Stereoselective Synthesis of (E)-α-Selenenylvinylsilanes via the Hydromagnesiation Reaction of Alkynylsilanes

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Abstract: (E)-α-Selenenylvinylsilanes have been synthesized stereoselectively via the hydromagnesiation of alkynylsilanes, followed by the reaction with arylselenenyl bromides. (E)-α-Selenenylvinylsilanes can undergo the desilylation reaction in the presence of a catalytic amount of hydriodic acid to give (E)-vinyl selenides in high yields.

Key words: hydromagnesiation, (E)-α-selenenylvinylsilane, alkynylsilane, stereoselectivity, (E)-vinyl selenide

Bifunctional-group reagents, which have two different functional groups linked to the olefinic carbon atoms, for example, Sn–Si, Si–Zr, Se–B, Se–Sn, and Se–Zr combinations, play an important role in organic synthesis, especially in developing many convenient methods for the stereoselective preparation of substituted alkenes. These reagents and their synthetic applications have been reported.1 Both vinylsilanes and vinyl selenides are important intermediates, but the bifunctional-group reagent containing selenium and silicon has rarely aroused attention. Recently, Xu et al.2 described that alkynylsilanes underwent hydrozirconation and the successive reaction with selenenyl bromides to give (E)-α-selenenylvinylsilanes. Hydromagnesiation has emerged as a unique hydrometalation with some attractive features, such as the high regioselectivity and stereoselectivity observed with alkynylsilanen.3,4 We now wish to report that (E)-α-selenenylvinylsilanes could be synthesized by hydromagnesiation of alkynylsilanes, followed by treatment with selenenyl bromides.

Alkynylsilanes 1 were prepared according to the literature procedure.5 Hydromagnesiation of alkynylsilanes at 25 °C in diethyl ether for 6 hours gave (Z)-α-silylvinyl Grignard reagents 2, which reacted with selenenyl bromides 3 in THF to afford (E)-α-selenenylvinylsilanes 4. The yields were 68–86% (Scheme 1).

Investigations of the crude products 4 by 1H NMR spectroscopy (300 MHz) showed their isomeric purities to be more than 96%. One olefinic proton signal of 4 splits characteristically into one triplet with a coupling constant J = 7.0 Hz, which indicated that the hydromagnesiation to the alkynylsilanes had taken place with strong preference for the addition of the magnesium atom at the carbon adjacent to the silyl group. The other results of the reaction are summarized in Table 1.

Table 1  Synthesis of (E)-α-Selenenylvinylsilanes

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Ar</th>
<th>Producta</th>
<th>Yieldb (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>n-C5H5</td>
<td>Ph</td>
<td>4a</td>
<td>81</td>
</tr>
<tr>
<td>b</td>
<td>n-C5H5</td>
<td>4-ClC6H4</td>
<td>4b</td>
<td>84</td>
</tr>
<tr>
<td>c</td>
<td>n-C5H5</td>
<td>4-MeC6H4</td>
<td>4c</td>
<td>78</td>
</tr>
<tr>
<td>d</td>
<td>i-C5H11</td>
<td>Ph</td>
<td>4d</td>
<td>80</td>
</tr>
<tr>
<td>e</td>
<td>i-C5H11</td>
<td>4-ClC6H4</td>
<td>4e</td>
<td>85</td>
</tr>
<tr>
<td>f</td>
<td>i-C5H11</td>
<td>4-MeC6H4</td>
<td>4f</td>
<td>79</td>
</tr>
<tr>
<td>g</td>
<td>n-C4H9</td>
<td>Ph</td>
<td>4g</td>
<td>82</td>
</tr>
<tr>
<td>h</td>
<td>n-C4H9</td>
<td>4-ClC6H4</td>
<td>4h</td>
<td>86</td>
</tr>
<tr>
<td>i</td>
<td>n-C4H9</td>
<td>4-MeC6H4</td>
<td>4i</td>
<td>80</td>
</tr>
<tr>
<td>j</td>
<td>PhCH2</td>
<td>Ph</td>
<td>4j</td>
<td>72</td>
</tr>
<tr>
<td>k</td>
<td>PhCH2</td>
<td>4-ClC6H4</td>
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<td>76</td>
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<tr>
<td>l</td>
<td>PhCH2</td>
<td>4-MeC6H4</td>
<td>4l</td>
<td>68</td>
</tr>
</tbody>
</table>

