A New Method for the Preparation of Oxazaborolidine Catalyst *In Situ* Using 1,2-Aminoalcohol, Sodium Borohydride, and Diiodomethane for the Asymmetric Reduction of Prochiral Ketones and *N*-Substituted Imines

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Abstract: An oxazaborolidine catalyst is readily prepared *in situ* at room temperature in THF using 1,2-aminoalcohols and borane generated from sodium borohydride/CH_2I_2 reagent system. The oxazaborolidine/BH_3 reagent system prepared in this way is useful for the reduction of prochiral ketones and *N*-substituted imines to the corresponding alcohols and amines with moderate to good enantiomeric excesses.

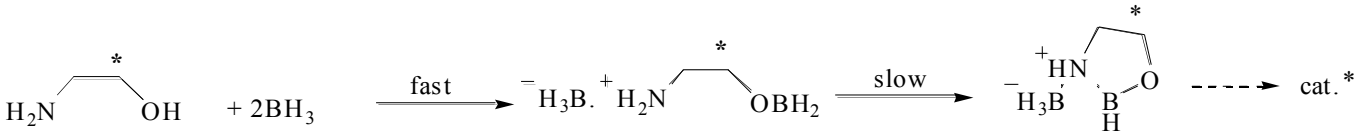
Keywords: Asymmetric reduction, oxazaborolidine, borane, ketone, imine.

1. INTRODUCTION

Chiral organoborane reagents, in particular 1,3,2- oxazaborolidines, have been extensively studied and applied as efficient Lewis acid catalysts to a wide range of asymmetric transformations [1,2]. B-H oxazaborolidines are commonly used as convenient catalyst for the enantioselective borane reduction of prochiral ketones, imines, and oximes [1a,c-f,3]. The most used method described in the literature for the preparation of B-H oxazaborolidines is by the *in situ* reaction of chiral aminoalcohols with an excess of borane without isolation and characterization of the catalyst [1-3]. We have reported from this laboratory that borane –THF prepared *in situ* using $NaBH_4$ and I_2 in THF is useful for several synthetic applications that require borane-THF (Table **1**). Unfortunately, the α,α-diphenylpyrrolidinemethanol and $NaBH_4/I_2$ combination gave poor results in the asymmetric reduction of acetophenone [4]. Herein we report that the $NaBH_4$, CH_2I_2 and 1,2-aminoalcohols combination is useful for the asymmetric reduction of ketones and imines to obtain the corresponding alcohols and amines with moderate to good enantiomeric excess.

2. RESULTS AND DISCUSSION

The $NaBH_4$ species has been reported to have good reactivity as a reducing agent [5]. This reagent has been used for the reduction of a wide large number of representative carbonyl functionalities. However, it has been widely employed in the reduction with $ZrCl_4$ [3C,6], Me_3SiCl [7, 8], $BF_3O.OEt_2$ [8], $ZnCl_2$ [9], I_2 [4,10,17], Lanthanoid [11], ($PhCO_2H$, H_3BO_3) [12], $SnCl_4$ [13a], $CoCl_3$ [13b], H_2SO_4 [14], etc, in THF solution instead of BH_3 reagents. Also chiral 1,2-aminoalcohol, such as valinol and leucinol [3c,6], 2-(α-hydroxybenzyl)benzimidazole [15], α,α-diphenylpyrroldinemethanol [4,7b], 12,sulfonamide [8], azacrownethers [16], ferrocenylaminoalcohol [17] has been used in the asymmetric reduction with $NaBH_4$.



Scheme 1. Mechanism of the catalyst formation.

It has been reported that $NaBH_4$ could not reduce diiodomethane to methyl iodide [18]. We have observed that the sodium borohydride ($NaBH_4$)/CH_2I_2 reagent system in the presence of 1,2- aminoalcohol affords a very easy and simple preparation of the oxazaborolidines catalyst (Fig. **1**, Scheme **1**), as well as the BH_3 species, which effectively reduces acetophenone within about 30 min at 25 °C and Phenyl(1-phenylethylidene)amine (**6**) within about 2 h at 25°C (Scheme **2**, Table **1**).

