

This article was downloaded by:

On: 28 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>

## Asymmetric Polyene Cyclization Via Episulfonium Ion

Hiroshi Kosugi; Hiroshi Tanaka; Issei Tsukamoto; Michiharu Kato

**To cite this Article** Kosugi, Hiroshi , Tanaka, Hiroshi , Tsukamoto, Issei and Kato, Michiharu(1999) 'Asymmetric Polyene Cyclization Via Episulfonium Ion', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 153: 1, 311 – 312

**To link to this Article:** DOI: 10.1080/10426509908546446

**URL:** <http://dx.doi.org/10.1080/10426509908546446>

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.

## Asymmetric Polyene Cyclization Via Episulfonium Ion

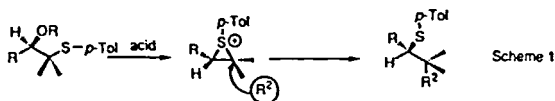
HIROSHI KOSUGI, HIROSHI TANAKA, ISSEI TSUKAMOTO and  
MICHIHARU KATO

*Institute for Chemical Reaction Science, Tohoku University Katahira 2-1-1,  
Aoba-ku, Sendai 980-8577 Japan*

Treatment of enantiomerically pure  $\beta$ -acetoxy sulfides, having alkene functionality in the side chain, with  $\text{SnCl}_4$  or  $\text{TMSOTf}$ , resulted in a stereoselective cyclization by a reaction initiated by an episulfonium cation.

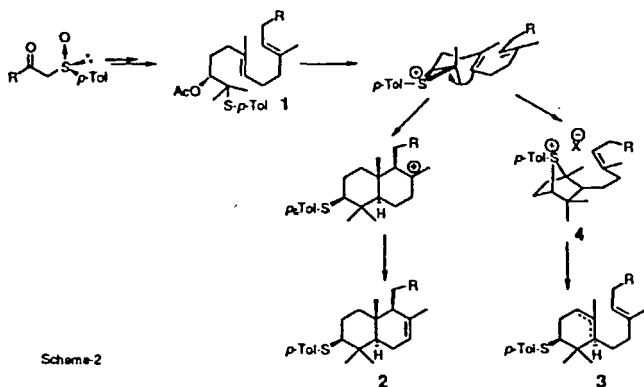
**Keywords:** polyene cyclization;  $\beta$ -acetoxy sulfide; episulfonium cation; sulfonium salt

Cationic polyene cyclization has become widely utilized for the synthesis of naturally occurring ring systems. However the chiral version of this methodology is limited only to use of chiral epoxides or acetals as the initiating group. Here we report the first examples of chiral polyene cascade cyclizations initiated by a "chiral" episulfonium ion (Scheme 1).

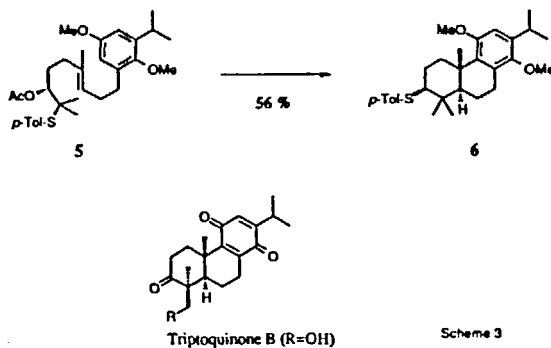


Chiral  $\beta$ -oxy sulfides **1** as the substrates for the cyclization reaction were readily prepared from the corresponding  $\beta$ -keto sulfoxides as reported earlier [1]. When **1** ( $\text{R}=\text{SO}_2\text{Ph}$ ) was subjected to cyclization with  $\text{SnCl}_4$  in  $\text{CH}_2\text{Cl}_2$ , the enantiomerically pure bicyclic product **2** was obtained in 58% yield along with the monocyclic product **3**. It is worth to note that the monocyclic products **3** were derived, during alkaline work-up, from a bridged sulfonium salt **4** which was formed by intramolecular trapping of a tertiary cation by the tolylthio group. The formation of the sulfonium salt **4** is confirmed by the NMR study of a model

compound (Scheme 2).



Application of the process to  $\beta$ -acetoxy sulfide **5** yields the tricyclic compound **6**, a promising intermediate for the synthesis of triptoquinones, a novel diterpenoid quinone with significant inhibitory activity against interleukin-1 release<sup>[2]</sup> (Scheme 3).



## References

- [1] H. Kosugi, O. Kanno, and H. Uda, *Tetrahedron: Asymmetry*, **1994**, *5*, 1139–1142.
- [2] Y. Takahashi, K. Shishido, N. Wariishi, M. Shibuya, K. Goto, M. Kido, and Y. Ono, *Tetrahedron Lett.*, **1992**, *33*, 7177.