MASTER'S THESIS

Unsaturated sulfinates and sulfoxides in organic synthesis

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Unsaturated Sulfinates and Sulfoxides

in

Organic Synthesis

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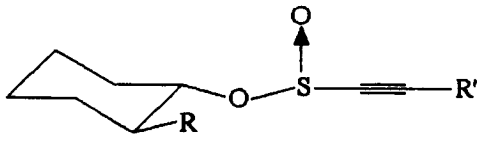
Abstract

Sulfinate and sulfoxide functionalities are used extensively in organic synthesis with much important chemical values. A novel method for the preparation of alkynesulfinate was developed in the first part of the research. The alcohols (cyclohexanol and (1*S*, 2*R*)-*trans*-2-phenylcyclohexanol) were converted to chlorosulfinates in the presence of a large excess of thionyl chloride at low temperature. Treatment of the labile chlorosulfinates with the corresponding lithium acetylide afforded in high yield of the sulfinates (**8**, **9**, **10**, **11a** and **11b**). The viability and reactivity of using these alkynesulfinates as dienophiles in the Diels-Alder reaction were demonstrated.

In the second part of this thesis, an enantioselective synthesis of the tetrahydroisoquinoline alkaloid (+)-calycotomine **32** was achieved using chiral acetylenic sulfoxide **23** as the starting material. Michael addition of 2-(3,4-dimethoxyphenyl)ethyl amine **26** onto **23** followed by acid induced cyclization reaction, a pair of separable diastereoisomers, **41** and **42**, were afforded after treatment with *p*-toluenesulfonyl chloride. Compound **41** could undergo trifluoroacetic acid anhydride induced Pummerer rearrangement and the corresponding hydroxyl compound could be obtained by LAH reduction. The enantioselective synthesis of **32** was then completed with the deprotection of the sulfonamide. In addition, racemization of the tetrahydroisoquinoline system was observed when **41** or **42** was treated with TFAA at room temperature.

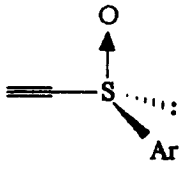


8 : R = H, R' = $SiMe_3$

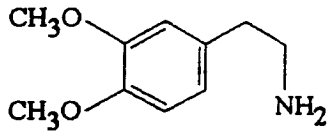
9 : R = H, R' = H

10 : R = H, R' = Bu

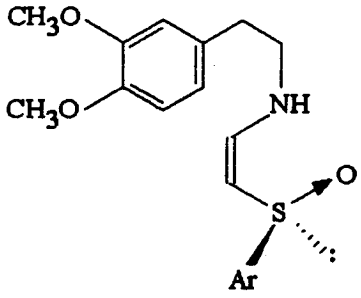
11 a, b : R = Ph, R' = H



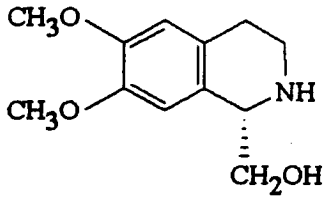
23 : Ar = *o*-NO_2-C_6H_4



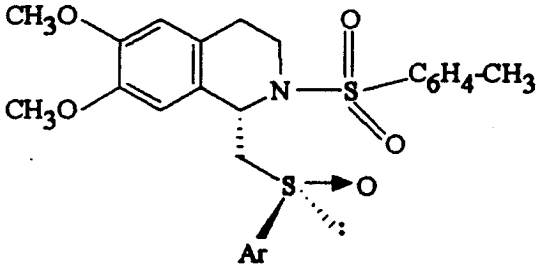
26



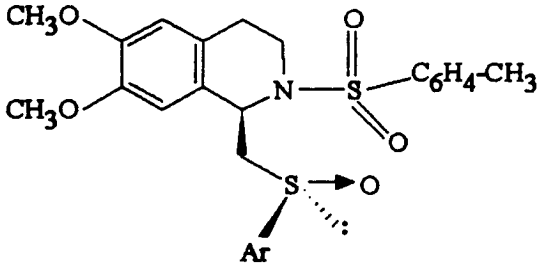
26 a : Ar = *o*-NO_2-C_6H_4



32



41 : Ar = *o*-NO_2-C_6H_4



42 : Ar = *o*-NO_2-C_6H_4

Contents