.4, 52.4, 68.4, 126.3, 127.1, 128.7, 129.5, 135.7, 139.4.

Resolution of racemic cis-*1-amino-1,2,3,4-tetrahydro-2-naphthalenol* ***1****. Optimum conditions*

To a solution of racemic **1** (16.3 g, 0.10 mmol) in isopropyl alcohol (200 cm^3) was added (−)-mandelic acid (15.1 g, 0.10 mmol) dissolved in the same solvent (100 cm^3) at 60°C. The resulting suspension was stirred for 3 hours at 60°C and then cooled to room temperature. The precipitate was collected by filtration, and washed with isopropyl alcohol. Recrystallization from ethanol (three times) gave pure diastereomeric salt of **1** (7.58 g, 24.0 mmol, 55.8% based on half of racemic **1** used) as colorless needles: $[\alpha]_D^{28}$ −95.8 (c=1.0, H_2O); mp 181.2–182.7°C; IR (KBr) 3354, 2881, 1541, 734.

A suspension of diastereomeric salt of **1** (7.58 g, 24.0 mmol) in water (500 cm^3) was made at pH 12 by the addition of aqueous NaOH solution and was extracted with CH_2Cl_2 (3×100 cm^3). Usual workup gave (1*R*,2*S*)-(−)-**1** (3.91 g, 24.0 mmol, 100%) as a colorless solid: $[\alpha]_D^{25}$ −75.0 (c=1.0, 0.1 M HCl in methanol); mp 95–96°C; IR (KBr) 3248, 2864, 1488, 726.

Enantioselective reduction of prochiral ketones catalyzed by ***1*** *and* ***2****. General procedure*

To a solution of a chiral amino alcohol (**1** or **2**, 0.8 mmol) in THF (24 cm^3) was added a BH_3–THF solution (1 M in THF, 7.15 g, 8.0 mmol) and the mixture was stirred for 4 hours, then the ketone (8.0 mmol) dissolved in THF (8 cm^3) was added dropwise over 10 minutes at three different temperatures (−13, 20 or 40°C). After stirring for 2 hours, the mixture was quenched with 10% aqueous HCl solution (10 cm^3). Extraction with CH_2Cl_2 (3×20 cm^3), drying over Na_2SO_4, and concentration afforded the alcohol. The e.e. value of the product was determined by a chiral HPLC analysis (CROWNPAK CR(−)).

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