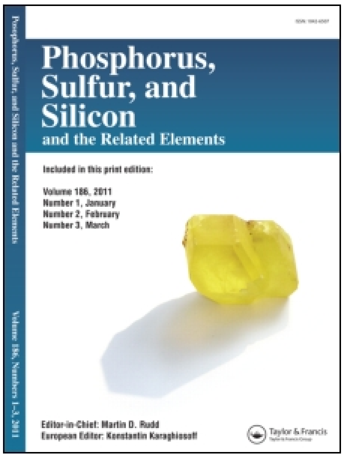


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Stereo- and Site-Selectivity in the Reaction of Chiral Episelenonium Ion with Carbon Nucleophile

Akio Toshimitsu[a]
[a] International Innovation Center, Kyoto University, Yoshida, Sakyo-ku, Kyoto, Japan

To cite this Article Toshimitsu, Akio(2005) 'Stereo- and Site-Selectivity in the Reaction of Chiral Episelenonium Ion with Carbon Nucleophile', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 3, 935 — 937

To link to this Article: DOI: 10.1080/10426500590906463

URL: http://dx.doi.org/10.1080/10426500590906463

Phosphorus, Sulfur, and Silicon, 180:935–937, 2005

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500590906463

Stereo- and Site-Selectivity in the Reaction of Chiral Episelenonium Ion with Carbon Nucleophile

Akio Toshimitsu
International Innovation Center, Kyoto University, Yoshida,
Sakyo-ku, Kyoto, Japan

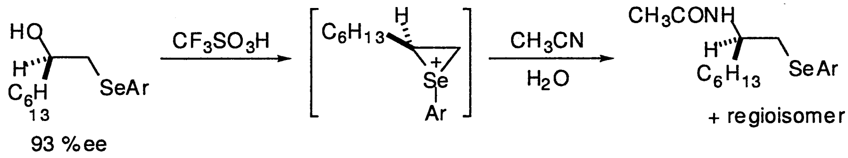
*There are two important aspects in the reaction of chiral episelenonium ion (episelenonium ion bearing chiral carbon in the three-membered ring) with carbon nucleophile; namely, (1) whether the chiral carbon racemizes during the reaction or not, and (2) the carbon nucleophile attacks the carbon atom (carbophilic attack) or selenium atom (selenophilic attack) in the three-membered ring. When carbon nucleophile such as alkenyl silyl ethers, trimethylsilyl cyanide, and allyltrimethylsilane are employed, steric protection of the selenium atom by the attachment of tri-*tert*-butylphenyl (TTBP) group to the selenium atom is inevitable to avoid both of the racemization of the chiral carbon atom and selenophilic attack of the carbon nucleophile. When aromatic compounds are employed as carbon nucleophile, on the other hand, selenophilic attack is rarely observed irrespective of the nature of the aryl group on the selenium atom and introduction of electron withdrawing group into the aryl group on the selenium atom is effective to retard the racemization of the chiral carbon atom.*

Keywords 2-Pyridylseleno group; 2,6-*bis*(trifluoromethyl)phenyl-seleno group; carbon-carbon bond formation; chiral episelenonium ion; phenylseleno group; tri-*tert*-butylphenylseleno group

RACEMIZATION OF CHIRAL CARBON

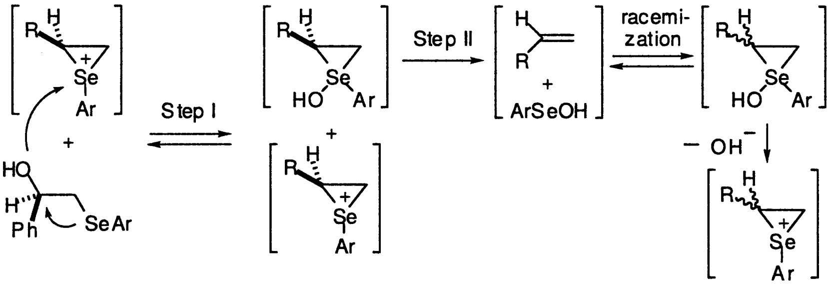
The mechanism of the racemization of the chiral carbon atom in the episelenonium ion intermediate was elucidated by the Ritter-type reaction of chiral alcohol bearing arylseleno group on the adjacent carbon atom in the presence of trufluoromethanesulfonic acid in acetonitrile as solvent (Scheme 1).[1] The important results are as follows: (1) enantiomeric excesses of the produced amide are better when the reactions are carried out at lower concentration of the reactant and when the chiral alcohol is added to the solution of the acid, and (2) enantiomeric excesses of the amide are better when bulky substituents are introduced

