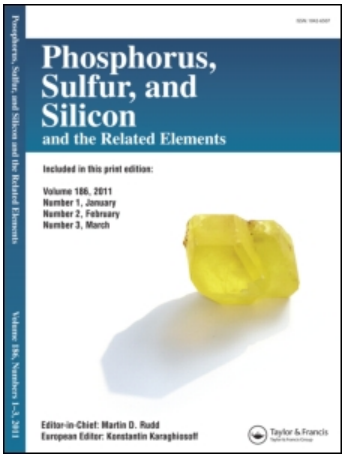


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Optically Active α,β-Unsaturated α-Phosphoryl Sulfoxides. Multifunctional Reagents for the Asymmetric Michael and Diels-Alder Reaction

Wanda H. Midura[a]; M. Mikołajczyk[a]
[a] Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Łódź, Poland

To cite this Article Midura, Wanda H. and Mikołajczyk, M.(1994) 'Optically Active α,β-Unsaturated α-Phosphoryl Sulfoxides. Multifunctional Reagents for the Asymmetric Michael and Diels-Alder Reaction', Phosphorus, Sulfur, and Silicon and the Related Elements, 95: 1, 397 — 398
To link to this Article: DOI: 10.1080/10426509408034249
URL: http://dx.doi.org/10.1080/10426509408034249

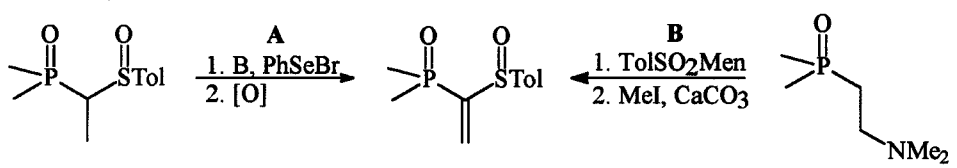
Phosphorus, Sulfur, and Silicon, 1994, Vol. 95-96, pp. 397-398
Reprints available directly from the publisher
Photocopying permitted by license only

OPTICALLY ACTIVE α,β-UNSATURATED α-PHOSPHORYL SULFOXIDES. MULTIFUNCTIONAL REAGENTS FOR THE ASYMMETRIC MICHAEL AND DIELS-ALDER REACTION

WANDA H.MIDURA, M.MIKOŁAJCZYK
Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90-363 Łódź, Sienkiewicza 112, Poland

Chiral sulfoxides are known as useful reagents in asymmetric synthesis. Currently, chiral α,β-unsaturated sulfoxides received also a considerable attention as dienophiles in asymmetric Diels-Alder reactions. However, because simple vinyl sulfoxides exhibit very low reactivity, it was necessary to activate the double bond by introduction of an additional electron-withdrawing group.

On the other hand, phosphonates having the electron-withdrawing group undergo the Horner reaction, which is one of the best among the numerous methods of olefin synthesis. Combination of both vinyl molecules in one structure led to creation of our target molecule α-phosphoryl vinyl p-tolyl α,β-unsaturated sulfoxide **1**. It was prepared by selenenylation of phosphorylethyl sulfoxide (method A)[1] or alternatively from β-amino-phosphonate (method B).

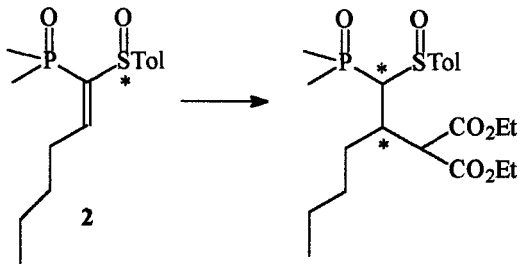


1

Optically active vinyl sulfoxide **1** was found to be a good acceptor in nucleophilic addition and easily reacted with different heteronucleophiles as mercaptane, amine and alcohol. The addition products were obtained in high yields (above 90%) as mixtures of diastereomers in a 2:1 ratio.

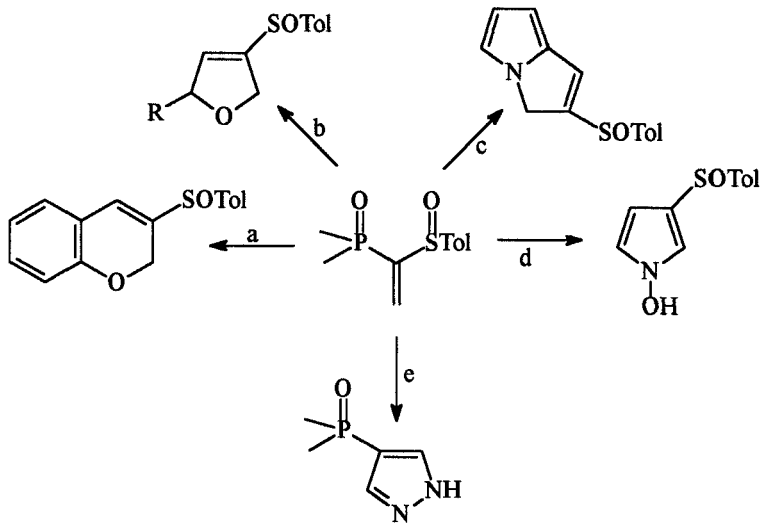
In order to define asymmetric induction on β-carbon atom in nucleophilic addition, β-substituted α,β-unsaturated α-phosphoryl sulfoxide **2** was synthesized starting from hexanephosphonate using method A. Isolated product **2** was pure E-isomer of optical rotation $[\alpha]_D$=+98.

When Me_2NH was used as nucleophile in addition to sulfoxide **2** the only isolated product was γ-hydroxy α,β-unsaturated phosphonate, formed by allylic rearrangement. Nucleophilic addition was accomplished using lithium salt of diethylmalonate. The addition product was formed as a mixture of two from four possible diastereomers, with a 5:3 ratio.



The phosphoryl group in α,β-unsaturated α-phosphoryl sulfoxides, functions not only as a double bond activating agent, but also allows to carry out the Horner reaction after the Michael addition.

If nucleophile contains a carbonyl group after Michael reaction the intramolecular Horner reaction takes place. The synthetic utility of vinyl α-phosphoryl sulfoxides as a key reagent for the construction of mono- and condensed heterocycles containing the chiral sulfoxide as substituent was illustrated by the synthesis of following examples.



It is interesting to underline that vinyl sulfoxide **1** undergoes also 1,3-dipolar cycloaddition with diazomethane, what shows the last example (e).

1. Mikołajczyk,M.; Midura,W.H.; Tetrahedron: Asymmetry, 1992. 3. 1515.