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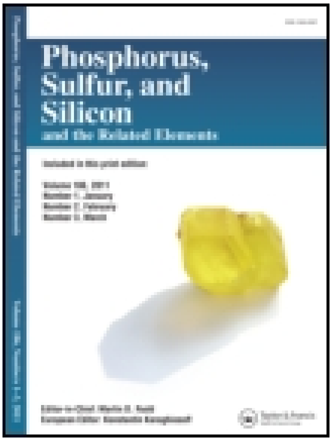

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Asymmetric Desymmetrization of σ-Symmetrical Diols Using Diastereoselective Acetal Cleavage of α-Sulfinyl Acetals

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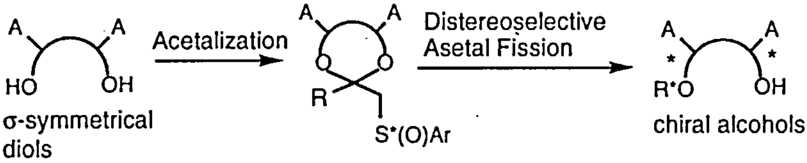
Asymmetric desymmetrization of σ-symmetrical diols was accomplished *via* diastereoselective C—O bond fission of α-sulfinyl acetals.

KEY WORDS asymmetrization σ-symmetrical diol chiral sulfoxide

INTRODUCTION

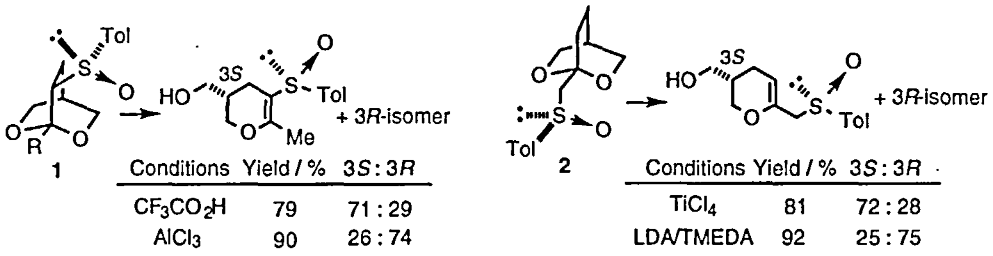
Asymmetric desymmetrization of σ-symmetrical diols has been widely used to prepare useful chiral building blocks for various natural products. To develop a novel asymmetric desymmetrization of σ-symmetrical diols, we planned an approach based on diastereoselective acetal cleavage of α-sulfinyl acetals (SCHEME 1). In this paper, we report the results of diastereoselective acetal cleavage reaction of various α-sulfinyl acetals.[1-4]



SCHEME 1

Asymmetric Desymmetrization of Prochiral 1,3-Diols.

On treatment with trifluoroacetic acid, the bicyclic acetal **1** was diastereoselectively cleaved to give mainly the alcohol with *S*-configuration. The selectivity was reversed on treatment with $AlCl_3$. Bicyclic acetal **2** with only one chirality also selectively gave the alcohol with *S*-configuration on treatment with $TiCl_4$. Opposite selectivity was observed when **2** was cleaved with bases *via* diastereoselective β-elimination followed by isomerization to the β,γ-unsaturated sulfoxides.



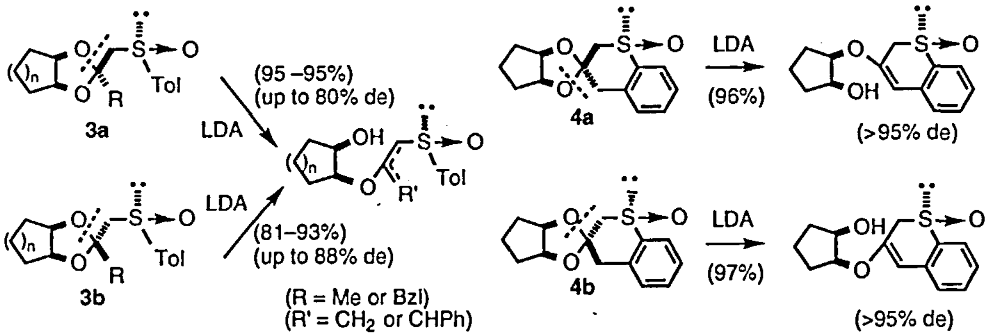
Conditions	Yield / %	3S : 3R
CF_3CO_2H	79	71 : 29
$AlCl_3$	90	26 : 74

Conditions	Yield / %	3S : 3R
$TiCl_4$	81	72 : 28
LDA/TMEDA	92	25 : 75

SCHEME 2

Asymmetric Desymmetrization of *meso*-1,2-Diols

Base promoted β-elimination proceeded diastereoselectively with both diastereomeric acetals **3a** and **3b** to afford the common product preferentially. The diastereomeric isomer with *endo*-methyl group showed better selectivity than the *exo*-one. In contrast to **3a** and **3b**, the acetals **4a** and **4b**, in which the sulfinylmethyl group was fixed in a ring, gave different alcohols exclusively. In this reaction, the C—O bond *syn* to the sulfinyl oxygen was selectively cleaved.



SCHEME 3

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