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## Phosphorus, Sulfur, and Silicon and the Related Elements

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## Asymmetric Desymmetrization of $\sigma$ -Symmetrical Diols Using Diastereoselective Acetal Cleavage of $\alpha$ -Sulfinyl Acetals

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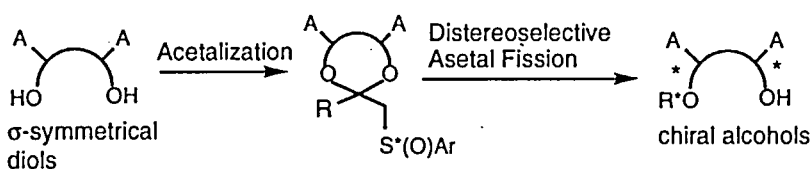
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Asymmetric desymmetrization of  $\sigma$ -symmetrical diols was accomplished via diastereoselective C—O bond fission of  $\alpha$ -sulfinyl acetals.

**KEY WORDS** asymmetrization  $\sigma$ -symmetrical diol chiral sulfoxide

### INTRODUCTION

Asymmetric desymmetrization of  $\sigma$ -symmetrical diols has been widely used to prepare useful chiral building blocks for various natural products. To develop a novel asymmetric desymmetrization of  $\sigma$ -symmetrical diols, we planned an approach based on diastereoselective acetal cleavage of  $\alpha$ -sulfinyl acetals (SCHEME 1). In this paper, we report the results of diastereoselective acetal cleavage reaction of various  $\alpha$ -sulfinyl acetals.<sup>1–4</sup>

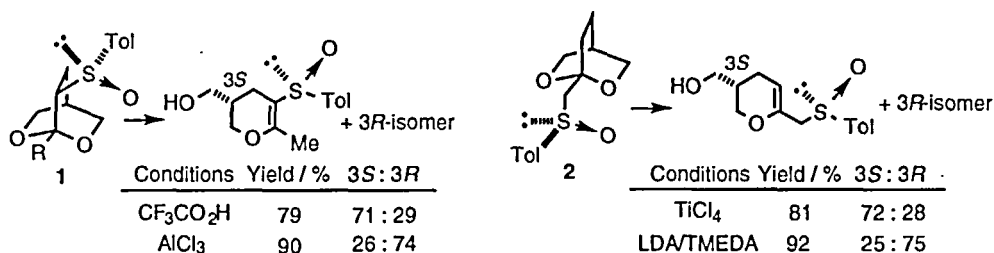


SCHEME 1

### 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  $\beta$ -elimination followed

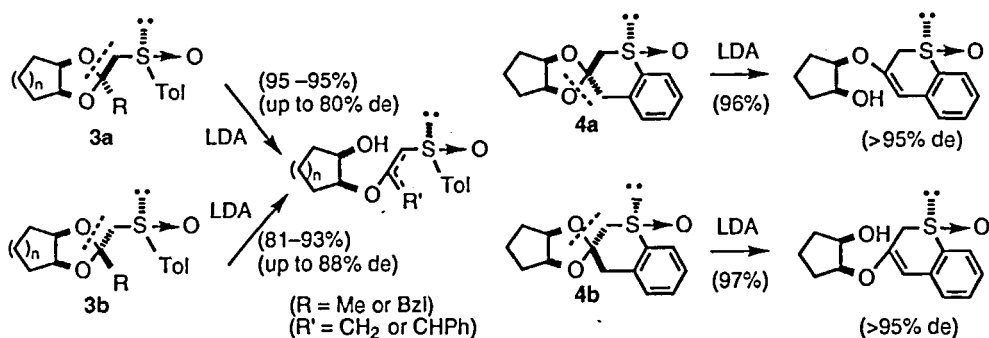
by isomerization to the  $\beta,\gamma$ -unsaturated sulfoxides.



SCHEME 2

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

Base promoted  $\beta$ -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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