

Activation of Sn-Se Bond: Regioselective Ring Opening Reaction of Epoxides with Tributylstannyl Phenylselenolate in the Presence of a Lewis Acid

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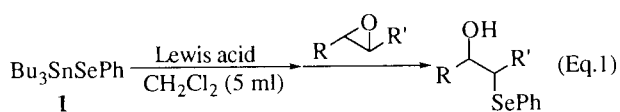
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When tributylstannyl phenylselenolate (Bu_3SnSePh) was allowed to react with epoxides in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ as a Lewis acid, the ring opening reaction of epoxides proceeded with complete regioselectivity to afford the β -hydroxy phenylselenides in moderate to good yields.

Recently, the synthesis of various organoselenium compounds possessing selenium-metal bonds such as Se-Al, Se-B, Se-Si, and Se-Sn has been reported, and there has been a considerable interest in the development of the synthetic reactions based on the characteristic features of these compounds.¹ However, the synthetic applications of organoselenium compounds having a Se-Sn bond still remain unexploited due to the lack of methods for activation of the selenium-tin bond.^{2,3}

We recently reported that the reaction of tributylstannyl phenylselenolate (Bu_3SnSePh) (**1**) with acetals gave monoselenoacetals in the presence of a Lewis acid.^{2a} During the course of our study on the utilization of compound **1**, we found that this reaction system, Bu_3SnSePh /Lewis acid, can be used for the regioselective transformation of epoxides to the corresponding β -hydroxy phenylselenides (Eq. 1).⁴



To a CH_2Cl_2 (5 ml) solution of tributylstannyl phenylselenolate (**1**) (0.5 mmol) and a small excess amount of $\text{BF}_3 \cdot \text{OEt}_2$ (1.2 equiv.), 1,2-epoxyoctane (**2**) (0.5 mmol) was added at -78°C and the solution was stirred at that temperature for 30 min. After workup, 1-(phenylseleno)-2-octanol (**3**), in which the phenylseleno group was introduced at the terminal carbon, was isolated in 86 % yield by column chromatography on silica gel, while the formation of the regioisomer, 1-hydroxy-2-phenylselenooctane (**4**), was not detected.

The results of the reaction of 1,2-epoxyoctane (**2**) with tributylstannyl phenylselenolate (**1**) using various Lewis acids are summarized in Table 1. Among the several Lewis acids screened, we found that $\text{BF}_3 \cdot \text{OEt}_2$ was the most effective (Run 1). In the presence of $\text{BF}_3 \cdot \text{OEt}_2$, the yield of **3** increased at the lower reaction temperature (-78°C) (Runs 1-3). The use of other Lewis acids such as SnCl_2 , AlCl_3 , Et_2AlCl , and EtAlCl_2 also gave the β -hydroxy phenylselenides **3** with excellent regioselectivity, but the yields of **3** were around 40 % (Runs 6-9). When TMSOTf was used as the Lewis acid, the starting materials were recovered in almost quantitative yields (Run 4). In contrast, the use of TiCl_4 led to several side reactions (Run 5).

It is interesting to note that the yield of the product is significantly influenced by the order of the addition of the epoxide and **1**. The reaction of **1** with $\text{BF}_3 \cdot \text{OEt}_2$ in CH_2Cl_2 followed by the addition of the epoxide provided **3** in 86 % yield (Run 3 in

Table 1. The effect of Lewis acid on the reaction of tributylstannyl phenylselenolate (Bu_3SnSePh) (**1**) with 1,2-epoxyoctane (**2**)

