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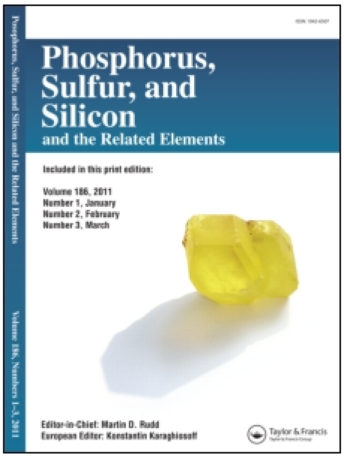

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Stereospecific Redox Reaction Directed by a Sulfinyl Group

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Stereochemistry of reductions of a pyridinium and quinoliniums with an asymmetric sulfinyl group has been studied. Dithionite and borohydride prefer the face characterized by a lone pair on sulfur atom. Dihydropyridine prefers the face characterized by a S-O bond.

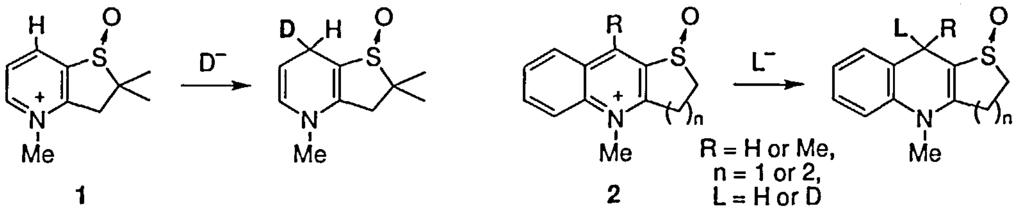
KEY WORDS: inherent stereochemistry, reduction, sulfinyl group, pyridinium, quinolinium

INTRODUCTION

We have found that a hydrogen is transferred to the face specified by the C=O bond in the side carbamoyl group in reduction of a pyridinium ion.[1)] In the reaction, conformational change and steric hindrance are not accounted because of the rigid configuration of the molecule. Therefore, the stereochemistry is called *nonsteric, inherent stereochemistry*. The sticking C=O bond out of the molecular plane seems to stabilize an encounter complex by some interaction. The reverse reaction, oxidation of a dihydropyridine, also exhibits the similar stereochemistry.[2)]

We interested in the inherent stereochemistry controlled by the orientation of the amide C=O bond, and elucidated stereochemistry of reductions of pyridinium ion **1**[3)] and quinolinium ions **2** with several reagents (Scheme 1). The side sulfinyl S-O is fixed to be out-of-plane orientation in these ions. The present systems are formally referred to as nucleophilic addition of a hydride ion to ß-sulfinyl carbocation. Comparing the reactions with different polar groups, the mechanism of asymmetric induction can be elucidated.

Scheme 1



RESULTS AND DISCUSSION

Reactions were carried out under an atmosphere of argon in the dark at room temperature. Stereochemistry of the reaction was estimated from the area ratio of characteristic peaks of diastereomeric products on ^{1}H NMR.

In dithionite reduction, a hydride preferably transfers in the *anti* face of **1** and **2** with respect to the S-O bond. Borohydride also reacts preferably in the *anti* face of **1**. On the contrary, dihydropyridines prefer to attack in the *syn* face of **1**. These preferences are independent of conformational change, steric hindrance, electrostatic interaction, and solvent. Stereochemistry inherent for the sulfinyl group was therefore observed.

We consider together the cases with the two side groups: the amide carbonyl group and the sulfinyl one. Stereochemistry of this type of reaction is directed by a polar bond or orbital. Moreover, in this study, reactivity of a reductant controls the face of preference: strong reductants prefer the face less activated by the lone pair orbital, and a weak reductant prefers the face more activated by the S-O bond.

The term "inherent" means that the reaction orbitals asymmetrically interact with the S-O bond or the lone pair orbital on the sulfur atom.

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