Received January 7, 2004; accepted October 1, 2004.
Address correspondence to Akio Toshimitsu, Kyoto University, International Innovation Center, Sakyo-ku, Kyoto 606-8501, Japan. E-mail: akiot@iic.kyoto-u.ac.jp



SCHEME 1

into the ortho-position of the aryl grop attached to the selenium atom or when electron-deficient aryl group was attached to the selenium atom. These results clearly indicate that the racemization does not proceed by the unimolecular reaction. It is highly probable that the racemization proceed by the contact of chiral episelenonium ion with starting alcohol. The attack of a certain nucleophile at the selenium atom and the formation of cationic selenium species seem to be included in the racemization. Based on these results, possible mechanism is proposed as shown in Scheme 2. Bulky substituent at the ortho position of the aryl group (TTBP group) seems to inhibit the step I and electron deficient aryl group (2,6-*bis*(trifluoromethyl)phenyl and 2-pyridyl group) seem to retard both of step I and II.



SCHEME 2

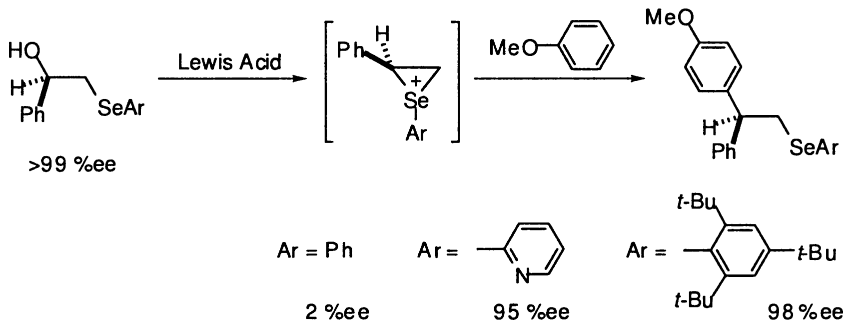
SITE-SELECTIVITY

Based on the results described above, the reaction of alcohol bearing TTBP- or *bis*(trifluorophenyl)phenylseleno group on the adjacent carbon atom with alkenyl silyl ether in the presence of Lewis acid were carried out. The carbon-carbon bond formation products were obtained selectively when TTBP group was present on the selenium atom, indicating that selenophilic attack of the carbon nucleophile was completely inhibited. In the case of episelenonium ion bearing *bis*(trifluorophenyl)phenyl group on the selenium atom, considerable amount of product due to the selenophilic attack was obtained.[3]

Thus, the reactions of chiral episelenonium ion bearing TTBP group on the selenium atom with other carbon nucleophile such as trimethylsilyl cyanide and allyltrimethyl-silane were carried out. It was confirmed that carbon nucleophiles selectively attacked on the carbon atom of the episelenonium ion without loss of the enantiomeric excesses of the chiral carbon atom.[2]

THE REACTION WITH AROMATIC COMPOUNDS

When aromatic compound such as anisole was employed as carbon nucleophile, selenophilic attack is rarely observed irrespective of the nature of the aryl group on the selenium atom. Enantiomeric excesses of the products, on the other hand, were found to depend greatly on the nature of the aryl group on the selenium atom. Thus, when phenyl group is attached to the selenium atom, the chiral carbon almost completely racemized during the reaction. When 2-pyridyl or TTBP group is attached to the selenium atom, optical purity was not lost during the substitution reaction (Scheme 3).



SCHEME 3

REFERENCES

[1] A. Toshimitsu, M. Ito, and S. Uemura, *J. Chem. Soc., Chem. Commun.*, 530 (1989).
[2] A. Toshimitsu, K. Nakano, T. Mukai, and K. Tamao, S., *J. Am. Chem. Soc.*, **118,** 2756 (1996).
[3] A. Toshimitsu, K. Nakano, and K. Tamao, S., *Phosphorus Sulphur, and Silicon*, **136–138,** 649 (1998).