

Jr. J. W. *Tetrahedron Lett.* 1985, 26, 1395.

6. Walker, K. A. M. *Tetrahedron Lett.* 1977, 4475.

7. **13**: mp 168.5-169.5 °C. IR (KBr); 1710 cm^{-1} . ^1H NMR (300 MHz, CDCl_3); δ 3.24-3.49 (m, 3H), 3.60 (dd, 1H, $J=9.6$ Hz, $J=5.4$ Hz), 4.68 (d, 1H, $J=5.4$ Hz), 6.81-7.54 (m, 14H). ^{13}C NMR (75 MHz, CDCl_3); δ 28.33, 38.59, 45.73, 50.88, 126.59, 126.93, 126.99, 128.01, 128.22, 128.47, 128.73, 128.99, 129.16, 131.87, 133.26, 134.24, 134.89, 136.90, 175.59, 178.04. **16**: IR (thin film); 1738 cm^{-1} . ^1H NMR (300 MHz, CDCl_3); 2.85 (dd, 1H, $J=17.1$ Hz, $J=11.9$ Hz), 3.09 (s, 3H), 3.22 (dd, 1H, $J=17.1$ Hz, $J=6.3$ Hz), 3.26 (dd, 1H, $J=11.6$ Hz, $J=3.7$ Hz), 3.61 (ddd, 1H, $J=11.9$ Hz, $J=11.6$ Hz, $J=6.3$ Hz), 3.75 (s, 3H), 3.88 (s, 3H), 5.19 (d, 1H, $J=3.7$ Hz), 6.68-7.57 (m, 8H). ^{13}C NMR (75 MHz, CDCl_3); δ 31.86, 37.70, 45.16, 46.65, 51.04, 52.04, 55.52, 108.27, 120.65, 124.28, 127.08, 128.50, 132.37, 133.65, 134.65, 136.11, 156.42, 171.40, 175.88.

Regio- and Stereoselective Oxyselenenylation of Allylic Alcohol and Its Derivatives

Kwan Soo Kim*, Ji Young Kim, Heung Bok Park,
and In Howa Jeong†

*Department of Chemistry, Yonsei University,
Seoul 120-749, Korea*

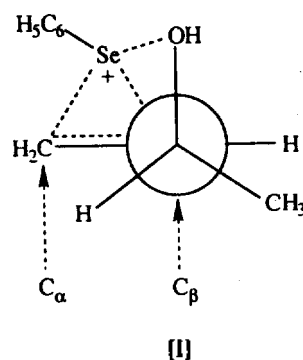
*†Department of Chemistry, Yonsei University,
Wonju 220-710, Korea*

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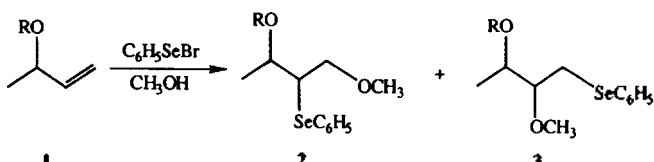
The electrophilic addition reaction of olefins with selenium species is of considerable interest with respect to the regio- and stereochemical outcome of this reaction¹⁻⁵ and versatile synthetic transformations of the phenylseleno group in the resultant product.⁶ A couple of reports^{2,5} showed that the phenylselenenyl chloride addition to allylic alcohols was performed in a highly regio- and stereoselective manner. Especially, the regio- and stereoselectivity are remarkably controlled in terminal acyclic allylic and cyclic allylic alcohol systems. However, the addition of phenylselenenyl chloride to internal acyclic allylic alcohol system afforded a relatively poor regioselectivity. In contrast to the systematic study of chloroselenylation to allylic alcohol systems, the oxyselenenylation to olefins is limited to the addition reaction of cyclic and acyclic olefins substituted by the alkyl or phenyl group.⁷⁻¹² The solvent plays an important role in the formation of regioisomers in the oxyselenenylation of cyclic system,¹² but the regiochemical outcome in the oxyselenenylation of acyclic system is affected by the steric hindrance or temperature.^{2,9} In spite of the synthetic importance of oxyselenenylation in olefin systems, much less attention has been paid to the oxyselenenylation of allylic alcohol systems which can be a potentially useful synthetic tool for the formation of regio- and stereocontrolled 1,2- or 1,3-diol compounds.^{13,14} Although the hydroxyselenenylation of 3-acetoxycyclohexene with *N*-phenyl-

selenophthalimide in the presence of water and that of allylic alcohols with phenylselenenyl chloride in the presence of water were studied in recent years, the oxyselenenylation of acyclic allylic alcohol derivatives has not been reported yet, specially from the regio- and stereochemical point of view.^{15,16} In this communication, we wish to describe a regio- and stereochemical aspect in the oxyselenenylation of acyclic allylic alcohol derivatives with phenylselenenyl bromide in methanol.

