Practical and Efficient Procedure for the *In Situ* Preparation of *B*-Alkoxyoxazaborolidines. Enantioselective Reduction of Prochiral Ketones

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Abstract: A new method for the in situ elaboration of B-alkoxyoxazaborolidines is presented. Their use in the enantioselective reduction of prochiral aromatic ketones provides excellent chemical and optical yields of chiral alcohols.

Since the development of Corey [1], the *B*-alkyloxazaborolidines (**OAB**) have gained reputation as efficient catalysts in the enantioselective reduction of prochiral ketones. In addition to provide alcohols in high optical purity [2], they can be employed in small quantities and their reaction mechanism allows the prediction of the stereochemistry of the newly generated chiral center.

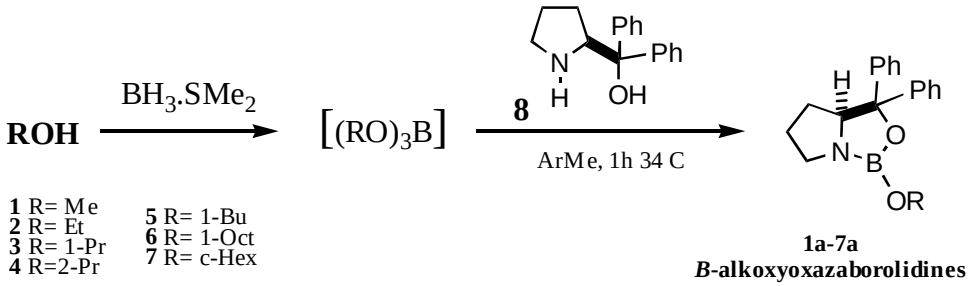
Numerous **OAB** synthesized from different aminoalcohols have been reported [3], however the most used **OAB** is that derived from α,α-diphenylpyrrolidinemethanol (**8**) developed by Corey.

In spite of the advantages of this new type of catalysts, the various methods described for their obtention, many times discourage their use, being time consuming [4] or requiring extensive separation steps prior to their use [5].

In order to avoid these inconvenients, we decided to study the synthesis of *B*-alkoxyoxazaborolidines, reacting alkyl borates with **8** by analogy with the strategies reported for the elaboration of alkyl-**OAB**, and then to evaluate the ability of the product to enantioselectively reduce prochiral aromatic ketones.

In this communication we introduce a new, practical and efficient method for the *in situ* elaboration of *B*-alkoxyoxazaborolidines employing inexpensive reagents and avoiding separation steps which could alter the optical quality of the reduction.

We also demonstrate the efficiency and capability of the *B*-alkoxyoxazaborolidines as catalysts through the reduction of several substituted acetophenones. The enantioselectivity obtained is generally comparable to that observed with the *B*-methyloxazaborolidine developed by Corey.



Product	*B*-alkoxy-**OAB**	ee(%)	Yield (%)
R-1-(3,4-dimethoxyphenyl)ethanol	**1a-7a**	>95	>93
R-1-(4-acetoxy-3-methoxyphenyl)ethanol	**5a**	97	≈100
R-1-(4-hydroxy-3-methoxyphenyl)ethanol	**6a**	>98	98
R-1-(2,4-dimethoxyphenyl)ethanol	**6a**	90	≈100
R-1(4-nitrophenyl)ethanol	**6a**	>95	≈100
R-1(4-aminophenyl)ethanol	**6a**	95	≈100
R-1(4-bromophenyl)ethanol	**6a**	97	98

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References and Notes

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