$\text{Bu}_3\text{SnSePh} \xrightarrow[\text{CH}_2\text{Cl}_2 (5 \text{ ml})]{\text{Lewis acid (0.6 mmol)}}$		$\xrightarrow{(0.5 \text{ mmol})} \text{O}$	
1		2	
$\text{CH}_2\text{Cl}_2 (5 \text{ ml})$		rt., 30 min.	
$\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{SePh}$		$\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{SePh}$	
3		4	
Run	Lewis acid	Yield/% ^{a,b}	
		3	4
1	$\text{BF}_3 \cdot \text{OEt}_2$	53	0
2 ^c	$\text{BF}_3 \cdot \text{OEt}_2$	70	0
3 ^d	$\text{BF}_3 \cdot \text{OEt}_2$	86	0
4	TMSOTf	No reaction	
5	TiCl_4	Complex mixture	
6	SnCl_2	21	0
7	AlCl_3	39	0
8	EtAlCl_2	27	0
9	Et_2AlCl	40	0

^aIsolated yield. ^bSelectivity was determined by 400MHz $^1\text{H-NMR}$. ^c -20°C . ^d -78°C .

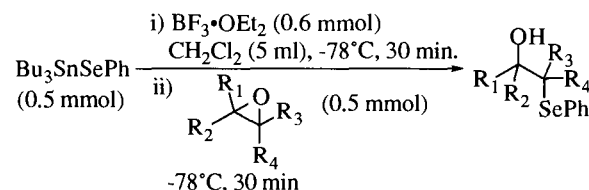
Table 1). In contrast, when $\text{BF}_3 \cdot \text{OEt}_2$ was first added to the CH_2Cl_2 solution of the epoxide followed by the addition of **1**, starting materials were almost quantitatively recovered.

Results of the reaction of **1** with various epoxides in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ at -78°C are shown in Table 2. When 1,2-epoxypropane and 1,2-epoxy-2-methylpropane were reacted with **1**, the corresponding 1-phenylseleno-2-hydroxyalkanes were obtained in 67 and 65 % yields, respectively, with complete regioselectivity (Runs 1 and 2). The reaction of 1,2-epoxycyclohexane or *cis*-2,3-epoxybutane with **1** stereospecifically gave *trans*-2-(phenylseleno)cyclohexanol or *threo*-3-(phenylseleno)-2-butane in moderate yields (Runs 3 and 4). The conversion of 1,2-epoxy-5-hexene and 1,2-epoxy-3-phenoxypropane to the corresponding β -hydroxy phenylselenides were successfully achieved without

affecting the carbon-carbon double bond and ether functions (Runs 6 and 7). It is interesting to note that the epoxide having a hydroxy group was also converted into the corresponding *vic*-diol derivative in moderate yield (Run 8).

The conversion of styrene oxide to the corresponding β -hydroxyphenylselenide has already been described,^{5c-d} however, there are a few examples on the regioselective ring opening reaction of styrene oxide with organoselenium compounds. In present case, the reaction of **1** with styrene oxide proceeded with complete regioselectivity to afford 1-phenyl-2-(phenylseleno)ethanol in 60% yield (Run 5).

Table 2. $\text{BF}_3 \cdot \text{OEt}_2$ Assisted reaction of Bu_3SnSePh with various epoxide



Run	Epoxide	Yield/% ^{a,b}
1	$\text{R}_1 = \text{CH}_3, \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{H}$	67
2	$\text{R}_1 = \text{R}_2 = \text{CH}_3, \text{R}_3 = \text{R}_4 = \text{H}$	31
3	$\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_4 = (\text{CH}_2)_4$	39
4 ^c	$\text{R}_1 = \text{R}_3 = \text{CH}_3, \text{R}_2 = \text{R}_4 = \text{H}$	60 ^d
5	$\text{R}_1 = \text{Ph}, \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{H}$	87
6	$\text{R}_1 = \text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ $\text{R}_2 = \text{R}_3 = \text{R}_4 = \text{H}$	78
7	$\text{R}_1 = \text{PhOCH}_2, \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{H}$	50
8	$\text{R}_1 = \text{HOCH}_2, \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{H}$	60

^aIsolate yield. ^bRegioisomer was not observed by 400MHz ^1H -NMR. ^c*cis*-2,3-Epoxybutane was used. ^d*Threo* isomer was formed.

