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7. **13**: mp 168.5-169.5 ℃. 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 Oxyselenylation of Allylic Alcohol and It's 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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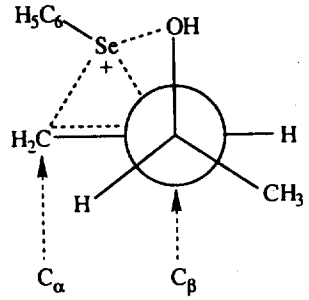
The electrophilic addition reaction of olefins with selenium species is of considerable interest with respect to the regio- and stereochemical outcome of this reaction[1~5] and versatile synthetic transformations of the phenylseleno group in the resultant product.[6] A couple of reports[2,5] showed that 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 oxyselenylation 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 oxyselenylation of cyclic system,[12] but the regiochemical outcome in the oxyselenylation of acyclic system is affected by the steric hindrance or temperature.[2,9] In spite of the synthetic importance of oxyselenylation in olefin systems, much less attention has been paid to the oxyselenylation 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 hydroxyselenylation of 3-acetoxycyclohexene with N-phenylselenophthalimide in the presence of water and that of allylic alcohols with phenylselenenyl chloride in the presence of water were studied in recent years, the oxyselenylation 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 oxyselenylation of acyclic allylic acohol derivatives with phenylselenenyl bromide in methanol.

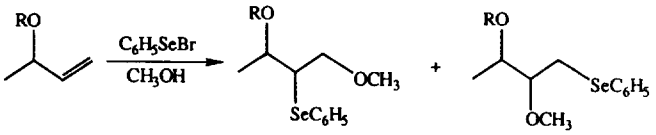
The first examination of the oxyselenylation was performed on terminal allylic alcohols. When the reaction of 3-buten-2-ol (**1a**) with phenylselenenyl bromide was performed in CH_2Cl_2 solvent containing 10 equiv. of methanol at 25 ℃, the oxyselenylation adducts **2a**, **3a** and bromoselenylation adducts were obtained in a 40 : 3 : 57 ratio. Despite the high regioselectivity between oxyselenylation adducts **2a** and **3a** (93 : 7) was shown, the formation of bromoselenylation adduct was a serious drawback. However, the treatment of allylic alcohol **1a** with phenylselenenyl bromide in methanol solvent at 25 ℃ produced an anti-Markovnikov adduct **2a** and a Markovnikov adduct **3a** in 49% yield (**2a** : **3a**=93 : 7).[17,18] The bromoselenylation 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 chloroselenylation of terminal allylic alcohols at 25 ℃, 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 hydroxyselenylation 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.



[I]

The same reaction at a raised temperature (60 ℃) provided the relatively poor regioselectivity (**2a** : **3a**=81 : 19). Therefore, the similar treatment of other allyic alcohols with phenylselenenyl bromide was carried in methanol solvent at 25 ℃. 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 bromoselenylation 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 bromoselenylation adduct indicates that the seleniranium ion intermediate formed during methoxyselenylation was in equilibrium somewhat with bromoselenylation adduct. The formation of **2b** in a relatively low yield may be due

Table 1. Oxyselenylation of terminal allylic alcohols with phenylselenenyl bromide in methanol at 25 ℃

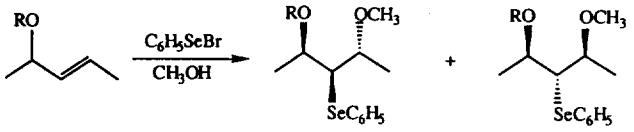


1 2 3

Compound No.	R	Product (ratio)	Yield (%)[a]
1a	H	**2a : 3a** (93 : 7)	49
1b	$CH_3C(O)$	**2b : 3b** (100 : 0)[b]	18
1c	$C_6H_5CH_2$	**2c : 3c** (100 : 0)	79

[a]Isolated yield. [b]A small amount (0.5%) of bromoselenation adducts are isolated.

Table 2. Oxyselenylation of internal allylic alcohols with phenylselenenyl bromide in methanol at 25 ℃



