SYNLETT
Spotlight 409

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

2-(Phenylsulfonyl)-3-phenyloxaziridine (Davis Reagent)

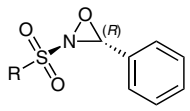
Compiled by Kottur Mohan Kumar

Kottur Mohan Kumar was born in 1980 in Mamidipally, Nizamabad, Andhra Pradesh, India. He received his B.Sc. degree in Chemistry (2001) from Osmania University, Hyderabad, and his M.Sc. degree in Organic Chemistry (2003) from Swami Ramanad Teerth University, Nanded, India. He worked as a research associate in Chembiotek Research International Pvt. Ltd, Kolkata and GVK-Bio Sciences Pvt. Ltd, Hyderabad. He is currently pursuing his Ph.D. degree under the tutelage of Dr. Srinivas Oruganti at the Institute of Life Sciences, University of Hyderabad. His current research interests are the development of novel synthetic methodologies and the synthesis of peptides containing both natural and unnatural amino acids, phospholipids and ^{13}C-labeled compounds.

Institute of Life Sciences, University of Hyderabad Campus, Gachibowli, Hyderabad 500046 (A. P), India
E-mail: mohankumark767@gmail.com

Introduction

In 1984, Davis and co-workers introduced a chiral derivative of *N*-sulfonyl oxaziridine[1] as a versatile reagent for different organic functional group transformations; it is known as Davis reagent (Figure 1).[2]



R = Alk, Ar

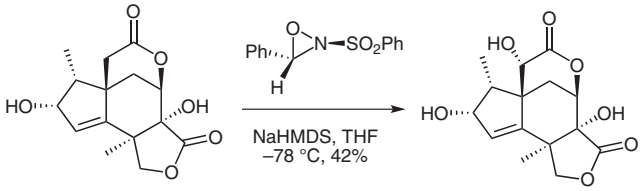
Figure 1

The Davis reagent can be prepared by the biphasic basic oxidation of the *N*-benzylidene benzene-sulfonamide with MCPBA or oxone.[3] It is a neutral, aprotic, mild and stable colorless powder (mp 92–94 °C) and can be stored in amber-colored bottles at 5 °C.

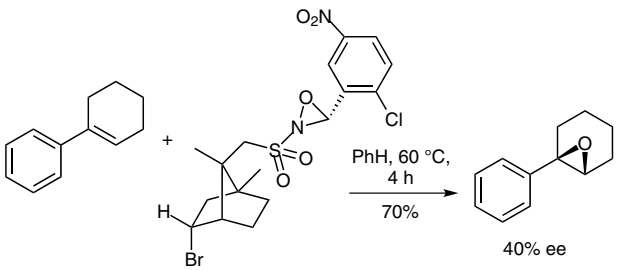
Sulfonyloxaziridines share many characteristics with dialkyldioxiranes and are widely used as versatile oxidizing reagents for the oxygenation of a variety of functional groups[4] such as sulfide (RSR) to sulfoxide (RSOR), disulfide (RSSR) to thiosulfinate (RSOSR), thiol (RSH) to sulfenic acid (RSOH) and selenide (RSeR) to selenoxide (RSeOR). Due to the stereoselective cleavage of the weak N–O bond and the chirality, the Davis reagent is significant for asymmetric functional group transformations.

Abstracts

(A) *Asymmetric Oxygenation*:
Danishefsky and co-workers used Davis oxaziridine for the selective α-hydroxylation as a key step in the synthesis of (+/–)-jiadifenin from the sodium enolate of the ester. The high preference for the *syn* arrangement can be rationalized by minimization of steric interactions leading to oxygen transfer from the side opposite to the largest substituent.[5]

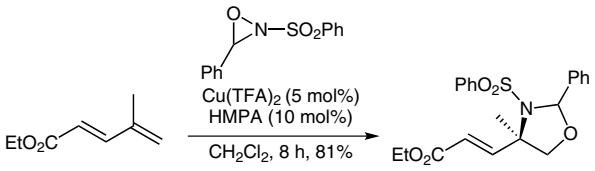


(B) *Asymmetric Epoxidation*:
Chiral oxaziridine is a more useful reagent for asymmetric epoxidation of alkenes compared to chiral peracids or hydroperoxides. The configuration of the oxaziridine three-membered ring controls the stereochemistry of the product.[6]

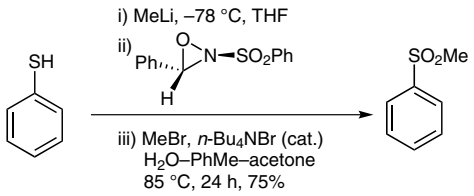


SYNLETT 2012, 23, 2572–2573
Advanced online publication: 28.09.2012
DOI: 10.1055/s-0032-1317327; Art ID: ST-2012-V0416-V

