Regio- and Stereoselective Oxyselenylation of Allylic Alcohol and Its Derivatives

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The electrophilic addition reaction of olefins with selenium species is of considerable interest with respect to the regio- and stereoselective outcome of this reaction1-3 and versatile synthetic transformations of the phenylseleneno group in the resultant product.4 A couple of reports5,6 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 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.7-9 The solvent plays an important role in the formation of regioisomers in the oxyselenylation of cyclic system,9 but the regiochemical outcome in the oxyselenylation of acyclic system is affected by the steric hindrance or temperature.9,10 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.11-14 Although the hydroxyoxyselenylation of 3-acetoxy-cyclohexene 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 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 alcohol 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 CH₂Cl₂ solvent containing 10 equiv. of methanol at 25 °C, the oxyselenylation adducts 2a, 3a and bromoselenenyl 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 bromoselenenyl 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 bromoselenenyl 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 °C, which afforded only Markovnikov adduct.1 The high regioselectivity can be understood in terms of the steric hindrance between the attacking methanol and seleniumium ion intermediate [I] which was also suggested in the hydroxyselenylation of allylic alcohols.14 Therefore, it is expected that the nucleophilic methanol attacks at the less hindered carbon site (Cα) rather than Cβ.

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-aceoxy-1-butene (1b) was reacted with phenylselenenyl bromide under the suggested reaction condition, an anti-Markovnikov adduct 2b and a small amount of the bromoselenenyl 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 bromoselenenyl adduct indicates that the selenenium ion intermediate formed during methoxyselenylation was in equilibrium somewhat with bromoselenenyl adduct.

The formation of 2b in a relatively low yield may be due
to the participation of acetyloxy group toward the seleniranium ion intermediate. The systematic study on this possibility is now underway. However, the oxylylenylation of 3-benzyl oxy-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 oxylylenylation of terminal allylic alcohols are summarized in Table 1.

The oxylylenylation 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 stereoisomorphic mixture 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 oxylylenylation 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 oxylylenylation of (E)-2-benzyl oxy-3-pentene (6c) and (E)-4-[(2-methoxyethoxy) methoxy]-2-pentene (6d) provided the similar results. Results of oxylylenylation of nonterminal allylic alcohols are summarized in Table 2.

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

The stereoselectivity in the oxylylenylation 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-

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

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>R</th>
<th>Product (ratio)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>H</td>
<td>2a : 3a (93 : 7)</td>
<td>49</td>
</tr>
<tr>
<td>1b</td>
<td>CH₂C(O)</td>
<td>2b : 3b (100 : 0)</td>
<td>18</td>
</tr>
<tr>
<td>1c</td>
<td>CH₃CH₂</td>
<td>2c : 3c (100 : 0)</td>
<td>79</td>
</tr>
</tbody>
</table>

*Isolated yield. *A small amount (0.5%) of bromoselenenyl adducts are isolated.

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

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>R</th>
<th>Product (ratio)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>H</td>
<td>7a : 8a (92 : 8)</td>
<td>73</td>
</tr>
<tr>
<td>6b</td>
<td>CH₂C(O)</td>
<td>7b : 8b (87 : 13)</td>
<td>55</td>
</tr>
<tr>
<td>6c</td>
<td>CH₃CH₂</td>
<td>7c : 8c (90 : 10)</td>
<td>93</td>
</tr>
<tr>
<td>6d</td>
<td>CH₃C(CH₃)OCH₂</td>
<td>7d : 8d (95 : 5)</td>
<td>80</td>
</tr>
</tbody>
</table>

*The ratio was determined by comparison with 1H NMR of authentie sample after conversion to 1,3-diol compounds. *Isolated yield.
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 Cα resulted in the formation of anti isomer. Four plausible conformations of seleniranium ion are shown in Figure 1.

In conclusion, the oxyselelenylation 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 adducts20 and the iodination of allylic alcohols provides a poor regioselectivity.21 In the case of the oxyselelenylation 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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References


17. Compound 2a: 1H NMR (300 MHz, CDCl3) 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: 1H NMR (300 MHz, CDCl3) 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: 1H NMR (300 MHz, CDCl3) 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: 1H NMR (300 MHz, CDCl3) 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).