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A Simple C_2 Symmetric Sulfide for a One Pot Ylide Mediated Asymmetric Conversion of Aldehydes into Epoxides

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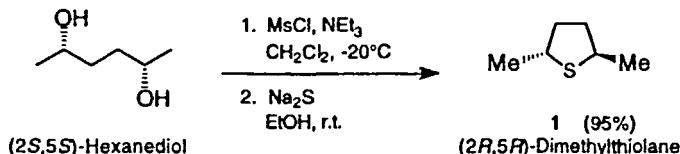
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The use of sulfur ylides in their reaction with aldehydes offers an attractive synthesis of oxiranes. Though it was developed in the early 60's, asymmetric versions only appeared in the 90's.¹⁻⁵ A major practical advantage of this route to enantioenriched oxiranes is that they are obtained in **one** step from aldehydes and organic halides whereas the oxidation of alkenes adds one step, *i.e.* the synthesis of the alkenes by a Wittig reaction which starts from the same substrates.

Our project was to design a new chiral sulfur ylide with emphasis on **simplicity**, in terms of structure of the chiral auxiliary, preparation, and epoxidation reaction conditions.

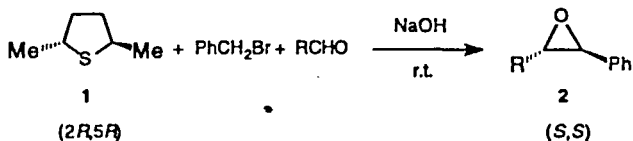
We wish to report the efficiency of (2*R*,5*R*)-dimethylthiolane **1** for the asymmetric ylide mediated epoxidation of carbonyl compounds.⁶ This sulfide^{6,7} was easily synthesised in two steps and 95% yield from commercially available material.



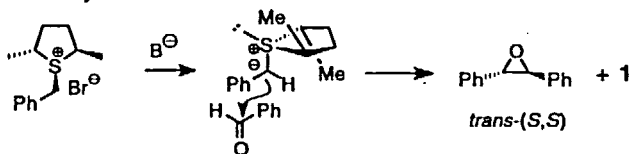
The C_2 symmetry of **1** allows the formation of a single sulfonium salt by reaction with a benzyl halide. After an extensive search of the reaction

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conditions, especially the nature of the solvent, we have found an extremely simple one-pot epoxidation procedure of aldehydes to afford oxiranes **2**. The reaction was performed in *t*-BuOH/H₂O 90:10, at room temperature, with a mineral base (NaOH).



As a representative example, *trans*-(2*S*,3*S*)-2,3-diphenyloxirane was obtained from benzaldehyde and benzyl bromide with **92% chemical yield**, **86% diastereomeric** and **88% enantiomeric excesses**. A range of non racemic epoxides have been synthesised using a variety of aldehydes and alkyl halides. The accompanying model is postulated to explain the stereoselectivity.



As compared to recently reported asymmetric versions of the epoxidation of aldehydes² our system has a number of advantages: i) the auxiliary has a low molecular weight and is chemically robust, ii) the reaction involves simple reagents and avoids harsh electrophiles, iii) the procedure is extremely simple to carry out and provides clean products with high ee's. Furthermore, an efficient catalytic version of the reaction (0.1 equiv. of sulfide **1**) has been shown to be possible.

Extension of this method to the synthesis of various oxiranes is in progress. Our new chiral sulfide might also be employed as an auxiliary for other reactions.

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