Initially, we examined the reduction of acetophenone (**5**) using the sodium borohydride ($NaBH_4$)/CH_2I_2 combination under the influence of (*R*)-leucinol (**1**) (10 mol%) in THF at 25 °C. In this case, the desired alcohol (**7**) was obtained in 84% yield and 72% ee. Stereoselectivities up to 87% ee in the presence of (*R*)-valinol (**2**) were reached with acetophenone (**5**). We observed that the $NaBH_4/CH_2I_2$ reagent system in the presence of catalyst (*R*)-prolinol (**4**) (10 mol%) yielded the desired alcohol **7** in 88% yield and 49% ee. The poor results were obtained with (*R*)-methioninol (**3**) (23%

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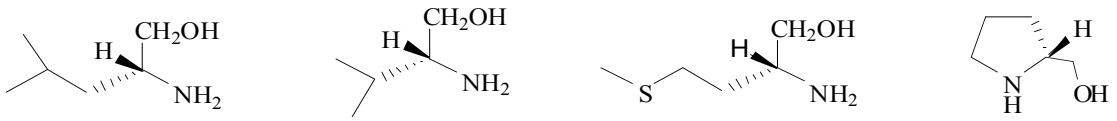
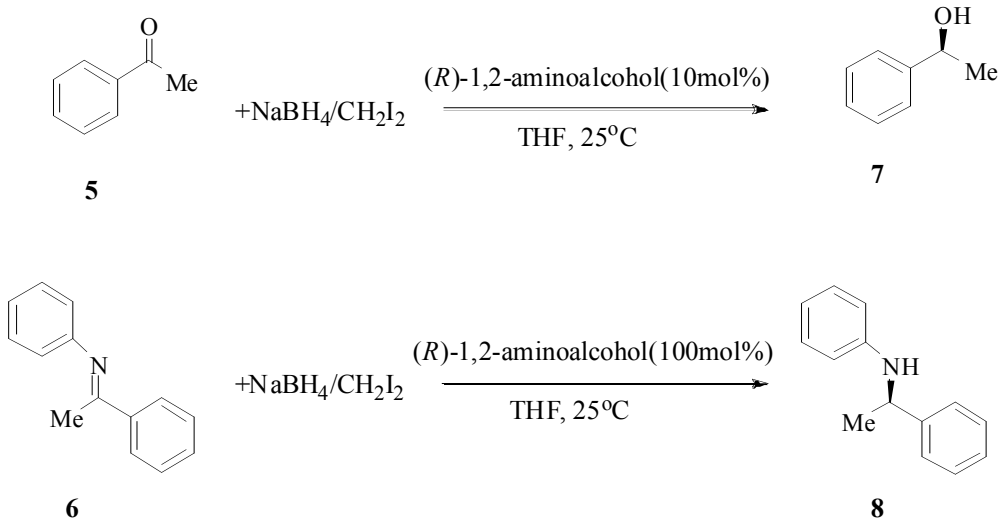


(*R*)-1 (*R*)-2 (*R*)-3 (*R*)-4

Fig. (1). Chiral aminoalcohols used to the preparation of chiral oxazaborolidine.



Scheme 2.

ee). In each case the (*S*)-enantiomer of the secondary alcohol (**7**) was formed preferentially.

The use of I_2 in place of CH_2I_2 led to a decreased ee and yield. In the absence of additive (CH_2I_2 and I_2), the acetophenone (**5**) and phenyl (1-phenylethylidene)amine (**6**) remained uninfected. Upon the addition of CH_2I_2, evolution of CH_4 was noticed, indicating that the formation of BH_3.THF *in situ* from sodium borohydride is essential for the reduction. Chiral aminoalcohol (*R*)-valinol (**3**) with 10 mol% or 100 mol% in THF gave maximum selectivity (Table **1**).

Table 1. Oxazaborolidine-Mediated Reduction of Acetophenone and Phenyl-(1-Phenylethylidene)Amine[a]

Substrat	Additive	Catalyst (mol %)	Yield (%)[b]	Configuaration[c]	ee (%)
Acetophenone	CH_2I_2	None	45	-	0[d]
	CH_2I_2	**1** (10)	84	*S*	72[d]
	I_2	**1**(10)	73	*S*	68[d]
	CH_2I_2	**2** (10)	94	*S*	87[d]
	I_2	**2** (10)	85	*S*	76[d]
	CH_2I_2	**3** (10)	51	*S*	23[d]
	CH_2I_2	**4** (10)	88	*S*	49[d]
Phenyl (1-phenylethylidene)amine	CH_2I_2	None	92	-	0[e]
	CH_2I_2	**1** (100)	65	*S*	70[e]
	I_2	**1**(100)	53	*S*	66[e]
	CH_2I_2	**2**(100)	72	*S*	74[e]
	I_2	**2** (100)	64	*S*	67[e]
	CH_2I_2	**3** (100)	49	*S*	32[e]
	CH_2I_2	**4** (100)	58	*S*	64[e]

