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

Varinder K. Aggarwal<sup>a</sup>; Richard S. Grainger<sup>a</sup>; Peter L. Spargo<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Sheffield, Sheffield, UK <sup>b</sup> Pfizer Central Research, Kent, UK

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

Varinder K. Aggarwal,\*<sup>a</sup> Richard S. Grainger<sup>a</sup> and Peter L. Spargo<sup>b</sup>

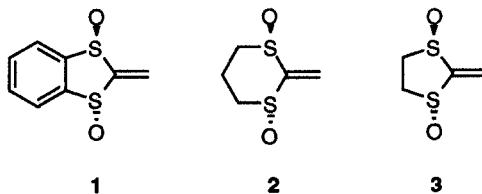
<sup>a</sup>Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK.

<sup>b</sup>Pfizer Central Research, Sandwich, Kent CT13 9NJ, UK.

**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

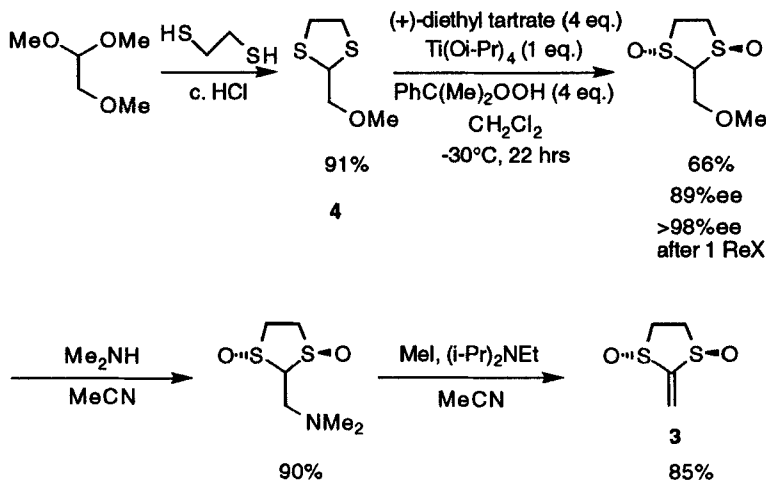
The use of cyclic alkenyl sulfoxides **1** and **2** as potential chiral ketene equivalents has been established.<sup>1</sup> Trans-2-methylene-1,3-dithiolane 1,3-dioxide **3** shows levels of reactivity and diastereoselectivity in Diels-Alder processes superior to **1** and **2**.<sup>2</sup> Reaction with cyclopentadiene at -78°C using BF<sub>3</sub>·OEt<sub>2</sub> catalysis, and with acyclic dienes at room temperature, gave single diastereomeric adducts in high yield. Reaction with furan at -78°C under SnCl<sub>4</sub> catalysis gave a 5:1 mixture of diastereomers.



### Asymmetric Synthesis of **3**

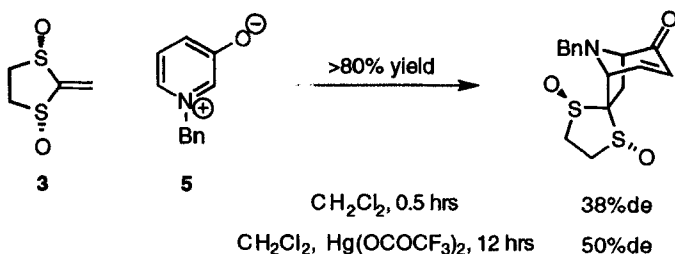
To fully realise the potential of our dienophile, we devised an asymmetric synthesis of **3** based on the chiral bisfunctionalisation of a suitable substrate, an approach which had already been shown to give rise to products with very high enantioselectivities.<sup>3</sup> Modena oxidation<sup>4</sup> 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.<sup>5</sup> Reaction with the relatively unreactive aromatic betaine **5** occurred readily at room temperature in  $\text{CH}_2\text{Cl}_2$  giving a 2,3:1 mixture of diastereomers. Addition of  $\text{Hg}(\text{OCOCF}_3)_2$  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).