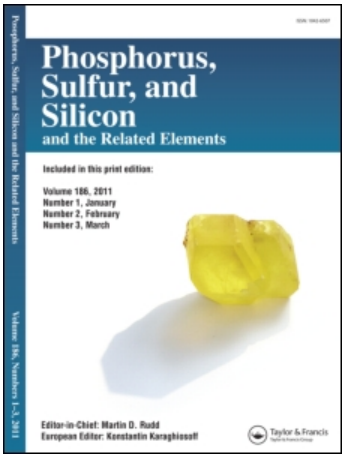

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Asymmetric Synthesis of Alkyl and Aryl Sulfinates of DAG: An Improved and General Route to Both Enantiomerically Pure Sulfoxides

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ASYMMETRIC SYNTHESIS OF ALKYL AND ARYL SULFINATES OF DAG: AN IMPROVED AND GENERAL ROUTE TO BOTH ENANTIOMERICALLY PURE SULFOXIDES.

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Abstract A short, efficient and general route for the preparation of o.p. alkyl and aryl sulfinates is described. Both epimers at sulfur can be obtained using DAG as unique inductor of chirality and, only by choosing the adequate base (Py or i-Pr_2NEt), the configuration at sulfur can be predicted. The efficiency of this methodology has been demonstrated by the synthesis of o.a. alkyl aryl and dialkyl sulfoxides with high e.e. (up to 100%).

INTRODUCTION

Optically active sulfoxides have proven themselves as powerful auxiliaries in highly efficient asymmetric synthesis.[1] Additionally, moleculas bearing a sulfinyl function are of great biological interest. This explains the considerable attention that the preparation of sulfoxides with high enantiomerically purity has received over the years.[2]

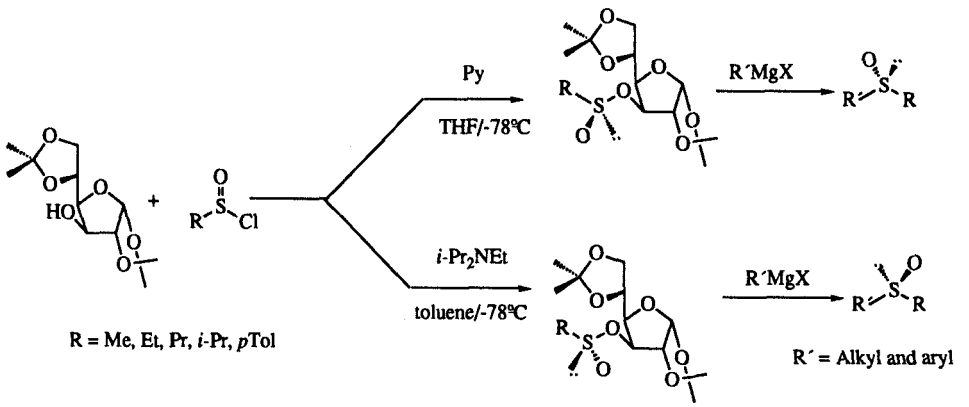
In this communication we present a new methodology that permits the obtantion of o.p. R and S sulfoxides (alkyl alkyl and alkyl aryl).

RESULTS AND DISCUSSION

Diacetone-D-glucose (DAG), a commercially available secondary alcohol, was found to react with alkyl and aryl sulfinyl chlorides in the presence of a base, in a very usefull manner. (-)-(S)-alkyl and aryl sulfinates are obtained with 70-90% d.e. and 56-87% yield, when i-Pr_2NEt was used as the base. With the simple change of the base, from i-Pr_2NEt to Py, (+)-(R)-alkyl and aryl sulfinates are obtained with 90-92% d.e. and 50-90% yield, (Scheme 1).

The d.e. were determined by 1H NMR. Optically pure alkyl and aryl sulfinates are obtained, either by recristallization or by column chomatography.

These sulfinates were transformed to both epimers of various enantiomerically pure sulfoxides (alkyl alkyl and alkyl aryl), by reaction with Grignard reagents (Scheme 1).



SCHEME 1 Synthesis of both sulfinate esters of DAG, epimers at sulfur.

This new methodology is cheap, quick and very convenient, when both epimers of a given sulfoxide are needed enantiomerically pure.

The effect of other type of bases was also studied, and other o.p. secondary alcohols were used in the same reaction to compare their behaviour with that of DAG.

To our Knowlege, this is the first time that it is reported that the stereocourse of formation of sulfinate esters is not only depending on the chiral alcohol but also on the nature of the base.

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