[a]All reactions were carried out using 4 mmol of $NaBH_4$, 2 mmol of CH_2I_2, 5 mmol of ketone or imine in 25 mL of solvent at 25 °C.
[b]Isolated yields of the corresponding secondary alcohol and amine.
[c]Absolute configurations were assigned by comparison of the sign of the specific rotation with that of a literature value.
[d]Based on reported maximum [20] $[\alpha]^{20}_D$ = -45,2 (*c* 2, MeOH) for (*S*)-isomer.
[e]Based on reported maximum [21] $[\alpha]^{24}_D$ = +17 (*c* 1, MeOH) for (*S*)-isomer.

The reduction of Ketone (**5**) with $NaBH_4/CH_2I_2$ in the absence of oxazaborolidines catalysts was sluggish. In contrast the uncatalysed reduction of imine (**6**) with this reducing agent was essentially complete within10 min.

To verify the rationale, a coordination between a sulfur atom which is a softer Lewis base in the (*R*)- methioninol, and borane provides low selectivity and yield. The results support our rationale.

In the reduction of *N*-substituted imine (**6**) the best enantioselectivety with up to 74% ee was achieved when (*R*)-valinol (**2**) with 100 mol% was utilized as catalyst whereas, the (*R*)-prolinol (**4**) gave the amine (**8**) in 64% ee (58% yield) and with (*R*)-methioninol (**3)** in 32% ee (49% yield). We observed that the $NaBH_4/CH_2I_2$ reagent system in the presence of catalyst (*R*)-leucinol (**1**) (100 mol%) yielded the desired amine (**8**) in 70% ee and 65% yield, reduction of imine (**6**) with $NaBH_4/CH_2I_2$ and 1,2 amino alcohol did indeed give rise predominantly to the (*S*)-amine (**8**).

Based on the rationale, the limited success shown in the reduction of *N*-substituted imine (**6**) due to the low electrophilicity of the imine carbon and the rapid equilibration between the *E* an *Z* isomer [19].

3. MECHANISTIC CONSIDERATION

In 1987, Corey *et al.* [3b] Reported ^{1}H NMR, ^{11}BNMR and infrared spectroscopic evidence of the structure of valinol chiral **3**. The oxazaborolidine **3** is unable to reduce ketones and imines [1a,c-f,3]. The addition of second equivalent of borane at the opposite site of the *iso*-propyl group gives the effective chiral reducing agent **3'**. The complex is sterically unfavorable **3''**.

Our adaptation of the mechanism for the reduction of ketones and imines to alcohols and amines agrees with high enantioselectivity observed. The nitrogen or oxygen of the the anti-geometric isomer is complexed by the endocyclic borane allowing the chiral hydrogene transfer *via* a six-membered cyclic transition state **9**.

At this stage, the stereogenic centre is formed, benzylic amines or alcohols and (*R*)-Valinol are obtained after work-up. This hypothetical mechanism illustrates a general feature of the reaction.

