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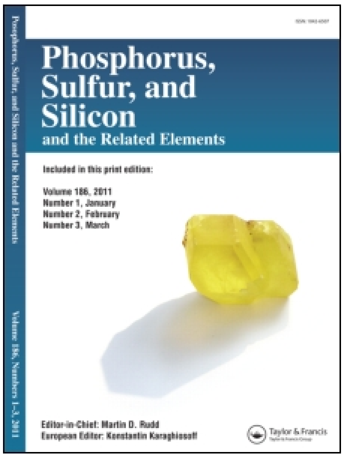

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Stereoselective Addition of Sulfur-Stabilized Carbanions

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STEREOSELECTIVE ADDITION OF SULFUR-STABILIZED CARBANIONS

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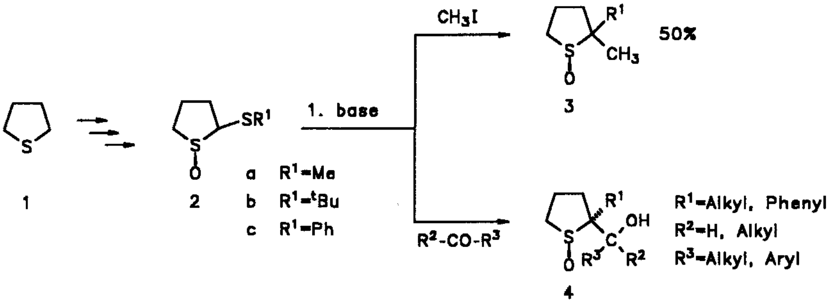
Abstract The reaction of dithioacetal sulfoxides **2** with different electrophiles was investigated. Sulfoxides **2** were easily deprotonated by different bases and reacted with variuos electrophiles. The carbanion of **2** exhibits configurational stability. Asymmetric induction was observed upon the reaction with prochiral electrophiles. Generation of the carbonyl functionality can easily be performed

INTRODUCTION

Dithioacetals and their related sulfoxides are known as "Umpolung" reagents in organic chemistry. One of the best known dithioacetals is 1,3-dithiane, introduced by *Corey* and *Seebach.*[1] Ogura and *Tsuchihashi* [2] have demonstrated that the methyl methylthiomethyl sulfoxide is a useful acylanion equivalent of formaldehyde that can be transformed to different aldehydes and also cyclic ketones of various ring sizes. As a consequence of our previous studies[3] we found the dithioacetal sulfoxide **2** to be a useful acylanion equivalent.

RESULTS AND DISCUSSION

Whereas 2-methylthio-thiolane sulfoxide (**2a**) has been described in 1970 [4] no further studies on this sulfoxide have yet been published. The sulfoxides **2** can be prepared in a three-step synthesis starting from thiolane (**1**). They were readily deprotonated by different bases and



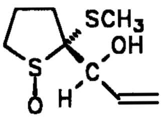
base = n-BuLi, LDA, n-BuLi/TMEDA, KO^{t}Bu, NaH

scheme I

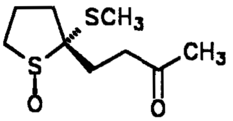
reacted with alkyl halides and carbonyl compounds to yield the compounds **3** and **4** in moderate to good yield (scheme I). The β-hydroxy sulfoxides **4** exhibit (E)-configuration, which demonstrates the configurational stability of the carbanions of **2**. Asymmetric induction at the prochiral center was observed upon the addition of carbonyl compounds. Diastereoisomeric ratios were in the range of 3:1.

Reactions of **2a** with bifunctional electrophiles such as diacetyl or p-cyanobenzaldehyde led to monoaddition products, exclusively.

The addition of α,β-unsaturated carbonyl compounds showed a remarkable selectivity. Sulfoxide **2a** reacted with acrolein in a 1,2-addition to form **5**, whereas methyl vinyl ketone was added in a Michael-type addition to give **6**.

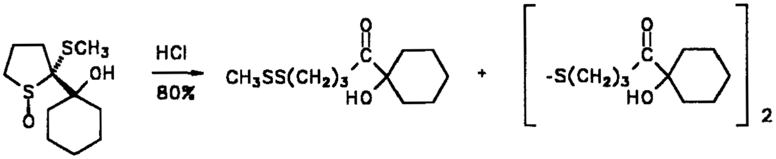


5



6

Generation of the carbonyl function can easily be performed with mineral acid in good yield (scheme II).



scheme II

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