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Highly catalytic enantioselective reduction of aromatic ketones using chiral polymer-supported Corey, Bakshi, and Shibata catalysts

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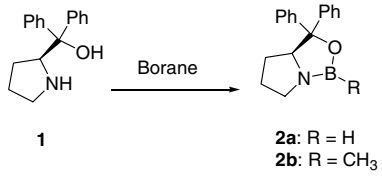
Abstract—A systematic study was conducted to formulate the optimal reaction parameters for polymer-supported (PS)-oxazaborolidine catalyzed enantioselective ketone reduction. The B-methylated chiral oxazaborolidine prepared in situ from the previously reported polymers by Degni et al. have been used in the enantioselective borane reduction of some substituted aromatic ketones to afford the corresponding optical active secondary alcohol products. While the linear-bound system shows low enantioselectivity, the cross-linked version affords enantioselectivities almost identical to those of the monomeric model (with up to 96% enantiomeric excesses).

1. Introduction

The enantioselective reduction of prochiral ketones leading to the corresponding optically active secondary alcohols is a topic of current interest.[1] One of the most successful methods has been based on the use of chiral 1,3,2-oxazaborolidines **2**, as catalysts (Scheme 1).[2,3]

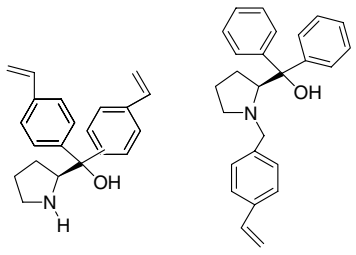
This method was developed by Itsuno and co-workers[2] and further improved by Corey et al.[3] (CBS reduction[3a]). Over the past decade, numerous examples describing the application of this method have been reported by several groups.[4] Some of these catalysts have been extensively studied with great success, however the development of cost-effective catalysts that exhibit high reactivity and enantioselectivity is still a challenging target in asymmetric synthesis. One approach to reduce the product-specific catalyst costs is to use the chiral catalyst repeatedly. In order to avoid lengthly recovery and purification, several polymer-bound heterogeneous catalysts have been prepared.[5]

In previous papers, Degni et al.[5e,6] described the facile anchoring of chiral L-prolinol derived amino alcohol ligands on mechanically 'stable' and chemically inert polyethylene (PE) fibers by electron beam (EB) preirradiation induced graft co-polymerization. Chiral styrenic ligand derivatives such as **3** and **4** (Fig. 1) were successfully immobilized on the fibrous support to generate the corresponding polymeric ligands **P1** and **P2** (Fig. 2) and were then employed in the reduction of prochiral ketones with borane from different sources.



1 **2a**: R = H **2b**: R = CH_3

Scheme 1. Some oxazaborolidine catalysts.



3 **4**

Figure 1. Chiral styrenic ligands **3** and **4**.

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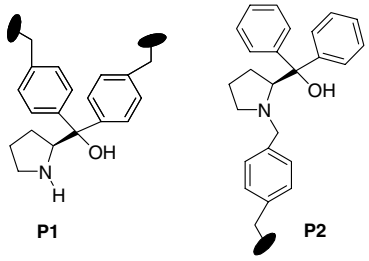
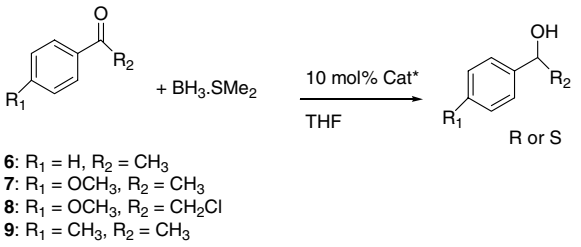


Figure 2. Previously described fibrous chiral polymer **P1** and **P2**.



6: $R_1 = H$, $R_2 = CH_3$
7: $R_1 = OCH_3$, $R_2 = CH_3$
8: $R_1 = OCH_3$, $R_2 = CH_2Cl$
9: $R_1 = CH_3$, $R_2 = CH_3$

Scheme 2. Me-CBS reduction of substituted aromatic ketones leading to the corresponding optically active secondary alcohols.