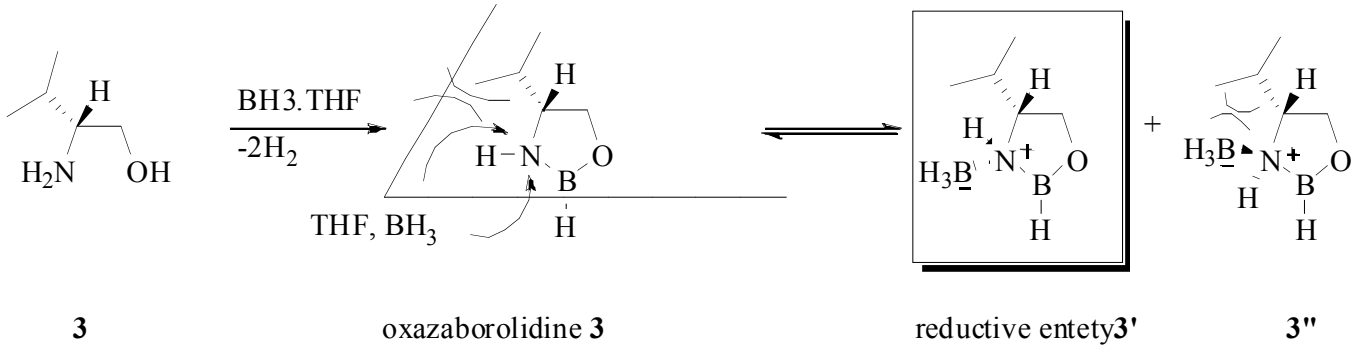
4. CONCLUSION

In conclusion, the asymmetric reduction of prochiral ketones and N-substituted imines using $NaBH_4/CH_2I_2$ reagent system gave the corresponding chiral secondary alcohol and amine in moderate to good selectivity. This method offers a relatively simple and inexpensive approach to this widely used transformation in syntheses.

5. EXPERIMENTAL

5.1. General

IR spectra were determined using a Shimadzu IR-435 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 100MHz using JNM-A400 spectrometer respectively. Mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer. Optical rotations were taken with a JASCO p-1010 polarimeter. Tetrahydrofurane (THF) was distilled from sodium benzophenone ketyl before use. TLC was carried out on Merck glass plates precoated with silica gel 60F-254 (0.25mm) and column chromatography was performed using Merck 23-400 mesh silica gel. All aminoal-



3 oxazaborolidine **3** reductive entety**3'** **3''**

9

X= N-Ph ou O

benzylic amines or alcohols (*R*)-valinol recycled

cohols and sodium borohydride were purchased from the Aldrich Chemical.

5.2. General Procedure for the Asymmetric Reduction of Acetophenone Utilizing the $NaBH_4/CH_2I_2$ Reagent System

Sodium borohydride (0.19 g, 4 mmol) and (*R*)-valinol (0.052 g, 0.5 mmol) in THF (12 mL) were taken in a two neck RB flask. The contents were stirred at 25 ^oC for 15 min under an argon atmosphere. Methylene iodide (0.54 g, 2 mmol) was added using a syringe and the reaction mixture was stirred for about 30 min. Acetophenone (**5**) (0.60 g, 5 mmol) in THF (12 mL) was added dropwise through a pressure equalizer for about 30 min under an argon atmosphere. The reaction mixture was stirred until the ketone had disappeared. The mixture was carefully quenched with 3 M HCl (10 mL). The organic layer was extracted with ether (3×30 mL). The combined organic extract was washed with brine (30 mL), dried over anhydrous Na_2SO_4, and the solvent was evaporated to give a yellow residue. The residue was purified on a silica gel column chromatography to obtain the (*S*)-1-phenylethanol (**7**) using hexane/ethyl acetate (973) as eluent, identified by comparison (GC, ^1H NMR) with an authentic sample. Conditions of GC analyses: β-DEX 120, 120column, 30m length, 0.25 mm internal diameter, isotherm temperature program, He as carier gas (2.4 mL/min). t_R *R* isomer 52.1min, t_R *S* isomer 55.7min.

5.3. General Procedure for the Asymmetric Reduction of Acetophenone Utilizing the $NaBH_4/I_2$ Reagent System

Sodium borohydride (0.19 g, 4 mmol) and (*R*)-leucinol (0.059 g, 0.5 mmol) in THF (12 mL) were taken in a two neck RB flask. The contents were stirred at 25 ^oC for 5 min under an argon atmosphere.I_2 (0.50 g, 2 mmol) dissolved in THF (12 mL) was added slowly for about 15-20 min through a pressure equalizer at 0 ^oC under an argon atmosphere and the reaction mixture was allowed to stir at 0 ^oC for about 30 min. The reaction mixture was then slowly brought to 25 ^oC and was stirred for about 10 min under an argon atmosphere. Acetophenone (**5**) (0.60 g, 5 mmol) in THF (15 mL) was added dropwise through a pressure equalizer for about 30 min. The reaction mixture was stirred until the ketone had disappeared. The mixture was carefully quenched with 3 M HCl (10 mL). The organic layer was extracted with ether (3×30 mL). The combined organic extract was washed with brine (30 mL), dried over anhydrous Na_2SO_4, and the solvent was evaporated to give a yellow residue. The residue was purified on a silica gel column chromatography to obtain the (*S*)-1-phenylethanol (**7**) using hexane/ethyl acetate (973) as eluent, identified by comparison (GC, ^1H NMR) with an authentic sample. Conditions of GC analyses: β-DEX 120, 120column, 30m length, 0.25 mm internal diameter, isotherm temperature program, He as carier gas (2.4 mL/min). t_R *R* isomer 52.1min, t_R *S* isomer 55.7min.

