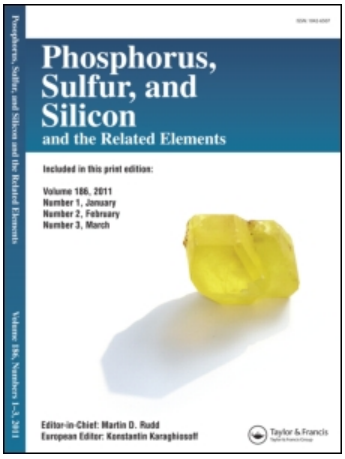

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Intramolecular Diels-Alder Reactions of Vinylsulfonates

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INTRAMOLECULAR DIELS-ALDER REACTIONS OF VINYLSULFONATES

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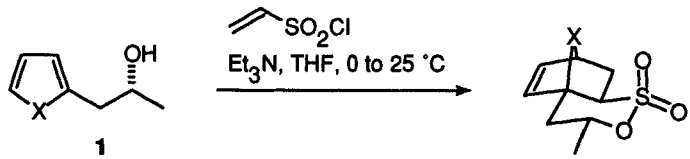
Abstract Control of side chain chirality is efficiently achieved by intramolecular Diels-Alder cycloaddition of vinylsulfonates and subsequent oxidative or reductive desulfurization of the resultant sultones. An alkoxide directed regio- and stereoselective 1,6-addition to dienyl sultones further enhances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

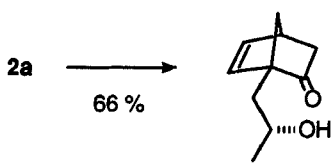


1

a : X = CH_2 64 %
b : X = O 90 %

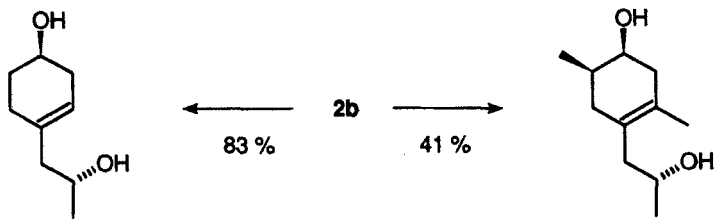
2

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



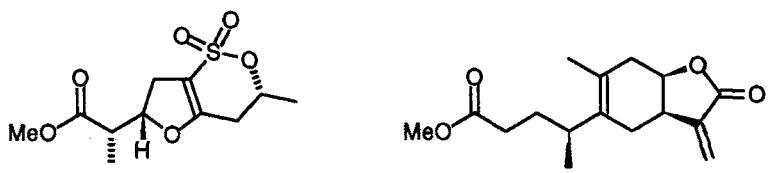
3

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**.



4 **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 acid[6], and a similar process has been applied for a short and highly stereoselective synthesis[7] of the 1,10-*seco*-eudesmanolide ivangulin (**7**)[8].



6 **7**

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