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Eva Cramer^a; Michael Fleischer^a; Uta Meiners^a; Jörn Stölting^a; Peter Metz^a ^a Organisch-Chemisches Institut der Universitét Münster, Münster, Germany

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INTRAMOLECULAR DIELS-ALDER REACTIONS OF VINYLSULFONATES

EVA CRAMER, MICHAEL FLEISCHER, UTA MEINERS, JÖRN STÖLTING. AND PETER METZ*

Organisch-Chemisches Institut der Universität Münster, Corrensstr. 40, D-48149 Münster, Germany

Abstract Control of side chain chirality is efficiently achieved by intramolecular Diels-Alder cycloaddition of vinylsulfonates and subsequent oxidative or reductive desulfurization of the resultant sultones. An alkoxide directed regio- and stereoselective 1,6-addition to dienyl sultones further enhances the utility of this reaction sequence.

Vinylsulfonates of hydroxyalkyl substituted furans, cycloalka-1,3-dienes, and acyclic 1,3-dienes undergo a smooth and often highly diastereoselective intramolecular [4 + 2] cycloaddition to δ -sultones (e.g. $2)^{1-3}$.

The resultant sultones lacking an oxygen atom β to sulfur allow for a one-pot oxidative desulfurization to hydroxy ketones (e.g. $2a \rightarrow 3$) via borylation and subsequent peracid treatment, thus establishing vinylsulfonyl chloride as a regio- and stereoselectively reacting ketene equivalent for the intramolecular Diels-Alder cycloaddition².

On the other hand, furan-derived sultones are efficiently elaborated to substituted cyclohexenols possessing a defined stereochemical relationship between acyclic and cyclic stereogenic moieties^{4,5}. Thus, hydrogenation of the unsaturated sultone 2b, followed by opening of the oxygen bridge via elimination and reduction of the resultant vinyl sultone afford 4, while a one-pot elimination/1,6-addition/alkylation and subsequent reductive desulfurization of an allyl sultone intermediate convert e.g. 2b to 5.

The tandem elimination/1,6-addition has been utilized in a 4-step route from 2b to sultone 6, an advanced intermediate for nonactic acid⁶, and a similar process has been applied for a short and highly stereoselective synthesis⁷ of the 1,10-seco-eudesmanolide ivangulin $(7)^8$.

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