CONVERSION OF ALLYL ARYL SELENIDES INTO SELENOCHROMAN DERIVATIVES

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Abstract — Several allyl aryl selenides were prepared and examined their reactions with aluminum bromide to give selenochroman derivatives in high to moderate yields. A plausible mechanism of this reaction is also discussed.

Heterocyclic compounds containing a selenium atom have attracted much attention in recent years because of their high reactivity and unique chemical properties.¹ The chemistries of selenium-containing molecules, as well as the tellurium analogs, have been intensively studied.² However, compared with sulfur heterocyclic compounds,³ the preparative methods for selenium-containing heterocyclic molecules are quite limited. For example, only a few methods for the preparation of benzoselenane derivatives such as selenochromans and isoselenochromans have been reported.⁴

In our previous studies,⁵,⁶ we demonstrated that when cinnamyl alcohol was treated with a reagent system of phenyl trimethylsilyl selenide — aluminum bromide in dichloromethane, 4-phenylselenochroman (1) was obtained as an unexpected product. ⁵ It was also found that this transformation involved the conversion of cinnamyl phenyl selenide (2) into 1 with the aid of aluminum bromide (Scheme 1).⁵

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{Se} & \quad \text{Se} \\
2 & \quad 1 \\
& \quad \text{AlBr}_3
\end{align*}
\]

Scheme 1

In order to generalize this convenient transformation of an allyl aryl selenide into a selenochroman, we prepared several allyl aryl selenides and examined their reactions in the presence of a Lewis acid. In preliminary experiments, aluminum bromide gave the best results as the additive compared to the other acids, such as AlCl₃, ZnBr₂, Yb(OTf)₃, Sc(OTf)₃, and p-toluenesulfonic acid. The other reaction conditions were optimized as shown in Table 1.

Allyl phenyl selenides (3–13) were prepared from allylic alcohols or allylic halides by nucleophilic substitution reactions⁷ with the phenylseleno group. The reactions of these substrates in the presence of
Table 1

<table>
<thead>
<tr>
<th>Allyl Phenyl Selenide</th>
<th>Reaction Time</th>
<th>Selenochroman</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2 h</td>
<td>1</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>5 min</td>
<td>14</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td>5 min</td>
<td>14</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>3 h</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5 min</td>
<td>15</td>
<td>68</td>
</tr>
<tr>
<td>7</td>
<td>5 min</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>5 min</td>
<td>16</td>
<td>58</td>
</tr>
<tr>
<td>9</td>
<td>2 h</td>
<td>17</td>
<td>43</td>
</tr>
<tr>
<td>10</td>
<td>5 min</td>
<td>18</td>
<td>71</td>
</tr>
<tr>
<td>11</td>
<td>5 min</td>
<td>19</td>
<td>49</td>
</tr>
<tr>
<td>12</td>
<td>5 min</td>
<td>20</td>
<td>85</td>
</tr>
<tr>
<td>13</td>
<td>5 min</td>
<td>20</td>
<td>67</td>
</tr>
</tbody>
</table>

* See ref. 5.  
* 86% of 5 was recovered.  
* Complicated mixture was obtained.

AlBr₃ at room temperature smoothly proceeded to afford the corresponding selenochromans in high to moderate yield, with the exception of 5 and 7 (Table 1). The cinnamyl type selenides (3, 4, 6, 8, and 10–13) generally showed good reactivity whereas the simple allyl selenide (5) did not give any products and was recovered in 86% yield. The low yield of 19 may be due to its unstability under the given reaction conditions. A quaternary carbon center at the benzylic position could be efficiently constructed in this reaction (14 and 17–20).

We suppose that this reaction pathway can be explained as shown in Scheme 2.³³ Initial coordination of selenium atom to aluminum bromide activates the allylic selenide to generate a positively charged allyl group (A). Then the Friedel-Crafts type C-C bond formation between the aromatic ring and the allyl group, followed by nucleophilic attack of aluminum selenolate (B) to the olefinic carbon leads to the
Further studies on the mechanistic aspect of this selenochroman synthesis are under way.

Scheme 2

**Typical Experimental Procedure**

To a stirred mixture of freshly purified AlBr₃ (46.4 mg, 0.17 mmol) and dry CH₂Cl₂ (0.7 mL), a solution of 3 (50.0 mg, 0.17 mmol) in dry CH₂Cl₂ (1.3 mL) was added under an argon atmosphere. After 5 min at ambient temperature, the reaction mixture was poured into a 1 N NaOH aqueous solution and extracted with CH₂Cl₂. The organic layer was washed with brine, dried over anhydrous MgSO₄, and concentrated in vacuo. The crude product was then purified on silica gel. Elution with hexane afforded 46.2 mg of **14** (92%) along with a trace amount of diphenyl diselenide.

**3,4-Dihydro-4-methyl-4-phenyl-2H-benzosele**

(14): Yellow oil. IR (CHCl₃) 2960, 1595, 1585, 1490, 1470, 1440, 1375, 1025, 905. ¹H-NMR (200 MHz, CDCl₃) δ: 1.73 (s, 3H), 2.15 (ddd, 1H, J = 14.0, 9.8, 3.8), 2.50 (ddd, 1H, J = 14.0, 7.4, 3.6), 2.72 (ddd, 1H, J = 11.2, 9.8, 3.8), 2.95 (ddd, 1H, J = 11.2, 7.4, 3.6), 6.98–7.16 (m, 5H), 7.16–7.32 (m, 4H). ¹³C-NMR (50 MHz, CDCl₃) δ: 16.2, 29.1, 39.3, 43.2, 124.8, 126.0, 126.6, 127.1, 128.0, 128.1, 129.0, 129.3, 143.3, 148.2. ⁷⁷Se-NMR (38 MHz, CDCl₃) δ: 220.0. MS (EI) m/z: 284, 285, 286, 288 (⁷⁷Se, M⁺), 290. (1:1:2.5:5:1)

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**REFERENCES AND NOTES**


8. Lewis acid promoted [3,3]-sigmatropic rearrangement mechanism can not be excluded. However, our results exhibit some differences from the previously reported seleno-Claisen rearrangement.\(^9\)\(^10\) Vallée et al. described that a five-membered ring product was mainly obtained in the thermal seleno-Claisen rearrangement of allyl phenyl selenide.\(^9\)\(^10\) And also, Murai et al. reported that the unsubstituted allyl selenide was more reactive than the prenyl compound\(^9\) whereas, in our results, the unsubstituted allyl compound (5) was inert as shown in Table 1.

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