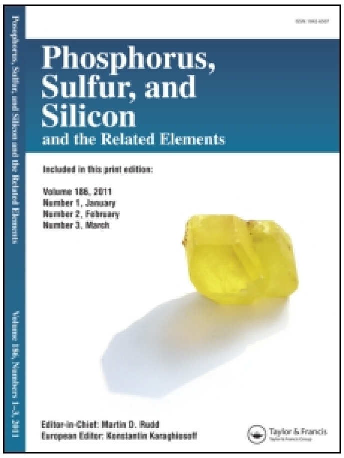

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Enantiopure 3-Alkylsulfinyl-1-Methoxybuta-1,3-Dienes in Target-Oriented Synthesis

MARIA C. AVERSA, ANNA BARATTUCCI, PAOLA BONACCORSI
and PLACIDO GIANNETTO

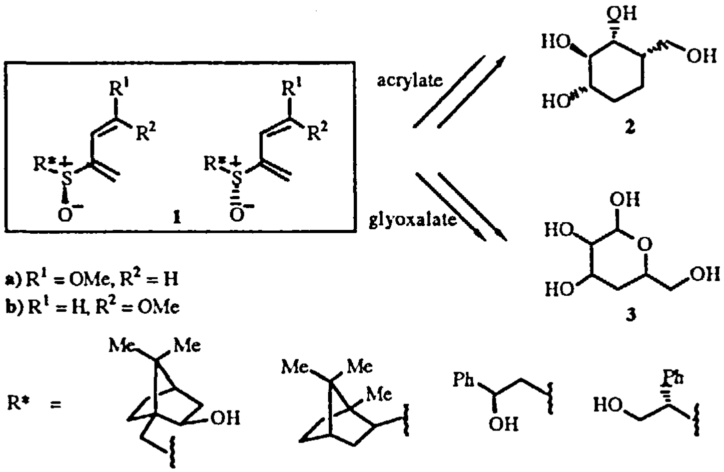
*Dipartimento di Chimica organica e biologica, Università di Messina,
Salita Sperone 31 (vill. S. Agata), 98166 Messina, Italy*

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[1] and points out the useful role that these diene systems may fulfil in enantioselective synthesis.[2]

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.[3] Mild conditions, complete *endo* and very high π-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.[1] 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 $MgBr_2$ 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.



a) R^1 = OMe, R^2 = H
b) R^1 = H, R^2 = OMe

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