a All the compounds were characterized using 1H NMR, IR, and MS or elemental analyses.
b Isolated yield based on the alkynylsilane used.
Vinyl selenides are promising synthetic intermediates owing to the versatile reactivity of the selenenyl group and the carbon–carbon double bond, but only a few methods for the synthesis of \((E)\)-vinyl selenides are available. The reaction of selenoacetylenes with LiAlH\(_4\) gave \((E)\)-vinyl selenides.\(^3\) Hydroboration of 1-alkynes afforded \((E)\)-alkenylboronic acids, which were treated with NaOH followed by PhSeBr to give stereoselectively \((E)\)-vinyl selenides.\(^9\) We carried out the desilylation reaction of \((E)\)-selenenylvinylsilanes 4 in the presence of a catalytic amount of 57\% hydriodic acid at room temperature in benzene for an hour to give \((E)\)-vinyl selenides 5 with high stereoselectivity and in high yields (Scheme 2). The experimental results are summarized in Table 2.  

**Scheme 2**  

**Table 2** Synthesis of \((E)\)-Vinyl Selenides  

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Ar</th>
<th>Product(^a)</th>
<th>Yield(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>(-\text{C}_3\text{H}_7)</td>
<td>Ph</td>
<td>5a</td>
<td>80</td>
</tr>
<tr>
<td>b</td>
<td>(-\text{C}_3\text{H}_7)</td>
<td>4-Cl(-\text{C}_6\text{H}_4)</td>
<td>5b</td>
<td>82</td>
</tr>
<tr>
<td>c</td>
<td>(-\text{C}<em>5\text{H}</em>{11})</td>
<td>Ph</td>
<td>5c</td>
<td>79</td>
</tr>
<tr>
<td>d</td>
<td>(-\text{C}<em>5\text{H}</em>{11})</td>
<td>4-Me(-\text{C}_6\text{H}_4)</td>
<td>5d</td>
<td>74</td>
</tr>
<tr>
<td>e</td>
<td>(-\text{C}<em>5\text{H}</em>{11})</td>
<td>Ph</td>
<td>5e</td>
<td>81</td>
</tr>
<tr>
<td>f</td>
<td>(-\text{C}<em>5\text{H}</em>{11})</td>
<td>4-Cl(-\text{C}_6\text{H}_4)</td>
<td>5f</td>
<td>83</td>
</tr>
</tbody>
</table>

\(^a\) All the compounds were characterized using \(^1\)H NMR, IR, and elemental analyses.  
\(^b\) Isolated yield based on the \((E)\)-selenenylvinylsilane used.

The stereochemistry of products 5 was easily established, since \(^1\)H NMR spectra of products 5a–f show a doublet at \(\delta = 6.3–6.5\) with a coupling constant of 15 Hz, typical of trans-positioned hydrogen atoms.\(^10\) In summary, compared to the reported method,\(^2\) the present method for the synthesis of \((E)\)-a-selenenylvinylsilanes has the advantages of readily available and cheap starting materials instead of the expensive \(\text{CP}_3\text{Zr}(\text{H})\text{Cl}\), straightforward and simple procedures, mild reaction conditions and high yields. The investigation on the synthetic applications of \((E)\)-a-selenenylvinylsilanes is in progress.  

\(^1\)H NMR spectra were recorded on an AZ-300MHz spectrometer with TMS as an internal standard. IR spectra were obtained on a Perkin-Elmer 683 instrument as neat films. Mass spectra were determined on a Finnigan 8230 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN micro elemental analyser. All solvents were dried, deoxygenated and freshly distilled before use.  

