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## Enantiopure 3-Alkylsulfinyl-1-Methoxybuta-1,3-Dienes in Target-Oriented Synthesis

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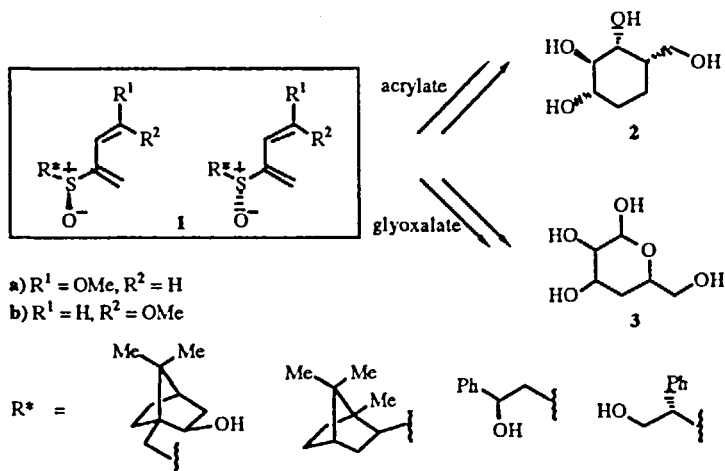
**Keywords:** 2-sulfinylbuta-1,3-dienes; cycloadditions; regioselectivity; stereoselectivity; chiral auxiliary removal

The high degree of stereochemical control exerted by the sulfinyl group in Diels-Alder reactions of enantiopure diene sulfoxides is well stated<sup>[1]</sup> and points out the useful role that these diene systems may fulfil in enantioselective synthesis.<sup>[2]</sup>

3-Alkylsulfinyl-1-methoxy-1,3-dienes **1**, which possess a strongly electron-donating methoxy substituent and a sulfinyl group suitably positioned to cooperate with OMe in mesomerism, showed a remarkable reactivity in Diels-Alder cycloadditions with electron-deficient carbo- and hetero-dienophiles.<sup>[3]</sup> Mild conditions, complete *endo* and very high  $\pi$ -facial diastereoselectivities were normally observed in the uncatalyzed additions of (*E*)-dienes **1a** with cyclic dienophiles, such as maleimide and *N*-phenylmaleimide. The cycloadditions of (*Z*)-dienes **1b** with various dienophiles occurred in a reasonable length of time and mild conditions. These results are in line with the higher reactivity of (*E*)-2-sulfinyldienes **1a**, with respect to 1-sulfinyldienes, pointed out by literature data.<sup>[1]</sup> Acyclic electron-deficient carbo- and hetero-dienophiles, such as methyl acrylate, dimethyl maleate, and ethyl glyoxalate, have been reacted with dienes **1a**, opening the way towards enantiomerically pure and highly

functionalized cyclohexenes, useful intermediates in the total synthesis of natural products such as validatol (**2**) and homochiral 4-deoxyaldohexoses **3**. These Diels-Alder reactions occurred in mild conditions, very high yields, and good (with glyoxalate as dienophile) up to complete diastereoselectivities (with maleate).

Removal of R\*SO chiral auxiliary was performed by oxidation of the sulfinyl cyclohexene adducts to sulfone epoxides and MgBr<sub>2</sub> cleavage. Stimulating results were achieved in parallel by the use of OMe cleaver iodotrimethylsilane, which apparently cleaved also the C-S bond of some cycloadducts. This unusual behaviour is still under study.



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