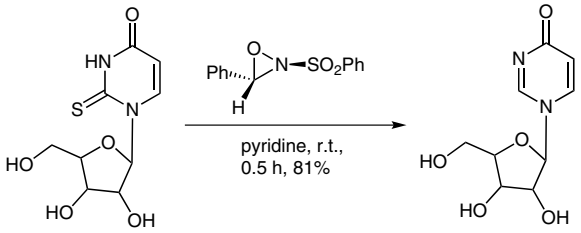
(C) *Oxaziridines as Nitrogen Transfer Reagents (Oxyamination)*:
N-Sulfonyl oxaziridine is an extensive source of electrophilic nitrogen, which upon activation by copper(II) catalysts reacts with alkenes to provide 1,3-oxazolidines.[7]



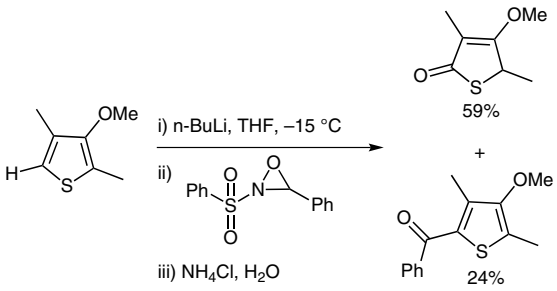
(D) *Oxidation of Thiolates to Sulfones*:
N-Sulfonyl (Davis) oxaziridine is an efficient reagent for the generation of sulfinate anions by oxidation of the corresponding thiolates. Subsequent S-alkylation of the sulfinates under phase-transfer catalysis affords sulfones.[8]



(E) *Desulfurization*:
Treatment of 2-thiouridine with an excess of *trans*-2-phenylsulfonyl-3-phenyloxaziridine in pyridine afforded 4-pyrimidinone in 81% yield with loss of sulfur during the oxidation.[9]



(F) *Thiophene Ring Hydroxylation*:
The hydroxylation of trisubstituted thiophene was successfully carried out using 2-(phenylsulfonyl)-3-phenyloxaziridine in THF, which upon hydrolysis furnished 59% of thiolactone and 24% of tetrasubstituted thiophene.[10]



References

(1) (a) Misra, J. K. *Synlett* **2005**, 543. (b) Li, J. J. *Name Reactions: A Collection of Detailed Reaction Mechanisms*; Springer: Berlin, **2006**, 185–186.

(2) (a) Davis, F. A.; Vishwakarma, L. C.; Billmers, J. M.; Finn, J. *J. Org. Chem.* **1984**, *49*, 3241. (b) Pearson, A. J.; Chang, K. *J. Org. Chem.* **1993**, *58*, 1228. (c) Mithani, S.; Drew, D. M.; Rydberg, E. H.; Taylor, N. J.; Moolbroex, S.; Dmotroemko, G. I. *J. Am. Chem. Soc.* **1997**, *119*, 1159.

(3) Vishwakarma, L. C.; Stringer, O. D.; Davis, F. A. *Org. Synth.* **1993**, *8*, 546.

(4) (a) Davis, F. A.; Jenkins, J. R.; Yocklovich, S. G. *Tetrahedron Lett.* **1978**, 5171. (b) Davis, F. A.; Awad, S. B.; Jenkins, J. R.; Billmers, R. L.; Jenkins, L. A. *J. Org. Chem.* **1983**, *48*, 3071. (c) Davis, F. A.; Rizvi, S. Q.; Ardecky, R.; Gosciniak, D. J.; Friedman, A. J.; Yocklovich, S. G. *J. Org. Chem.* **1980**, *45*, 1650. (d) Davis, F. A.; Jenkins, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 7967. (e) Davis, F. A.; Billmers, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7016. (f) Davis, F. A.; Stringer, O. D.; Billmers, J. M. *Tetrahedron Lett.* **1983**, *24*, 1213.

(5) Cho, Y. S.; David, D. A.; Tian, Y.; Li, Y. M.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2004**, *126*, 14358.

(6) Davis, F. A.; Harakal, M. E.; Awad, S. B. *J. Am. Chem. Soc.* **1983**, *105*, 3123.

(7) (a) Michaelis, D. J.; Ischay, M. A.; Yoon, T. P. *J. Am. Chem. Soc.* **2008**, *130*, 6610. (b) DePorter, S. M.; Jacobsen, A. C.; Partridge, K. M.; Williamson, K. S.; Yoon, T. P. *Tetrahedron Lett.* **2010**, *51*, 5223.

(8) Sandrinelli, F.; Perrio, S.; Beslin, P. *Org. Lett.* **1999**, *1*, 1177.

(9) Sochacka, E.; Fratczak, I. *Tetrahedron Lett.* **2004**, *45*, 6729.

(10) Cruz-Almanza, R.; Hernández-Quiroz, T.; Breña-Valle, L. J.; Pérez-Flores, F. *Tetrahedron Lett.* **1997**, *38*, 183.