Though the details of the reaction mechanism remain unclear at the present time, the results obtained from the present work indicate that this reaction is sensitive to steric hindrance. We therefore propose that the ring opening is likely to involve an $\text{S}_{\text{N}}2$ -like cleavage of the C-O bond by the selenium species generated *in situ* from **1** and Lewis acid.^{6,7}

Further investigations on the utilization of this reagent and the reaction mechanism are now in progress.

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References and Notes

- 1 A. Krief and L. Hevesi, in "Organoselenium Chemistry," Springer Verlag, Berlin (1988), Vol. 1; b) C. Paulmier, in "Selenium Reagents and Intermediates in Organic Synthesis," Pergamon Press, Oxford, (1986); S. Patai and Z. Rappoport, in "The Chemistry of Organic Selenium and Tellurium Compounds," Vol. 1 and 2, 1986. c) K. Shimada, N. Jin, M. Kawaguchi, K. Dobashi, Y. Nagano, M. Fujimura, E. Kudoh, T. Kai, N. Saito, J. Masuda, M. Iwaya, H. Fujisawa, S. Aoyagi, and Y. Takikawa, *Bull. Chem. Soc. Jpn.*, **70**, 197 (1997) and references cited therein.
- 2 a) Y. Nishiyama, S. Aoyama, and S. Hamanaka, *Phosphorus, Silicon, and Sulfur*, **65** 1245 (1993); b) K. Shimada, S. Okuse, and Y. Takikawa, *Bull. Chem. Soc. Jpn.*, **65**, 2848 (1992). c) M. Segi, A. Kojima, T. Nakajima, and S. Suga, *Tetrahedron Lett.*, **32**, 7427 (1991). d) M. Segi, A. Kojima, T. Nakajima, and S. Suga, *Synlett*, **1991**, 105. e) D. N. Harpp and M. Gingras, *J. Am. Chem. Soc.*, **110**, 7737 (1988). f) K. Steliou and M. Mrani, *J. Am. Chem. Soc.*, **104**, 3104 (1982). g) M. Baudler, H. Suchomel, G. Fuerstenberg, and O. Schings, *Angew. Chem.*, **93**, 1087 (1981). h) B. C. Crosse and G. V. Hutson, *J. Chem. Soc. (A)* **1967**, 2014.
- 3 The bond energy of the Se-Sn bond is $D_{298}^0 = 98.2 \pm 3$ kcal/mol. See: K. C. M. Ho, in "Thermodynamic Data for Inorganic Sulfides, Selenides, and Tellurides" Rechood Press, England (1974), p. 594.
- 4 The reaction of epoxides with organoselenium reagents has already been reported.⁵ However, many of these reactions suffer from lack of generality and poor regioselectivity.
- 5 a) N. Y. Derkach, N. A. Pasmurtseva, and E. S. Levchenko, *Zh. Org. Khim.*, **7**, 1543 (1971). b) K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, **95**, 2697 (1973). c) M. R. Detty, *Tetrahedron Lett.*, **1978**, 5087. d) N. Miyoshi, K. Kondo, S. Murai, N. Sonoda, *Chem. Lett.*, **1979**, 909. e) A. Cravador and A. Krief, *Tetrahedron Lett.*, **26**, 2491 (1981).
- 6 J. March, in "Advanced Organic Chemistry; Reactions, Mechanisms, and Structure" 4th ed., John Wiley & Sons, Inc. (1992), p. 368-369.
- 7 The ZnI_2 -catalyzed ring opening reaction of styrene oxide with PhSeSiMe_3 has already been reported by N. Sonoda *et al.* However, in this reaction, 2-phenyl-2-(phenylseleno)ethanol, in which the phenylseleno group was introduced at the inner carbon, was formed in 83 % yield.^{5d} They suggested that this reaction proceeded *via* the partially stabilized carbonium ion (**5**) to afford 2-phenyl-2-(phenylseleno)ethanol.

