

MASTER'S THESIS

Unsaturated sulfinates and sulfoxides in organic synthesis

Lee, Ka Ming Danny

Date of Award:
1995

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Unsaturated Sulfinates and Sulfoxides

in

Organic Synthesis

Danny LEE Ka Ming

**A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Philosophy**

May, 1995

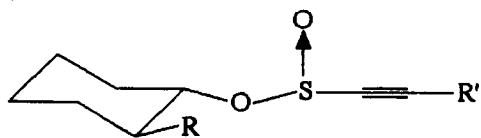
Hong Kong Baptist University



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 chlorosulfonates in the presence of a large excess of thionyl chloride at low temperature. Treatment of the labile chlorosulfonates with the corresponding lithium acetylide afforded in high yield of the sulfonates (8, 9, 10, 11a and 11b). The viability and reactivity of using these alkynesulfonates 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.

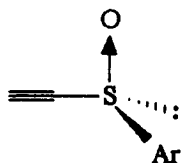


8 : R = H, R' = SiMe₃

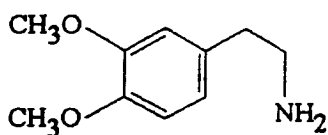
10 : R = H, R' = Bu

9 : R = H, R' = H

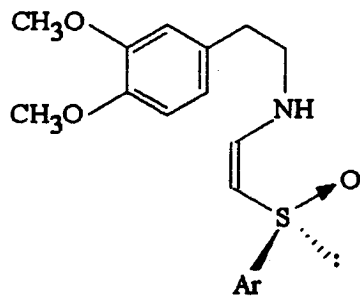
11 a, b : R = Ph, R' = H



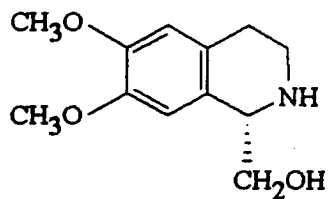
23 : Ar = *o*-NO₂-C₆H₄



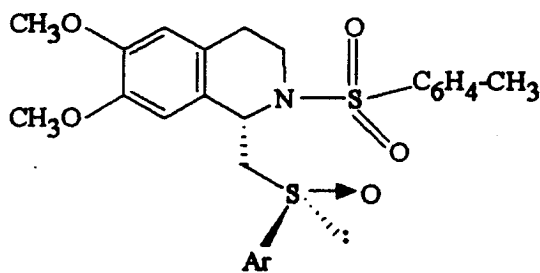
26



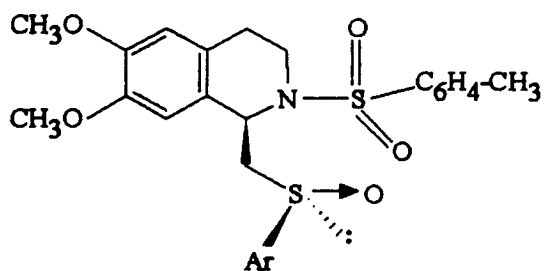
26 a : Ar = *o*-NO₂-C₆H₄



32



41 : Ar = *o*-NO₂-C₆H₄



42 : Ar = *o*-NO₂-C₆H₄

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