The first examination of the oxyselenenylation was performed on terminal allylic alcohols. When the reaction of 3-buten-2-ol (**1a**) with phenylselenenyl bromide was performed in CH_2Cl_2 solvent containing 10 equiv. of methanol at 25 °C, the oxyselenenylation adducts **2a**, **3a** and bromoselenenylation adducts were obtained in a 40 : 3 : 57 ratio. Despite the high regioselectivity between oxyselenenylation adducts **2a** and **3a** (93 : 7) was shown, the formation of bromoselenenylation adduct was a serious drawback. However, the treatment of allylic alcohol **1a** with phenylselenenyl bromide in methanol solvent at 25 °C produced an anti-Markovnikov adduct **2a** and a Markovnikov adduct **3a** in 49% yield (**2a** : **3a** = 93 : 7).^{17,18} The bromoselenenylation product was not observed in this reaction and the isomerization of **2a** to **3a** did not occur at all under the employed reaction condition. The regioselectivity of this reaction sharply contrasts to that obtained from the chloroselenenylation of terminal allylic alcohols at 25 °C, which afforded only Markovnikov adduct.⁵ The high regioselectivity can be understood in terms of the steric hindrance between the attacking methanol and seleniranium ion intermediate [I] which was also suggested in the hydroxyselenenylation of allylic alcohols.¹⁶ Therefore, it is expected that the nucleophilic methanol attacks at the less hindered carbon site (C_α) rather than C_β .

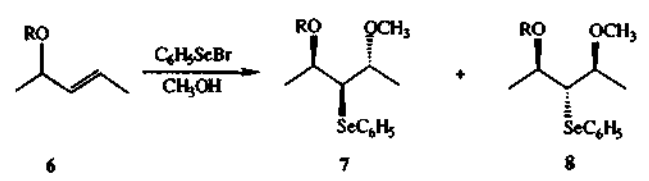


The same reaction at a raised temperature (60 °C) provided the relatively poor regioselectivity (**2a** : **3a** = 81 : 19). Therefore, the similar treatment of other allylic alcohols with phenylselenenyl bromide was carried in methanol solvent at 25 °C. When 3-acetoxy-1-butene (**1b**) was reacted with phenylselenenyl bromide under the suggested reaction condition, an anti-Markovnikov adduct **2b** and a small amount of the bromoselenenylation adduct were isolated in 18% and 0.5% yield, respectively, although the improved regioselectivity was shown. The other regioisomer **3b** was not detected. The isolation of bromoselenenylation adduct indicates that the seleniranium ion intermediate formed during methoxyselenenylation was in equilibrium somewhat with bromoselenenylation adduct. The formation of **2b** in a relatively low yield may be due

Table 1. Oxyseleenylation of terminal allylic alcohols with phenylselenenyl bromide in methanol at 25 °C


Compound No.	R	Product (ratio)	Yield (%) ^a
1a	H	2a : 3a (93 : 7)	49
1b	CH ₃ C(O)	2b : 3b (100 : 0) ^b	18
1c	C ₆ H ₅ CH ₂	2c : 3c (100 : 0)	79

^aIsolated yield. ^bA small amount (0.5%) of bromoselenation adducts are isolated.

