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 stereochemical outcome of this reaction and versatile synthetic transformations of the phenylseleno group in the resultant product. A couple of reports 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 alcohols was afforded a relatively poor regioselectivity. In contrast to the systematic study of chloroselenenylation 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.

The solvent plays an important role in the formation of regioisomers in the oxyselenenylation of cyclic system, but the regiochemical outcome in the oxyselenenylation of acyclic system is affected by the steric hindrance or temperature. 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. Although the hydroxyselenenylation 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 oxyselenenylation of acyclic allylic alcohol derivatives has not been reported yet, specially from the regio- and stereochemical point of view.

In this communication, we wish to describe a regio- and stereochemical aspect in the oxyselenenylation of allylic 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 CH2Cl2 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 adduct 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) and 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. The high regioselectivity can be understood in terms of the steric hindrance between the attacking methanol and seleniumium ion intermediate [1] which was also suggested in the hydroxyselenenylation of allylic alcohols. Therefore, it is expected that the nucleophilic methanol attacks at the less hindered carbon site (Cα) rather than Cβ.

[Diagram]

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 seleniumium ion intermediate formed during methoxyselenenylation was in equilibrium somewhat with bromoselenenylation adduct. The formation of 2b in a relatively low yield may be due to...
to the participation of acetoxy group toward the seleniranium ion intermediate. The systematic study on this possibility is now underway. However, the oxyselenylation of 3-benzylxoy-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 °C afforded stereoisomeric mixture of 7b and 8b in 55% yield (7b : 8b = 87 : 13). The oxyselenylation of (E)-2-benzylxoy-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.

Table 1. Oxyselenylation 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>CH(_2)C(O)</td>
<td>2b : 3b (100 : 0)*</td>
<td>18</td>
</tr>
<tr>
<td>1c</td>
<td>CH(_2)CH(_2)</td>
<td>2c : 3c (100 : 0)</td>
<td>79</td>
</tr>
</tbody>
</table>

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

Table 2. Oxyselenylation 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>CH(_2)C(O)</td>
<td>7b : 8b (87 : 13)</td>
<td>55</td>
</tr>
<tr>
<td>6c</td>
<td>CH(_2)CH(_2)</td>
<td>7c : 8c (90 : 10)</td>
<td>93</td>
</tr>
<tr>
<td>6d</td>
<td>CH(_2)OC(_2)H(_2)OCH(_3)</td>
<td>7d : 8d (96 : 5)</td>
<td>80</td>
</tr>
</tbody>
</table>

*The ratio was determined by comparison with \(^{1}H\) NMR of authentic sample after conversion to 1,3-diol compounds. Isolated yield.

Scheme 1. Determination of stereochemistry of oxyselenylation adducts.

The assignment of stereoisomers 7 and 8 was made by the comparison with \(^{1}H\) 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 7e and 8e, in which the phenylseleno group can be easily removed by using tributyltin hydride. After the major isomer 7e\(^\bullet\) was isolated from a stereoisomeric mixture (7e and 8e), the deprotection of 7e with trimethylsilyl iodide afforded the (2R, 4R)-pentanediol 7f\(^\bullet\) which was confirmed by comparison with \(^{1}H\) 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 Cα 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 and the iodonation of allylic alcohols provides a poor regioselectivity. 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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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 (d, J=12.5, 7.0 Hz, 1H), 3.06 (dd, J=12.5, 5.2 Hz, 2H), 2.31 (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), 3.83-3.74 (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 (sietet, 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=6.5 Hz, 6H).