

This article was downloaded by:

On: 30 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## 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>

### SYNTHESIS AND STEREOCHEMISTRY OF MEDIUM SIZE (8-10) THIACYCLOALKENES FORMED BY 2,3-SIGMATROPIC SHIFT OF NON-STABILIZED SULFONIUM YLIDES. BARRIERS TO CHIRAL INVERSION IN TRANS-THIACYCLOALK-4-ENES

E. Sandri<sup>a</sup>; V. Ceré<sup>a</sup>; C. Paolucci<sup>a</sup>; S. Pollicino<sup>a</sup>; L. Lunazzi<sup>a</sup>; A. Fava<sup>a</sup>

<sup>a</sup> Istituto di Chimica Organica, Università di Bologna, Bologna, Italy

**To cite this Article** Sandri, E. , Ceré, V. , Paolucci, C. , Pollicino, S. , Lunazzi, L. and Fava, A.(1979) 'SYNTHESIS AND STEREOCHEMISTRY OF MEDIUM SIZE (8-10) THIACYCLOALKENES FORMED BY 2,3-SIGMATROPIC SHIFT OF NON-STABILIZED SULFONIUM YLIDES. BARRIERS TO CHIRAL INVERSION IN TRANS-THIACYCLOALK-4-ENES', Phosphorus, Sulfur, and Silicon and the Related Elements, 6: 1, 265

**To link to this Article:** DOI: 10.1080/03086647908080406

**URL:** <http://dx.doi.org/10.1080/03086647908080406>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

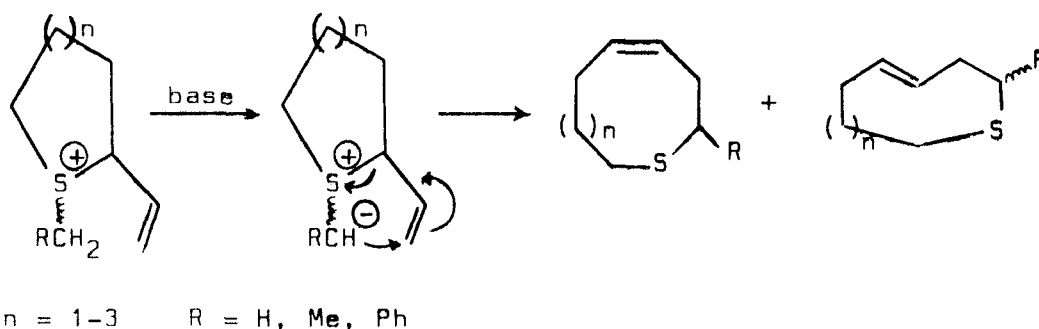
The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SYNTHESIS AND STEREOCHEMISTRY OF MEDIUM SIZE (8-10) THIACYCLOALKENES FORMED BY 2,3-SIGMATROPIC SHIFT OF NON-STABILIZED SULFONIUM YLIDES. BARRIERS TO CHIRAL INVERSION IN *trans*-THIACYCLOALK-4-ENES.

E. Sandri, V. Ceré, C. Paolucci, S. Pollicino, L. Lunazzi, and A. Fava.

Istituto di Chimica Organica, Università di Bologna, Bologna, Italy

The experimental conditions will be discussed under which unstabilized sulfonium ylides generated in situ from 2-vinyl substituted cyclic sulfonium salts may undergo 3-carbons ring expansion to give thiacycloalk-4-enes:



For  $n = 1$ , the *cis* olefin normally predominates (40 to 95%), while for  $n \geq 2$  the *trans* olefin is the nearly exclusive product. The relation between the stereochemistry of the starting sulfonium salt and that of the product olefin will be discussed.

When  $R \neq H$ , two diastereomeric *trans*-2-R-cycloalk-4-enes are formed, indicating restricted conformational inversion around the chiral plane arising from the *trans* double bond. For  $n = 1$  (8-membered ring) the two diastereoisomers are capable of separate existence and their interconversion has been followed by conventional kinetics. For the larger rings the barriers to chiral inversion can be obtained by dynamic  $^1H$  and/or  $^{13}C$  NMR. These inversion barriers will be discussed and compared with those of the corresponding carbocyclics.