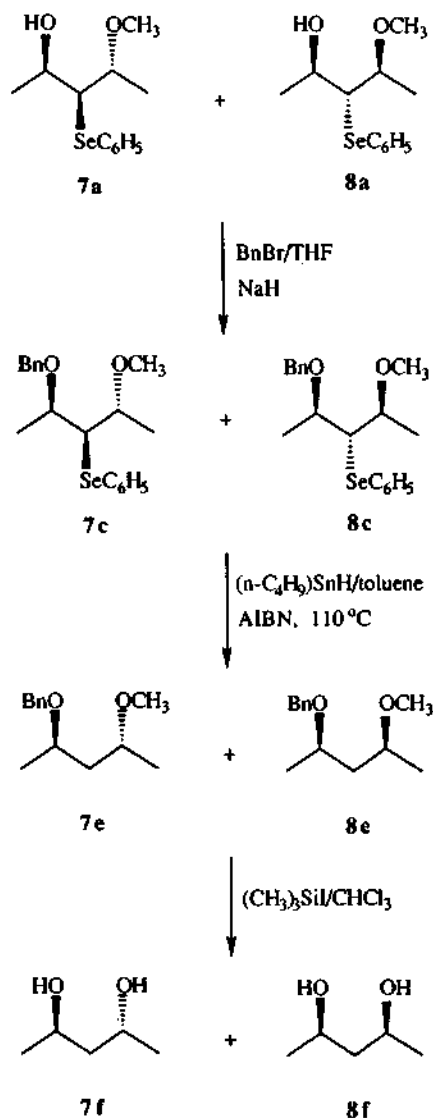
Table 2. Oxyseleenylation of internal allylic alcohols with phenylselenenyl bromide in methanol at 25 °C


Compound No.	R	Product (ratio) ^a	Yield (%) ^b
6a	H	7a : 8a (92 : 8)	73
6b	CH ₃ C(O)	7b : 8b (87 : 13)	55
6c	C ₆ H ₅ CH ₂	7c : 8c (90 : 10)	93
6d	CH ₃ OC ₂ H ₅ OCH ₂	7d : 8d (95 : 5)	80

^aThe ratio was determined by comparison with ¹H NMR of authentic sample after conversion to 1,3-diol compounds. ^bIsolated yield.

to the participation of acetoxy group toward the seleniranium ion intermediate. The systematic study on this possibility is now underway. However, the oxyseleenylation of 3-benzyloxy-1-butene (1c) with phenylselenenyl bromide resulted in the formation of only anti-Markovnikov adduct 2c in 79% yield. Markovnikov adduct 3c and other regioisomers were not detected in this reaction. Results of the oxyseleenylation of terminal allylic alcohols are summarized in Table 1.

The oxyseleenylation of internal allylic alcohols under the suggested reaction condition are regioselective and stereoselective reaction. For example, the addition of phenylselenenyl bromide to (E)-3-penten-2-ol (6a) resulted in the formation of only stereoisomeric mixtures 7a and 8a in 73% yield (7a : 8a = 92 : 8). No other regioisomers were observed. This regioselectivity can be explained in the same manner which was mentioned in the oxyseleenylation of terminal allylic alcohols. The similar treatment of (E)-2-acetoxy-3-pentene (6b) with phenylselenenyl bromide in methanol at 25 °C afforded stereoisomeric mixture of 7b and 8b in 55% yield (7b : 8b = 87 : 13). The oxyseleenylation of (E)-2-benzyloxy-3-pentene (6c) and (E)-4-[(2-methoxyethoxy)methoxy]-2-pentene (6d) provided the similar results. Results of oxyseleenylation of nonterminal allylic alcohols are summarized in Table 2.

**Scheme 1.** Determination of stereochemistry of oxyseleenylation adducts.

The assignment of stereoisomers 7 and 8 was made by the comparison with ¹H NMR of authentic samples after the conversion to 1,3-diol compounds. Since the removal of phenylseleno group from adducts 7a, 7b, 8a, and 8b by using tributyltin hydride was not satisfied, we converted these compounds to 7c and 8c, in which the phenylseleno group can be easily removed by using tributyltin hydride. After the major isomer 7e¹⁹ was isolated from a stereoisomeric mixture (7e and 8e), the deprotection of 7e with trimethylsilyl iodide afforded the (2R, 4R)-pentanediol 7f²⁰ which was confirmed by comparison with ¹H NMR of authentic (2R, 4R)-pentanediol. Stereoisomers 7d and 8d were assigned in a similar manner as was in the case of 7c and 8c. The determination of stereochemistry of oxyseleenylation adducts was shown in Scheme 1.

