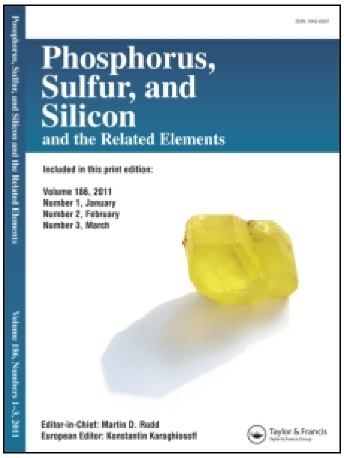

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Asymmetric Synthesis and Cycloaddition Chemistry of Trans-2-Methylene-1,3-Dithiolane 1,3-Dioxide

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ASYMMETRIC SYNTHESIS AND CYCLOADDITION CHEMISTRY OF TRANS-2-METHYLENE-1,3-DITHIOLANE 1,3-DIOXIDE

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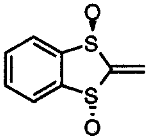
Abstract A study on the Modena oxidation of some 2-substituted 1,3-dithiolanes has led to an asymmetric synthesis of the chiral ketene equivalent trans-2-methylene-1,3-dithiolane 1,3-dioxide. Its reaction as a dipolarophile with aromatic betaines is also discussed.

Introduction

The use of cyclic alkenyl sulfoxides **1** and **2** as potential chiral ketene equivalents has been established.[1] Trans-2-methylene-1,3,dithiolane 1,3-dioxide **3** shows levels of reactivity and diastereoselectivity in Diels-Alder processes superior to **1** and **2**.[2] Reaction with cyclopentadiene at -78°C using $BF_3.OEt_2$ catalysis, and with acyclic dienes at room temperature, gave single diastereomeric adducts in high yield. Reaction with furan at -78°C under SnCl4 catalysis gave a 5:1 mixture of diastereomers.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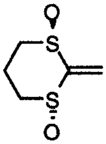
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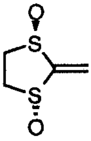
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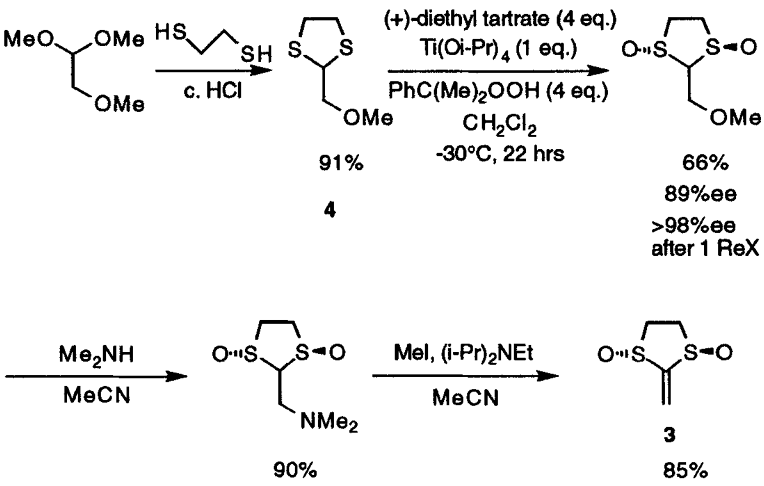
Asymmetric Synthesis of 3

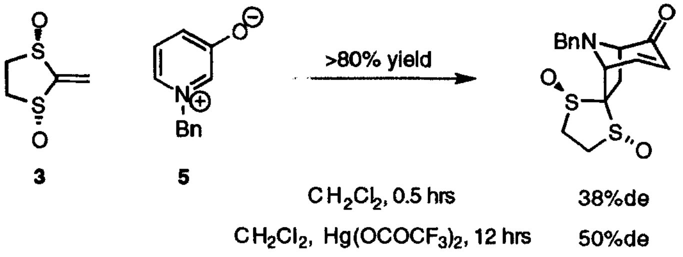
To fully realise the potential of our dienophile, we devised an asymmetric synthesis of **3** based on the chiral bisfunctionalisation of a suitable substrate, an approach which had already been shown to give rise to products with very high enantioselectivities.[3] Modena oxidation[4] of 2-substituted-1,3-dithiolanes was found to be highly substrate dependent.

Oxidation of methyl ether **4** was found to be not only highly enantioselective, but highly diastereoselective in favour of the trans isomer. A single recrystallisation gave rise to optically pure material, which could be easily converted to the alkene **3** in two steps.



1,3-dipolar cycloadditions with aromatic betaines

3 has also been found to be a highly reactive diporophile in 1,3-dipolar cycloaddition chemistry.[5] Reaction with the relatively unreactive aromatic betaine **5** occured readily at room temperature in CH_2Cl_2 giving a 2.3:1 mixture of diastereomers. Addition of $Hg(OCOCF_3)_2$ increased diastereoselectivity to 3:1.



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5 For 1,3-dipolar cycloadditions of vinyl sulfoxides see T. Takahashi, A. Fujii, J. Sugita, T. Hagi, K. Kitano, Y. Arai and T. Koizumi, Tet. Asym., 2, 1379, (1991).