

New Chiral Ligand Derived from (+)- α -Pinene Used in the Enantioselective Addition of Diethylzinc to Aldehydes

Gustavo Frensch¹, Francisco A. Marques^{1*}, Celso L. Wosch¹, Ricardo Labes¹, Beatriz Helena L. N. Sales Maia¹, Palimecio G. Guerrero Jr.², Cesar A. Lenz³

¹Departamento de Química, Universidade Federal do Paraná, Centro Politécnico, Jardim das Américas, 81531-990 – Curitiba, PR, Brazil. ²Departamento de Química e Biologia, Universidade Tecnológica Federal do Paraná, Centro, 80230-901 – Curitiba, PR, Brazil. ³Instituto de Tecnologia do Paraná, Cidade Industrial, 81350-010 – Curitiba, PR, Brazil

*Corresponding author. Tel.: 00 55 41 3361-3177 Fax: 00 55 41 3361-3186 e-mail: tic@ufpr.br

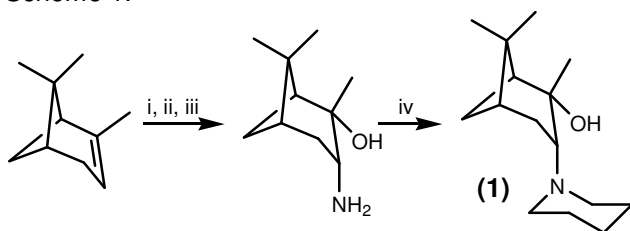
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INTRODUCTION

Several examples have been reported for highly enantioselective alkylation of aldehydes by organometallic compounds combined with chiral modifiers. In general, dialkylzincs present low reactivity towards carbonyl compounds, but their reactivity can be enhanced by the structural modification by appropriate ligands or auxiliaries. Replacement of one alkyl group by an electronegative substituent increases the acceptor character of the zinc atom and the donor property of the remaining alkyl group, thereby accelerating the reaction with carbonyl substrates¹. Here we report our results involving the addition of diethylzinc to some aromatic aldehydes using a compound derived from α -pinene (**1**) as chiral auxiliary.

RESULTS AND DISCUSSION

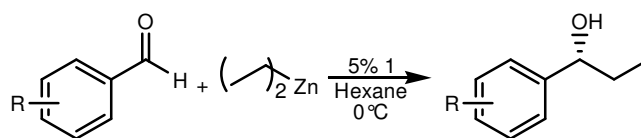
The first stage of the work involved the synthesis of chiral auxiliary through the reactions described in Scheme 1.



i: KMnO_4 , $\text{H}_2\text{O}/\text{Acetone}$, 0°C ; ii: $\text{NH}_2\text{OH}\cdot\text{HCl}$, AcONa , $\text{H}_2\text{O}/\text{Ethanol}$; iii: LAH, THF, reflux; iv: $\text{Br}(\text{CH}_2)_5\text{Br}$, K_2CO_3 , Ethanol

Scheme 1. Synthesis of the chiral auxiliary

Then, diethylzinc was added to several aromatic aldehydes, using compound (**1**) as chiral auxiliary, as show in Scheme 2. The best enantiomeric excess was achieved in the addition of diethylzinc to *p*-anisaldehyde and in all cases the *R*-enantiomer was the major one.



Scheme 2. Addition of Et_2Zn to aldehydes.

Table 1. Yields and e.e. of addition of Et_2Zn to aldehydes

Aldehyde	Alcohol	
	Yield (%)	e.e. (%)
Benzaldehyde	91	75,4
<i>p</i> -chlorobenzaldehyde	98	85,2
<i>o</i> -anisaldehyde	93	68,8
<i>m</i> -anisaldehyde	73	84,2
<i>p</i> -anisaldehyde	75	85,2

CONCLUSION

The new chiral ligand **1** presented good properties as chiral auxiliary in addition of diethylzinc to aldehydes, leading to the corresponding alcohols with moderate to good enantiomeric excesses.

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