For example, the fibrous ligand **P1** gave 1-phenylethanol in 99% yield and 5–6% ee[5e] whereas, the monomer analogue **3** in the presence of $NaBH_4/Me_3SiCl$[5e] combination gave the secondary alcohol in 98% yield and 94% ee in the reduction of acetophenone.

It has been reported that diborane can be generated by treating $NaBH_4$ with Me_3SiCl[5e] or $BF_3{\cdot}OEt_2$.[7] Herein, to the best of our knowledge, we report the first asymmetric reduction of acetophenone by employing $NaBH_4/BF_3{\cdot}OEt_2$ as reducing agent, and chiral ligand **3** as the catalyst (Table 1, entry 8).

To take our investigation of this general approach a step further, we prepared, in situ, some polymer-supported oxazaborolidines, together with their nonpolymeric analogues using $BH_3{\cdot}SMe_2$ as the borane source. The various catalysts were used to catalyze the asymmetric reduction of substituted aromatic ketones (Scheme 2). The results of this study are presented herein.

The use of polymer-supported (PS) chiral catalysts to achieve asymmetric synthesis promises to become a major area of development, which is of particular interest to the pharmaceutical industry.[8] The interest can be expected to increase as the enantiomeric excesses (ees) achieved increase and the range of reactions, which afford high ees increases.

2. Results and discussion

The syntheses of all chiral monomeric ligands, together with chiral polymeric ligands **P1** and **P2** presented in this paper are described previously.[5e,6] We have now turned our attention to the preparation of their corresponding oxazaborolidine catalysts using $BH_3{\cdot}SMe_2$. A survey of the literature reveals that a variety of conditions have been recommended for the preparation of different oxazaborolidines, for example, with –BH substituent, by stirring the amino alcohol at 35 °C with 2 equiv of $BH_3{\cdot}THF$ followed by sublimation,[3a] refluxing the amino alcohol with 2 equiv of $BH_3{\cdot}THF$ under moderate pressure (1.7 bar),[9] and more recently, stirring a mixture of amino alcohol with excess of $BH_3{\cdot}SMe_2$ at room temperature for 10 h.[10] Clearly the last mentioned procedure could provide the most convenient route for laboratory as well as an industrial scale procedure. We thought that this procedure could work well for the preparation of simple oxazaborolidines, but could not

Table 1. Enantioselective reduction of substituted aromatic ketones at 45 °C (or otherwise mentioned)

Entry	Catalyst	Borane source 'BH_3'	Ketone	Yield (%)[a] of product	Ee %[c]
1	**2a**	$NaBH_4/Me_3SiCl$	**6**	Quant.[b]	96[5e]
2	**2a**	$NaBH_4/BF_3{\cdot}OEt_2$	**6**	98 (Reflux)	95.1[7]
3	**2b**	SMe_2	**6**	99	**98**
4	**2b**	SMe_2	**7**	90	**95**
5	**2b**	SMe_2	**8**	78	**98**
6	**2b**	SMe_2	**9**	80	**94**
7	**3a**	$NaBH_4/Me_3SiCl$	**6**	98	94[5e]
8	**3a**	$NaBH_4/BF_3{\cdot}OEt_2$	**6**	78	**70**
9	**4a**	$NaBH_4/Me_3SiCl$	**6**	>99 (Reflux)	**28**
10	**4b**	SMe_2	**6**	Quant.[b]	**17**
11	**5**	SMe_2	**6**	Quant.[b]	**95**
12	**P1a**	$NaBH_4/Me_3SiCl$	**6**	99 (rt)	6[5e]
13	**P1b**	SMe_2	**6**	90	**95.2**[d]
14	**P1b**[*]	SMe_2	**6**	90	**78**[d]
15	**P1b**	SMe_2	**8**	Quant.[b]	**88**
16	**P1b**[*]	SMe_2	**8**	Quant.[b]	**86**
17	**P1b**	SMe_2	**9**	57	**96**
18	**P2b**	SMe_2	**6**	99	**44**

[a] Isolated yield.
[b] No ketone was detected by GC or ^1H NMR.
[c] Enantiomeric excess (ee) was determined by HPLC.
[d] Enantiomeric excess (ee) was determined by CGC.
[*] Reuse.

be satisfactory on our L-prolinol-based fiber catalysts. We believe that the formation of **2**, which involves a strained [3.3.0] fused ring system, would be incomplete under the conditions described.[11]

The reaction of a homochiral 1,2-substituted amino alcohol in the presence of excess BH_3 is likely to proceed as described in Scheme 3. The excess borane renders the nitrogen atom acidic and cyclization takes place easily. Such a mode of cyclization explains why the intermediate 'ate'-complex obtained by using 1 equiv of borane requires prolonged heating at 100 °C to cyclize,[12] whereas the cyclization is facile in the presence of excess borane.[10]

At the outset, we decided to use a 2 M solution of $BH_3{\cdot}SMe_2$ in THF. The choice was based on the consideration that the fiber-supported ligand swelled well in THF. As we have mentioned earlier, the temperature at which the reduction should be conducted, remains controversial,[4c,13] although there has been a definitive study dealing with the preparation of –BMe and –BPh derivatives of oxazaborolidine.[14]

When we stirred the amino alcohol (L-prolinol derivatives) with an excess of $BH_3{\cdot}SMe_2$ at 45 °C for 16–22 h (monomers) and 24 h (polymers). The polymer catalyst **P1b** thus obtained, reduced acetophenone **6** providing the corresponding secondary alcohol in 90% yield and 95.2% ee and ketone **9** in 57% yield and 96% ee using 10 mol% of the supported-oxazaborolidine catalyst (Table 1, entries 13 and 17, respectively) compared to the soluble analogue **2b** (99% yield, 98% ee for ketone **6** and 80% yield, 94% ee for ketone **9** (Table 1, entries 3 and 6, respectively). Thus, the aforementioned chiral oxazaborolidines, easily prepared by the reaction of the corresponding amino alcohols with $BH_3{\cdot}SMe_2$ complex according to our optimized reaction conditions, reduced the substituted aromatic ketones **6**–**9** in high yields and high enantioselectivities.

Catalysts **2b** and **4b** (prepared, respectively, from **2** and **4** with $BH_3{\cdot}SMe_2$) were generated in situ and used as models in order to test the influence of substitution on the pyrrolidine ring nitrogen on the enantioselectivity of the reduction. As shown in Table 1 (entries 3 and 10), the enantioselectivity obtained with **2b** (98% ee) is far higher than that reached with **4b** (17% ee). Obviously the substitution on the nitrogen atom has created an unfavorable interaction in the case of ligand **4**.[4f] This would lead to a weaker coordination of borane (BH_3) to the nitrogen atom and hence slower catalysis. Quallich et al.[4f] have done a nice study dealing with the oxazaborolidine structure and enantioselectivity. Even though, the pyrrolidine moiety appears to be the ideal substitution for oxazaborolidine catalysts, the Quallich et al. investigation however fell short of describing 'the ideal' structure of an oxazaborolidine structure.

According to the literature and our results, the conclusion may be drawn that the enantioselectivity of oxazaborolidine-catalyzed borane reduction of ketones is dependent on both catalyst structure and the temperature of the reduction (Table 1, entries 12 and 13). It is difficult to provide a straightforward explanation in the case of **4b** and **P2b** (Table 1, entries 10 and 18, respectively), because in general, the enantioselectivity of this asymmetric reduction is likely to be a result of many complex factors.[15a]

Zhou et al.[15b] have prepared and used amino alcohols of squaric acid as examples of bifunctional chiral catalysts for the reduction of prochiral ketones to the corresponding optical active secondary alcohols. Those amino alcohols of squaric acid could be considered as another substituted pattern of **1** and **5** with the characteristics of having in the substituent groups, heteroatoms that could effectively coordinate with BH_3. We therefore believed that the second functional group (the ester group) in **5** (Fig. 3) could also preferentially coordinate with borane and lead to an intramolecular delivery of hydride to a carbonyl group in a selective manner.

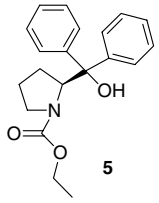
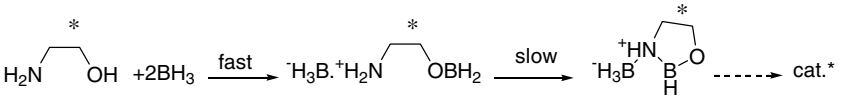


Figure 3. Chiral amino alcohol **5**.

Thus applying the same reaction conditions as mentioned above, 10 mol% of **5b** prepared using **5** in the presence of $BH_3{\cdot}SMe_2$, was found to reduce acetophenone, **6** to the corresponding secondary alcohol in quantitative yield and 95% ee. This result implies that the oxygen atoms in the N-substituent of **5** has effectively coordinated with BH_3 and has directed the hydride to approach selectively one of the prochiral faces of the carbonyl group in the substrate ketone.

We are not the first to work toward a polymer-bound oxazaborolidine catalysts. Itsuno et al. have published[5a,b] their preparation of several ligands covalently bonded to various polymer supports and subsequent generation of oxazaborolidine catalysts for the reduction of ketones, imines, and oximes. But as we mentioned earlier, here we describe the first attempt to develop such an optimal catalyst by preparing a polyethylene (PE)-bound oxazaborolidine.



Scheme 3. Mechanism of the catalyst formation.

Though the results obtained by Itsuno et al.[5a,b] and Caze et al.[5c] are comparable to ours, our approaches are not related, in terms of the support, polymer synthesis and polymer-bound oxazaborolidine catalyst preparation.

Our goal was to develop an environmental-friendly stable PE-ligand with potential for industrial use (scale-up application) as well as university laboratories applications (small scale) concerned with simplicity of recovery.

3. Conclusion

In conclusion, we have prepared and examined the performance of what we believe are the first two polyethylene-grafted CBS catalysts. The readily accessible crosslinked fibrous **P1** is clearly superior to the N-substituted pendant-linked **P2** ligand and comparable to the conventional solution-phase ligands **1**, **2**, and **5** in its ability to direct stereoselective ketone reduction. While several factors may contribute to these observed differences, the substitution on the nitrogen atom characteristic of **P2** relative to **P1** would create unfavorable interaction and lead to weaker coordination of borane ($-BH_3$) to the nitrogen atom and hence slower catalysis. Probably it is for this reason, the unsubstituted *N*-pyrrolidine moiety appears to be the ideal substitution for an oxazaborolidine catalyst. Also, catalyst structure as well as temperature effects are non-neglectable factors in the reduction systems. We were surprised with results obtained using the monomer chiral ligand **4** compared with its polymeric analogue **P2**. We hope that our ongoing work will allow us to explain these observations.

As we have already demonstrated in earlier work,[5e,6] the chiral ligands grafted on the polyethylene fiber **P1** and **P2** are recyclable and reusable without significant loss of activity and selectivity. As we aimed to improve the use of these catalysts for continuous asymmetric reactions, we once more demonstrated the reusability of, especially **P1** in repetitive enantioselective reduction of substituted aromatic ketones to synthetically very important chiral secondary alcohol intermediates.

