

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>

## Carbon-Carbon Bond Formation Using Alkenylsulfides

Keiji Tanino; Isao Kuwajima

**To cite this Article** Tanino, Keiji and Kuwajima, Isao(1997) 'Carbon-Carbon Bond Formation Using Alkenylsulfides', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 120: 1, 369 — 370

**To link to this Article:** DOI: 10.1080/10426509708545553

**URL:** <http://dx.doi.org/10.1080/10426509708545553>

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.

## Carbon-Carbon Bond Formation Using Alkenylsulfides



KEIJI TANINO and ISAO KUWAJIMA\*

*Department of Chemistry, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan*

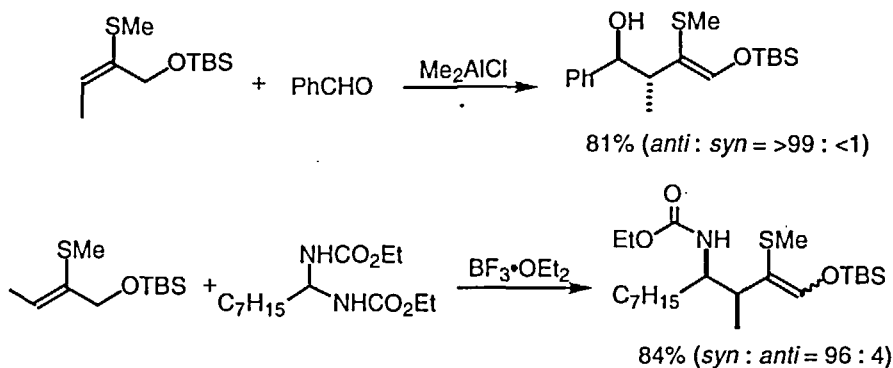
Highly stereoselective C-C bond forming reactions were developed on the basis of nucleophilic addition of alkenylsulfides to aldehydes, imines, and  $\alpha,\beta$ -unsaturated carbonyl compounds.

**KEY WORDS:** ene reaction, diastereoselection, Lewis acid

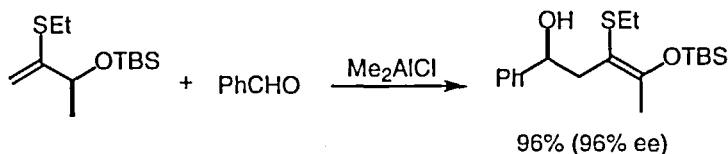
Although nucleophilic addition of enol ethers to electrophiles has been found widespread use in organic synthesis, much less attention has been given to alkenylsulfides as a nucleophile. The HOMO energy level of an alkenylsulfide is even higher than that of an enol ether. On the other hand, alkenylsulfides also show electrophilic character which is attributable to low LUMO energy level.

 SMe	Energy Levels* (eV)	 OMe	Energy Levels* (eV)	
	HOMO -8.69		HOMO -9.52	
	LUMO 0.32		LUMO 1.30	*calculated by PM3.

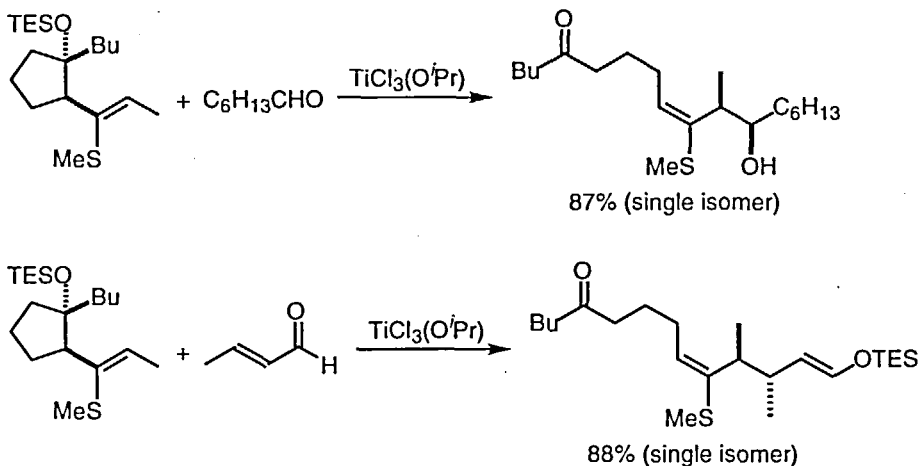
On the basis of these characteristic features of alkenylsulfides, we designed 2-(alkylthio)allyl silyl ethers to develop a carbonyl ene reaction which is applicable to a wide range of aldehydes. Under the influence of  $\text{Me}_2\text{AlCl}$ , the reactions of 2-(methylthio)crotyl silyl ether with aldehydes afforded corresponding adducts with high diastereoselectivity.<sup>1</sup> A highly stereoselective ene reaction of aldimines was also achieved by using geminal biscarbamates as enophiles.<sup>2</sup>



On the other hand, optically active products were obtained through chirality transfer by the reaction of an optically pure ene substrate.<sup>3</sup>



A novel method involving intermolecular C-C bond formation and C-C bond cleavage was also developed utilizing the propensity of alkenylsulfides to undergo double-bond shifts.<sup>4</sup> The diastereoselectivity of the reaction with an aldehyde could be explained by assuming the cyclic transition state which imposes coordination of both carbonyl oxygen and sulfur to the titanium atom.



## REFERENCES

- (a) K. Tanino, T. Nakamura, and I. Kuwajima, *Tetrahedron Lett.*, **31**, 2165 (1990). (b) T. Nakamura, K. Tanino, and I. Kuwajima, *Chem. Lett.* 1425 (1992). (c) T. Nakamura, K. Tanino, and I. Kuwajima, *Tetrahedron Lett.*, **34**, 477 (1993).
- (a) Y. Tohyama, K. Tanino, and I. Kuwajima, *J. Org. Chem.*, **59**, 518 (1994). (b) K. Sato, T. Koga, K. Masuya, K. Tanino, and I. Kuwajima, *Synlett*, *in press*.
- (a) K. Tanino, H. Shoda, T. Nakamura, and I. Kuwajima, *Tetrahedron Lett.*, **33**, 1337 (1992). (b) A. Adachi, K. Masuya, K. Tanino, and I. Kuwajima, *J. Org. Chem.*, **58**, 4189 (1993). (c) K. Masuya, K. Tanino, and I. Kuwajima, *Tetrahedron Lett.*, **35**, 7965 (1994).
- (a) M. Takayanagi, N. Umamori, K. Tanino, and I. Kuwajima, *J. Am. Chem. Soc.*, **115**, 12635 (1993). (b) M. Takayanagi, K. Tanino, and I. Kuwajima, *Synlett*, 173 (1995).