The stereoselectivity in the oxyseleenylation of internal allylic alcohols can be rationalized in terms of the neighboring group participation by allylic oxygen and the conformational factor of seleniranium ion intermediate. There are four pos-

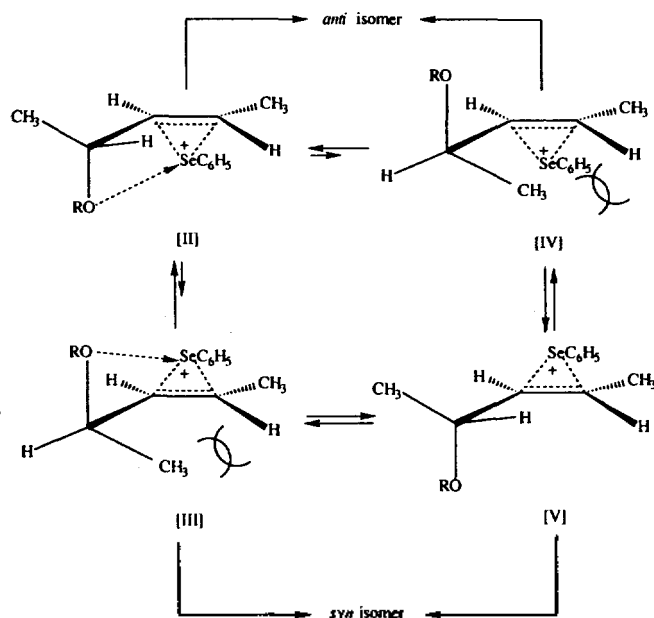


Figure 1. Four plausible conformations of seleniranium ion.

sible conformations [II], [III], [IV], and [V] which can be suggested. The relatively stable conformations involve the seleniranium ions [II] and [III] in which the seleno group is directed to the syn-face of oxygen, since the carbocation of seleniranium ion can be stabilized by the seleno-oxonium ion formation. However, the seleniranium ion [II] is more stable conformation than [III] because of the steric hindrance between the methyl group and proton in [III]. Consequently, the ring opening of [II] by the anti-addition of methanol at less hindered site C_a resulted in the formation of anti isomer. Four plausible conformations of seleniranium ion are shown in Figure 1.

In conclusion, the oxyselenylation of terminal allylic alcohols with phenylselenenyl bromide in methanol resulted in the different regiochemical outcome as comparing with oxymercuration and iodination. Generally, the oxymercuration of allylic alcohols produces Markovnikov adducts²¹ and the iodination of allylic alcohols provides a poor regioselectivity.²² In the case of the oxyselenylation of internal allylic alcohols, a high stereoselectivity as well as regioselectivity were observed. The high stereoselectivity can be understood in terms of the steric hindrance between attacking methanol and substituents in the stable conformer of seleniranium ion.

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- Compound 2a: ^1H NMR (300 MHz, CDCl_3) δ 7.61-7.57 (m, 2H), 7.29-7.25 (m, 3H), 4.13-4.11 (m, 1H), 3.76-3.73 (m, 2H), 3.36 (s, 3H), 3.33-3.28 (m, 1H), 2.89 (d, $J=3.6$ Hz, 1H), 1.35 (d, $J=6.3$ Hz, 3H).
- Compound 3a: ^1H NMR (300 MHz, CDCl_3) δ 7.56-7.53 (m, 2H), 7.29-7.25 (m, 3H), 4.05-4.01 (m, 1H), 3.43 (s, 3H), 3.36-3.31 (m, 1H), 3.17 (dd, $J=12.5, 7.0$ Hz, 1H), 3.06 (dd, $J=12.5, 5.2$ Hz, 2H), 2.01 (d, $J=3.3$ Hz, 1H), 1.17 (d, $J=6.6$ Hz, 3H).
- A stereoisomeric mixture, 7e and 8e: ^1H NMR (300 MHz, CDCl_3) δ 7.39-7.27 (m, 5H), 4.63 and 4.44 (ABq, $J=11.6$ Hz, 2H), 3.81-3.74 (m, 1H), 3.59-3.52 (m, 1H), 3.28 (s, 3H), 1.83-1.51 (m, 2H), 1.22 (d, $J=6.2$ Hz, 3H), 1.14 (d, $J=6.2$ Hz, 3H).
- Compound 7f: ^1H NMR (300 MHz, CDCl_3) δ 4.18 (s, $J=6.2$ Hz, 2H), 2.43-2.41 (bs, 1H), 1.61 (dd, $J=5.5, 5.5$ Hz, 2H), 1.24 (d, $J=6.3$ Hz, 6H).
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