\((E)\)-\(\alpha\)-Selenenylvinylsilanes 4a–l; General Procedure  
To a solution of isobutylmagnesium bromide (4.5 mmol) in Et\(_2\)O (7 mL) was added \(\text{CP}_3\text{TiCl}\) (50 mg, 0.2 mmol) at 0°C under Ar, and the mixture was stirred for 30 min at that temperature. To this solution was added alkynylsilane 1 (4.0 mmol), and the mixture was stirred for 6 h at 25°C. After removal of the Et\(_2\)O under reduced pressure (2 h, r.t./2 Torr), the residue was dissolved in THF (6 mL), cooled to –10°C, and a solution of ArSeBr (4.0 mmol) in THF (6 mL) was added dropwise over 30 min with stirring. The reaction mixture was brought to 30°C gradually and stirred for 8 h, quenched with sat. aq \(\text{NH}_4\text{Cl}\) (25 mL) and extracted with Et\(_2\)O (2 × 30 mL). The organic layer was washed with sat. aq \(\text{NH}_4\text{Cl}\) (20 mL) and \(\text{H}_2\text{O}\) (3 × 30 mL) and dried (\(\text{MgSO}_4\)). Removal of solvent under reduced pressure gave an oil, which was purified by column chromatography on silica gel using light petroleum (bp 30–60°C) as eluent.  

4a  
\(^1\)H NMR (CDCl\(_3\)): \(\delta = 7.43–7.35\) (m, 2 H), 7.32–7.14 (m, 3 H), 6.63 (t, \(J = 7.0\) Hz, 1 H), 2.31–2.17 (m, 2 H), 1.45–1.25 (m, 4 H), 0.91 (t, \(J = 5.4\) Hz, 3 H), 0.15 (s, 9 H).  
MS: \(m/z = 312\) (M\(^+\)).  
Anal. Calcd for \(\text{C}_{15}\text{H}_{23}\text{SiSe}\): C, 52.05; H, 6.65. Found: C, 51.89; H, 6.44.  

4b  
IR (film): 3070, 3016, 2962, 2930, 2865, 1590, 1495, 1249, 839, 735 cm –1 .  
\(^1\)H NMR (CDCl\(_3\)): \(\delta = 7.40–7.01\) (m, 4 H), 6.55 (t, \(J = 7.0\) Hz, 1 H), 2.45–2.01 (m, 2 H), 1.54–1.10 (m, 4 H), 0.92 (t, \(J = 5.4\) Hz, 3 H), 0.15 (s, 9 H).  
MS: \(m/z = 346\) (M\(^+\)).  
Anal. Calcd for \(\text{C}_{15}\text{H}_{24}\text{SiSe}\): C, 57.88; H, 7.72. Found: C, 57.61; H, 7.58.  

4c  
IR (film): 3070, 3017, 2956, 2926, 2865, 1589, 1489, 1247, 839, 800, 753 cm –1 .  
\(^1\)H NMR (CDCl\(_3\)): \(\delta = 7.38–6.79\) (m, 4 H), 6.41 (t, \(J = 6.9\) Hz, 1 H), 2.50–2.01 (m, 5 H), 1.56–1.12 (m, 4 H), 0.91 (t, \(J = 5.4\) Hz, 3 H), 0.15 (s, 9 H).  
MS: \(m/z = 326\) (M\(^+\)).  
Anal. Calcd for \(\text{C}_{15}\text{H}_{32}\text{SiSe}\): C, 51.89; H, 6.64.  

4d  
IR (film): 3070, 2955, 2915, 2870, 1578, 1475, 1384, 1366, 1249, 860, 839, 734, 690 cm –1 .  
\(^1\)H NMR (CDCl\(_3\)): \(\delta = 7.39–6.87\) (m, 5 H), 6.41 (t, \(J = 6.9\) Hz, 1 H), 2.42–2.01 (m, 2 H), 1.70–1.11 (m, 3 H), 0.88 (d, \(J = 6.7\) