Effect of the Secondary Reduction on the Enantioselectivity and Function of Additives in the Chiral Oxazaborolidine-Catalyzed Asymmetric Borane Reduction of Ketones

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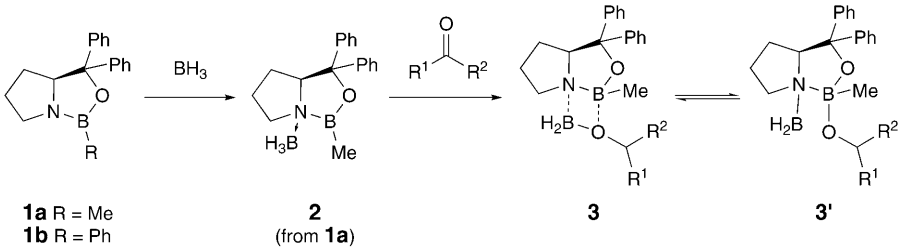
The secondary reduction in the direct and oxazaborolidine-catalyzed asymmetric borane reduction of ketones was investigated by the use of GC/MS tracing titration and control experiments. The results indicate that the secondary reduction affects the enantioselectivity only in noncoordinated solvents at low temperature and not under the usual catalytic reduction conditions because the intermediate alkoxyborane is unstable and quickly converts to borane and dialkoxyborane. The function of an alcohol additive in the asymmetric borane reduction of ketones is to consume excess borane in the reduction system thus inhibiting noncatalytic reduction, which leads to increased enantioselectivity in the catalytic reduction.

1. Introduction. – Chiral oxazaborolidine (OAB)-catalyzed borane reduction of prochiral ketones to chiral secondary alcohols is considered to be one of the most important reactions in asymmetric syntheses (for recent reviews, see [1]). Numerous new efficient oxazaborolidine catalysts have been reported, and a lot of applications have appeared until now [1]. In comparison with the numerous attempts to search for new catalysts to improve the enantioselectivity and to carry out the mechanistic investigation of the catalytic asymmetric reduction [2][3], some investigators have studied the factors which affect the enantioselectivity in the asymmetric reduction, such as the structure [1][2][4], the stability [2a][5] (including dimerization), and the loading amount [2a][5a][6] of the catalyst, the borane source [7] and amount [2a][6c], the order and rate of the addition of a ketone or borane into a reductive system [1d][6c], the reduction temperature [5d][6c][8], the solvent [5a][6c][7c], the additive [8g][9][10], the secondary reduction [9a][11], the stabilizer in borane [12], the electronic effects of both ketones [4a][5a][10][13] and catalysts [10][14], *etc*. Although a few studies have dealt with the effects of the secondary reduction [9a][11] and the additives [8g][9][10] on the enantioselectivity of the asymmetric reduction, these effects are still unclear. However, it is highly desirable to understand all factors which affect the enantioselectivity in order to apply the asymmetric reaction effectively. Herein, we wish to present our investigation about the effect of the secondary reduction on the enantioselectivity and about the function of additives in the asymmetric borane reduction of ketones.

2. Results and Discussion. – *Effect of the Secondary Reduction on the Enantioselectivity.* After our investigations on the effects of the temperature [5d][6c], of the electronic nature of the substrate ketones [10] and catalysts [14], and of anions [10] on the enantioselectivity, we now studied the effect of the secondary reduction on the enantioselectivity of the asymmetric reduction. In 1993, *Cai et al.* first established the concept of the secondary reduction [9a]. These authors investigated the stoichiometric asymmetric reduction of an N-containing ketone, a key intermediate in the synthesis of the drug candidate MK-0499, with the OAB·BH_3 complex **2** as a chiral reductant in the noncoordinated solvent CH_2Cl_2 (*Scheme 1*). The chiral reductant **2** was prepared from (5*S*)-2-methyl-4,4-triphenyl-3,1,2-oxazaborabicyclo[3.3.0]octane (*B*-Me catalyst; **1a**) and borane. Moreover, Et_3N was used as an additive which improved the enantioselectivity of the reduction. To interpret the phenomenon, a monoalkoxyborane·OAB complex **3** or **3′** was postulated as intermediate which can also reduce a ketone to an alcohol by a second H-transfer occuring, however, with lower enantioselectivity. The role of the added Et_3N would be the destruction of complex **3** by coordination with this monoalkoxyborane. In 1994, *Shi*, *Cai et al.* discovered that ^{i}PrOH and other alcohols could also improve the enantioselectivity in both the stoichiometric and catalytic asymmetric reduction processes [9b]. They considered that ^{i}PrOH could react with the monoalkoxyborane·OAB complex **3** and inhibit the secondary reduction. In 1996, the same group established by ^{1}H-, ^{13}C-, and ^{11}B-NMR studies that the monoalkoxyborane·OAB complex **3** was indeed generated on mixing OAB·BH_3 and *p*-methoxyacetophenone at $-100°$, was still observed at $-75°$, but vanished when the temperature was raised to $-50°$ [11]. The resulting alcohol was formed with 98% ee. Moreover, complex **3** reacted with another subsequently added molecule of *p*-methoxyacetophenone, resulting in only 85% ee for this secondary reduction. It was postulated that addition of ^{i}PrOH destroyed complex **3** on forming an inactive dialkoxyborane.

Scheme 1. *Formation of the Monoalkoxyborane·OAB Complex*

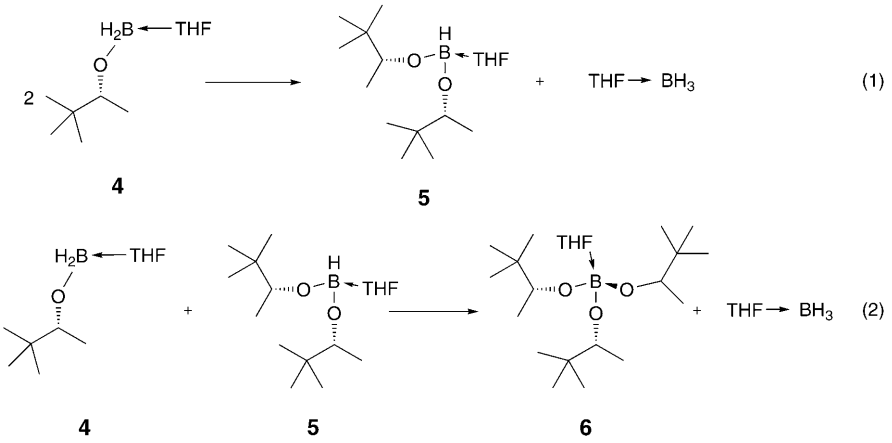


Corey et al. reported that 0.6 equiv. of borane is enough to reduce 1 equiv. of a ketone [2b], indicating that two H-atoms of borane can be transferred to the ketone. Thus, an alkoxyborane seemed to be able to reduce the ketone, and in [9a,b][11] it was assumed that the reduction of a ketone with monoalkoxyborane occurs with a relatively lower enantioselectivity than with borane in the presence of a catalyst under the same conditions. However, in our and others' previous works [1][2][6b,c,d][10], a lot of prochiral ketones were reduced catalytically with excellent enantioselectivities, and no obvious influence of the secondary reduction on the enantioselectivity was observed.

To better understand and evaluate the effect of the secondary reduction on the enantioselectivity, we first collected and analyzed published kinetics data [15].

Schmidt and co-workers have investigated the kinetics of both direct and catalytic borane reduction of ketones in solution [15]; in all these studies, monoalkoxyborane was not observed. Only *Fehlner* observed it in a gas-phase reaction by mass spectrometry [16]. In 1968, *Pasto et al.* reported results on the disproportionation of alkyl-, alkoxy-, and haloboranes and found that monoalkoxyborane **4** could disproportionate into dialkoxyborane **5** and borane (*Scheme 2*, *Eqn. 1*), and dialkoxyborane **5** could react with monoalkoxyborane **4** to yield trialkyl borate·THF complex **6** and borane·THF complex (*Eqn. 2*) [17]. Because no monoalkoxyborane **4** was detected, they only determined the equilibrium constant of *Eqn. 2* and postulated that the equilibrium constant of *Eqn. 1* is much larger, and both equilibriums could be achieved rapidly. In 1997, *Schmidt et al.* reported the rate constant of *Eqn. 1* in the solvent THF, with pinacolone (=3,3-dimethylbutan-2-one) as substrate [15b]. They determined the constant indirectly by numerical integration. According to their results, the disproportionation of monoalkoxyborane was nearly 100 times faster than the reactions between the borane·THF complex or the monoalkoxyborane·THF complex and pinacolone ($k=0.0037\pm0.0006$ and 0.003 ± 0.001 mol^{-1} l s^{-1}, resp.). The rate constant of *Eqn. 1* ($k=0.2\pm0.1$ mol^{-1} l s^{-1}) was similar to that in the catalyzed reduction with *B*-Ph oxazaborolidine **1b** as a catalyst ($k=0.23\pm0.02$ mol^{-1} l s^{-1}).

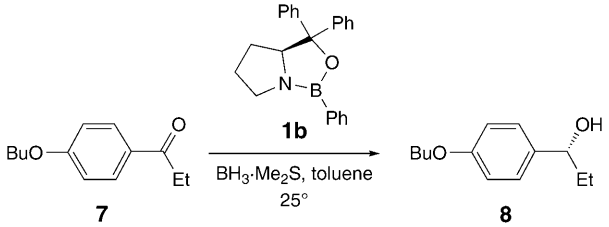
Scheme 2. *Reaction of Monoalkoxyborane and Dialkoxyborane*



On the basis of the above information, we are inclined to consider that the secondary reduction is not an important factor in the catalytic asymmetric reduction of ketones. It might exist only in the stoichiometric process at lower temperature when complex **2** is used as a stoichiometric reductant in noncoordinated CH_2Cl_2 as solvent. Since in this case, there are no THF or other molecules present (such as an amine or dimethyl sulfide) that are able to coordinate with the electron-deficient B-atom, the formed complex **3** is relatively stable and can react with another molecule of a ketone. However, in the presence of THF, complex **3** could be rapidly transformed into oxazaborolidine **1** and complex **4**. Two molecules of complex **4** react then with each other to

form the borane·THF and the dialkoxyborane·THF complex **5** as shown in *Eqn. 1*. Complex **5** could react with complex **4** to form the borane·THF complex and trialkyl borate·THF complex **6** as shown in *Eqn. 2*. The rate of the latter reaction is much slower, and equilibrium can not be achieved during the time scale of the reduction. Nearly all molecules of the ketone are reduced to the corresponding alcohol through the catalytic process with borane as a reductant, and not with monoalkoxyborane or dialkoxyborane. To support this viewpoint, we reduced 4-butoxypropiophenone (**7**) to **8** with 0.5 and 1.0 equiv. of borane in toluene at 25° in the presence of *B*-Ph catalyst **1b**. The enantioselectivities were 91.5 and 93.7%, respectively, *i.e.*, they were nearly equal (*Table 1*, *Entries 1* and *2*). If the secondary reduction was an important factor in our system, the enantioselectivity in the reduction with 0.5 equiv. of borane should be substantially lower than in the reduction with 1.0 equiv. of borane. This is not verified by the experimental results.

Table 1. *Catalytic Asymmetric Borane Reduction of a Ketone under Different Conditions*



7 **8**

Entry	Borane [equiv.]	Additive ^{i}PrOH [equiv.]	Addition time [h]	Yield [%][a])	e.e. [%][b])
1	0.5	0	1	86.5	91.5
2	1.0	0	1	93.4	93.7
3	0.5	1.0	0	87.4	85.6
4	1.0	1.0	0	92.5	79.6
5	1.5	1.0	0	85.3	80.4

[a]) Isolated yield after column chromatography. [b]) The ee values were determined by HPLC analysis (*OD* chiral column (4.6×250 mm, *Chiralcel*), hexane/^{i}PrOH 98.5:1.5, flow 0.8 ml/min, detection at 220 nm). The configuration of the product was assigned according to its optical rotation value. In each case, a positive optical rotation was obtained, indicating that the selectivity was in favor of the (*R*)-enantiomer, in agreement with reported work [6c].

Function of Additives in the Catalytic Process. In the study reported in [9b], ^{i}PrOH and other alcohols were used in both catalytic and stoichiometric asymmetric reductions of ketones to improve the enantioselectivity, and their function was assumed to inhibit the secondary reduction (see above). As aforementioned, we conclude that the secondary reduction does not play an important role in the catalytic process. Therefore, the effect caused by addition of ^{i}PrOH should be reinvestigated. We now elucidated its effect by GC/MS tracing experiments and control experiments.

To understand the function of ^{i}PrOH, we must know its initial form in the reduction medium. To the best of our knowledge, ^{i}PrOH is active enough to react with borane rapidly, *i.e.*, added to borane, it cannot survive in the reaction mixture. Thus, borane will react with ^{i}PrOH faster than with a ketone. There will be no ^{i}PrOH left when com-

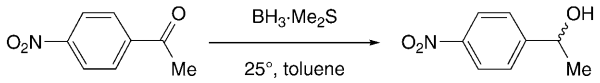
plex **3** has been generated. To ascertain the product of the reaction between borane and ^{i}PrOH, we titrated the borane·dimethyl sulfide complex in toluene with ^{i}PrOH at room temperature, the temperature generally used for the catalytic asymmetric reduction of ketones, and analyzed the reaction mixture by GC/MS. Thus, to 1 mmol of borane·dimethyl sulfide complex in 5 ml of anhydrous toluene under N_2 was added sequentially 0.1 equiv., 0.1 equiv., 0.2 equiv., 0.4 equiv., 0.2 equiv., 0.5 equiv., 0.5 equiv., and 1.0 equiv. of ^{i}PrOH. The resulting soln. was stirred for 10 min after each addition and analyzed by GC/MS. No MS signal of monoalkoxyborane was found even when only 0.1 equiv. of ^{i}PrOH had been added, but the signal of dialkoxyborane was present. After a total addition of 0.8 equiv. of ^{i}PrOH, both dialkoxyborane and triisopropyl borate were detected. These results are in good accordance with previous reports [18].

The formation of isopropoxyborane in the reduction solution can also be excluded in another way. *Shi*, *Cai*, *et al.* reported in [9b] that reduction of a ketone by the complex of monoalkoxyborane and oxazaborolidine, prepared at low temperature as a stoichiometric chiral reductant, occurred with lower enantioselectivity than the catalytic borane reduction. If isopropoxyborane was generated when ^{i}PrOH is added, the reductants would be a mixture of isopropoxyborane and borane, and the enantioselectivity would decrease. This is not verified by the experimental results and indicates that the formed alkoxyborane in the first reduction is converted into dialkoxyborane and borane immediately after it is formed. And then borane serves as a reducing reagent in the further reduction, and not alkoxyborane.

Having established the generation of dialkoxyborane when ^{i}PrOH is added, we can conclude that the real reductant in the borane reductive system is borane and not a mixture of borane and alkoxyborane. In the reduction system described in [9b], 1 equiv. of an N-containing ketone was reduced with 2.5 equiv. of borane and 1 equiv. of ^{i}PrOH, as an additive to the key intermediate of the drug candidate MK-0499. Considering that 1 equiv. of borane would coordinate tightly with the N-atom in the ketone, and 1 equiv. of ^{i}PrOH would consume 0.5 equiv. of borane to form 0.5 equiv. of dialkoxyborane, there would be 1 equiv. of free borane left, which is the generally used amount of borane under the catalytic asymmetric reduction conditions. Both the free borane and the dialkoxyborane can reduce the ketone. In order to know which reductant reacts preferentially, we directly (without catalyst) reduced *p*-nitroacetophenone (**9**) in toluene at 25° for 5 h with 1 equiv. of borane, 0.5 equiv. of borane/0.5 equiv. of diisopropoxyborane (generated *in situ* by adding 1 equiv. of ^{i}PrOH to 1 equiv. of borane), 1.0 equiv. of dialkoxyborane, and 0.5 equiv. of borane to afford the corresponding alcohol **10** in 84, 62, 25, and 79% yield, respectively (*Table 2*). The results indicate that the dialkoxyborane can reduce a ketone, but the reaction is much slower than that with borane, *i.e.*, when a similar amount of borane and diisopropoxyborane is present, the reduction caused by diisopropoxyborane can be neglected. Addition of ^{i}PrOH leads only to the decrease of the amount of borane. In our previous study [6c], we observed that increasing the amount of borane could lower the enantioselectivity due to the competition of noncatalyzed reduction and catalytic reduction. So, we conclude that the addition of ^{i}PrOH or other alcohols enhances the enantioselectivity by decreasing the amount of borane.

To confirm the conclusion, we also conducted the catalytic asymmetric reduction of 4-butoxypropiophenone (**7**) in toluene at 25° in the presence of *B*-Ph catalyst **1b** with 0.5 equiv., 1 equiv., and 1.5 equiv. of borane, in the presence of 1 equiv. of ^{i}PrOH

Table 2. *Direct Borane Reduction of a Ketone under Different Conditions*



9 **10**

Entry	Borane [equiv.]	Additive ^{i}PrOH [equiv.]	Addition time [h]	Yield [%][a])
1	1.0	0	5	84
2	1.0	1.0	5	62
3	1.0	2.0	5	25
4	0.5	0	5	79

[a]) Isolated yields after the column chromatography.

(equal to the mixture of 1 equiv. of borane and 0.5 equiv. of diisopropoxyborane) (*Table 1*, *Entries 3–5*). In our asymmetric reduction, the *B*-Ph catalyst **1b** was prepared from phenylboronic acid and (2*S*)-α,α-diphenylpyrrolidine-2-methanol as described in [15b]. After the addition of borane or a mixture of borane and diisopropoxyborane (generated in another flask under N_2), ketone **7** dissolved in toluene was added all at once at 25°. Indeed, an enhanced addition rate makes the effect of noncatalyzed reduction more obvious. These conditions are similar to those used by *Shi*, *Cai*, *et al.* [9b]. Our results indicate that the enantioselectivities are similar with 1.0 and 1.5 equiv. of borane and 1 equiv. of ^{i}PrOH (*Table 1*, *Entries 4* and *5*) and lower than with 0.5 equiv. of borane and 1 equiv. of ^{i}PrOH (*Table 1*, *Entry 3*). These results are also in accordance with our conclusion.

3. Conclusions. – In summary, we investigated the effect of the secondary reduction on the enantioselectivity in the catalytic asymmetric borane reduction of ketones and the function of the ^{i}PrOH additive by means of GC/MS tracing and control experiments. The secondary reduction may play an important role in the stoichiometric asymmetric reduction at low temperature in noncoordinated solvent, but it is not an important factor in the catalytic asymmetric process. The addition of an alcohol can generate dialkoxyborane and concomitantly decrease the amount of borane in the reduction system, thus improving the enantioselectivity due to a decrease of the competition of the noncatalyzed reduction. We hope the current results can be beneficial to both laboratory and industry since decreasing the amount of borane is more cost-efficient than using additives.

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Experimental Part

1. *General.* Borane·dimethyl sulfide complex and phenylboronic acid were purchased from *Acros Chemicals Co*. Toluene was heated under reflux over Na and distilled prior to use. HPLC: *Hewlett-Packard 1100* HPLC equipment; *Chiralcel-OD* column (4.6×250 mm). ^{1}H- and ^{13}C-NMR spectra: *Varian Mercury Plus 300* (300 and 75 MHz, resp.) spectrometer: $CDCl_3$ soln. with $SiMe_4$ as an internal standard; chemical shifts δ in ppm. GC/MS: *HP-5971* GC/MS.

2. *Determination of the Reaction Mixture of Borane and* ^{i}*PrOH*. To borane · dimethyl sulfide complex (1 mmol) in anh. toluene (5 ml) under N_2 was added sequentially 0.1 equiv., 0.1 equiv., 0.2 equiv., 0.4 equiv., 0.2 equiv., 0.5 equiv., 0.5 equiv., and 1.0 equiv. of ^{i}PrOH in this order. The resulting soln. was stirred for 10 min after each addition and analyzed by GC/MS.

3. *(5*S*)-2,4,4-Triphenyl-3,1,2-oxazaborabicyclo[3.3.0]octane* (= *(3a*S*)-Tetrahydro-1,3,3-triphenyl-1*H*, 3*H*-pyrrolo[1,2-*c*][1,3,2]oxazaborole* = B-*Ph Catalyst*; **1b**). In a round-bottomed flask equipped with a 10-ml pressure-equalizing addition funnel (containing a cotton plug and *ca.* 10 g of 5-Å molecular sieves, and functioning as a *Soxhlet* extractor), a mixture of (*S*)-diphenylprolinol (0.05 mmol, 12.7 mg) and phenylboronic acid (0.05 mmol, 6.1 mg) was dissolved under stirring in dry toluene (15 ml). The resulting soln. was heated to reflux for 12 h. Then, most of the solvent was distilled and the residue (*ca.* 3 ml) was cooled to r.t. The addition funnel was removed, and the flask was airproofed quickly to avoid moisture.

4. *General Procedure for the Asymmetric Reduction of Ketones*. To a soln. of catalyst **1b** (17 mg, 0.05 mmol, 10 mol-%), freshly prepared in dry toluene, 2M borane · dimethyl sulfide complex in THF (0.25 ml, 0.5 mmol; or the amount given in *Table 1*) was added under N_2 at r.t. A soln. of 4-butoxypropiophenone (=1-(4-butoxyphenyl)propan-1-one; **7**, 103 mg, 0.5 mmol) in toluene (4 ml) was added dropwise over 1 h or all at once. After the addition, the mixture was stirred for 4 h and then quenched with MeOH (0.5 ml) in an ice-water bath. After evaporation, the residue was purified by column chromatography (silica gel, petroleum ether (60–90°)/AcOEt 5 : 1): chiral secondary alcohol as colorless oil. The spectral and anal. data of all obtained alcohols were in agreement with those reported in [6c]. The ee value was determined by chiral HPLC analysis.

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