4. Experimental

4.1. General

All reactions were carried out under argon atmosphere using flame-dried glasswares. Borane-dimethyl sulfide ($BH_3{\cdot}SMe_2$ a 2 M solution in THF) was purchased from Acros Organics, $NaBH_4$ powder 98% and $BF_3{\cdot}OEt_2$ (ca. 48% BF_3) were purchased from Acros Organics and used as received. Me_3ClSi, 99% was purchased from ABCR and used as received. The chiral reference amino alcohol **1** was purchased from Fluka. Synthesis of **3**, **5**, and **P1** have been described in our previous paper.[5e] The synthesis of ligands **4** and **P2** is reported in Ref. 6. Ketones **6** (99%), **7** (98%), **8** (96.5%) were purchased from Acros Organics and used as received. Ketone **9** (97%) was purchased from Riedel-de Häen and used as received. THF was freshly distilled over sodium benzophenone ketyl. All other commercially available chemicals and solvents used were of puriss p.a. quality, or purified and dried according to standard methods. TLC: precoated silica gel 60 F254 (Merck); visualization by irradiation with UV light. Flash chromatography (FC): silica gel 60 (0.04–0.063, Merck). ^1H NMR spectra were recorded on Bruker AC 250 MHz at rt with a broad band probe. Enantiomeric excesses (ees) were determined either by capillary gas chromatography (CGC) on an HP-5 GC (Crosslinked 5% PH ME siloxane, column: 15 m × 0.53 mm × 1.5 μm film β-cyclodextrin, 30 m × 0.25 mm × 1.5 μm film thickness) or by HPLC using an HP 1090 Liquid chromatograph system equipped with a Chiralcel OD column (Daicel Chemical Industries), 5% isopropanol in hexane mixture as mobile phase and detection by UV–vis detector at 254 nm. GC/MS analyzes were performed using an HP-5890 SERIES II Gas chromatograph equipped with a 5971 A mass selective detector (column: 30 m × 0.25 mm × 0.25 μm-HP-1MS).

4.2. General procedure for the soluble CBS–oxazaborolidine-catalyzed borane reduction of subsubstituted aromatic prochiral ketones

To a solution of the soluble ligand (10 mol%) in THF (10 mL) was added a solution of borane-dimethyl sulfide ($BH_3{\cdot}SMe_2$ 2 M in THF solution, 1.3 equiv) at rt. The solution was stirred at 45 °C for 16–18 h under argon atmosphere. To this mixture was added slowly a solution of the ketone (1 equiv in 5 mL of THF) at 45 °C for 3 h. After the addition, the reaction mixture was stirred for 50 min, then cooled to rt. The solution was then cautiously quenched at 0 °C with saturated ammonium chloride solution (15 mL) and extracted with diethyl ether (3 × 20 mL). The extracts were combined and washed with brine (2 × 10 mL). The solvent was evaporated under reduced pressure. All crude residues were further purified by flash column chromatography on 30 g of silica gel using diethyl ether–*n*-pentane (40:60) as eluent. All the secondary alcohols were obtained in relatively good yields (see Table 1). ^1H NMR data[16,17] matched with authentic samples. Enantiomeric excesses of all alcohols were determined by HPLC analysis using Chiralcel OD chiral column, isopropanol–*n*-hexane = 5:95; 0.5 mL/min, UV 254 nm.[17]

As a general rule,[18] the use of the (*R*)-enantiomer of the catalysts gives the (*S*)-configured alcohol and vice versa. According to published work,[4c,5f,19] (*R*)-configured alcohols are obtained for the reduction of ketones **6**, **7**, and **9**; subsequently, the (*S*)-configured alcohol is obtained for the reduction of 4-methoxy-α-chloroacetophenone[1,7,8,19,20] when using the (*S*)-enantiomer of the catalysts derived from (*S*)-prolinol.

4.3. General procedure for the PS CBS–oxazaborolidine-catalyzed borane reduction of subsubstituted aromatic prochiral ketones

To a solution of the PS ligand (10 mol%) in THF (15 mL) was added a solution of Borane-dimethyl sulfide

($BH_3{\cdot}SMe_2$ 2 M in THF solution, 1.3 equiv) at rt. The solution was stirred at 45 °C for 24 h under argon atmosphere. To this mixture was added slowly a solution of the ketone (1 equiv in 5 mL of THF) at 45 °C for 3 h. After the addition, the reaction mixture was stirred for 50 min, then cooled to rt. The solution was then cautiously quenched at 0 °C with methanol solution (15 mL) and filter (glass filter no 4). The fiber was washed with methanol (50 mL). The filtrate was evaporated and the residue was dissolved in diethyl ether (20 mL). The ether phase was washed saturated ammonium chloride and extracted with diethyl ether (3×20 mL). The extracts were combined and washed with brine (2×10 mL) then dried over anhydrous $MgSO_4$ The solvent was evaporated under reduced pressure. The alcohols were purified and identified as above mentioned.

The fiber ligands were successively washed with THF (100 mL), methanol (100 mL) and dried under high vacuum at rt for several hours, then reused in repetitive runs.

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