5.4. General Procedure for the Asymmetric Reduction of Phenyl-(1-Phenylethylidene)Amine Utilizing the $NaBH_4/CH_2I_2$ Reagent System

Sodium borohydride (0.19 g, 4mmol) and (*R*)-valinol (0.52 g, 5 mmol) in THF (12 mL) were taken in a two neck RB flask. The contents were stirred at 25 ^oC for 15 min under an argon atmosphere. Methylene iodide (0.54 g, 2 mmol) was added using a syringe and the reaction mixture was stirred for about 30 min. Phenyl-(1-phenylethylidene)amine (**6**) (0.98 g, 5 mmol) in THF (3 mL) was slowly added at 0 ^oC under an argon atmosphere. After 2 h, a 3 M sodium hydroxide (5 mL) was added dropwise, and stirring was continued for 1 h. layers were separated and the aqueous layer was extracted with diethyl ether (3×5 mL). The extracts were combined and dried with magnesium sulphate. Evaporation of the solvents and flash column chromatography on silica gel (petroleum ether / ethyl acetate, 8:2) afforded (*S*)-phenyl-(1-phenylethyl)amine (**8**), identified by comparison (GC, ^1H NMR) with an authentic sample. Elemental analysis, Calcd C, 85.24; H, 7.66; N, 7.10. Found: C, 85.39; H, 7.7; N, 7.15. for *S* isomer $[\alpha]^{24}_D = +17^o$ (*C* l,CH_3OH); lit. [21] $[\alpha]^{24}_{578} = +18.5^o$ (*C* 1, CH_3OH). for *R* isomer $[\alpha]^{24}_D = \sim -16^o$ (*C* 1, CH_3OH); lit. [21] $[\alpha]^{24}_{578} = -17.7^o$ (*C* 1, CH_3OH).

5.5. General Procedure for the Asymmetric Reduction of Phenyl-(1-Phenylethylidene)Amine Utilizing the $NaBH_4/I_2$ Reagent System

Sodium borohydride (0.19 g, 4 mmol) and (*R*)-leucinol (0.59 g, 5 mmol) in THF (12 mL) were taken in a two neck RB flask. The contents were stirred at 25 ^oC for 5 min under an argon atmosphere.I_2 (0.50 g, 2 mmol) dissolved in THF (12 mL) was added slowly for about 15-20 min through a pressure equalizer at 0 ^oC under an argon atmosphere and the reaction mixture was allowed to stir at 0 ^oC for about 30 min. The reaction mixture was then slowly brought to 25 ^oC and was stirred for about 10 min under an argon atmosphere, Phenyl-(1-phenylethylidene)amine (**6**) (0.98 g, 5 mmol) in THF (3 mL) was slowly added through a pressure equalizer for about 30 min at 0 ^oC under an argon atmosphere. After 2 h, a 3 M sodium hydroxide (5 mL) was added drop wise, and stirring was continued for 1 h. layers were separated and the aqueous layer was extracted with diethyl ether (3×5 mL). The extracts were combined and dried with magnesium sulphate. Evaporation of the solvents and flash column chromatography on silica gel (petroleum ether / ethyl acetate, 8:2) afforded (*S*)-phenyl-(1-phenylethyl)amine (**8**), identified by comparison (GC, ^1H NMR) with an authentic sample. Elemental analysis, Calcd C, 85.24; H, 7.66; N, 7.10. Found: C, 85.39; H, 7.7; N, 7.15. for *S* isomer $[\alpha]^{24}_D = +17^o$ (*C* l,CH_3OH); lit. [21] $[\alpha]^{24}_{578} = +18.5^o$ (*C* 1, CH_3OH). for *R* isomer $[\alpha]^{24}_D = \sim -16^o$ (*C* 1, CH_3OH); lit. [21] $[\alpha]^{24}_{578} = -17.7^o$ (*C* 1, CH_3OH).

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