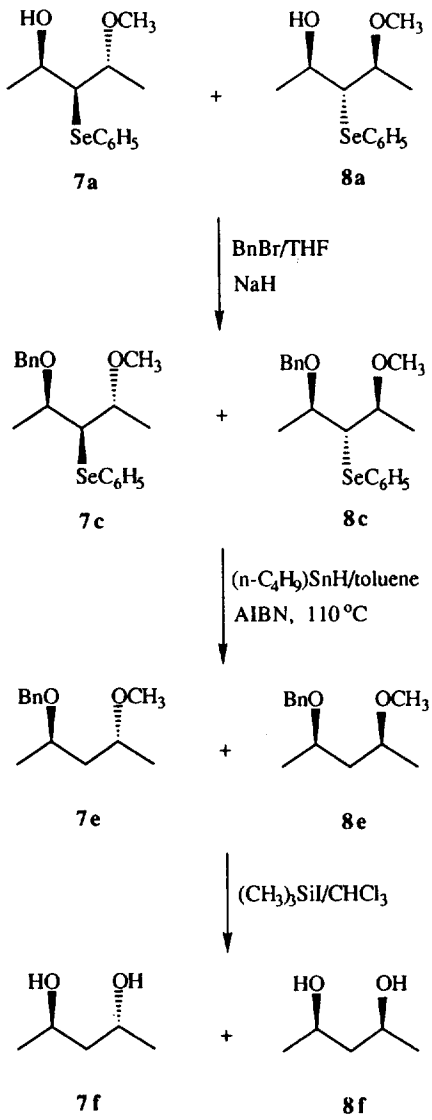
6 7 8

Compound No.	R	Product (ratio)[a]	Yield (%)[b]
6a	H	**7a : 8a** (92 : 8)	73
6b	$CH_3C(O)$	**7b : 8b** (87 : 13)	55
6c	$C_6H_5CH_2$	**7c : 8c** (90 : 10)	93
6d	$CH_3OC_2H_5OCH_2$	**7d : 8d** (95 : 5)	80

[a]The ratio was determined by comparison with ^1H NMR of authetnic sample after conversion to 1,3-diol compounds. [b]Isolated yield.

to the participation of acetyloxy group toward the seleniranium ion intermediate. The systematic study on this possibility is now underway. However, the oxyselenylation 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 oxyselenylation of terminal allylic alcohols are summarized in Table 1.

The oxyselenylation of internal allylic alcohols under the suggested reaction condition are regiospecific 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 regiospecificity can be explained in the same manner which was mentioned in the oxyselenylation of terminal allylic alcohols. The similar treatment of (E)-2-acetoxy-3-pentene (**6b**) with phenylselenenyl bromide in methanol at 25 ℃ afforded stereoisomeric mixture of **7b** and **8b** in 55% yield (**7b** : **8b**= 87 : 13). The oxyselenylation of (E)-2-benzyloxy-3-pentene (**6c**) and (E)-4-[(2-methoxyethoxy)methoxy]-2-pentene (**6d**) provided the similar results. Results of oxyselenylation of nonterminal allylic alcohols are summarized in Table 2.



Scheme 1. Determination of stereochemistry of oxyselenylation 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 **7e**[19] was isolated from a stereoisomeric mixture (**7e** and **8e**), the deprotection of **7e** with trimethylsilyl iodide afforded the (2R, 4R)-pentanediol **7f**[20] 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 oxyselenylation adducts was shown in Scheme 1.

The stereoselectivity in the oxyselenylation 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-

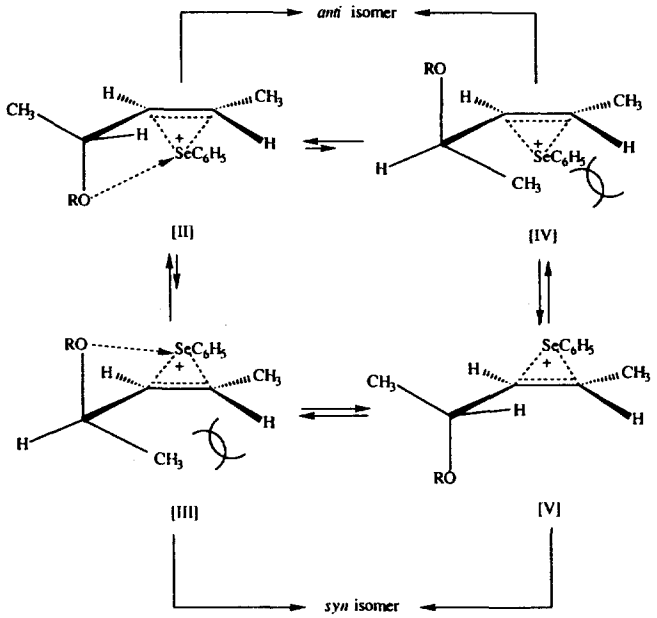


Figure 1. Four plausible conformations of seleniranium ion.

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_α 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 iodonation. Generally, the oxymercuration of allylic alcohols produces Markovnikov adducts[21] and the iodonation of allylic alcohols provides a poor regioselectivity.[22] In the case of the oxyselenylation of internal allylic alcohols, a high stereoselectivity as well as regiospecificity 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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17. Compound **2a**: ^{1}H 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).
18. Compound **3a**: ^{1}H 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).
19. A stereoisomeric mixture, **7e** and **8e**: ^{1}H 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).
20. Compound **7f**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.18 (sixtet, 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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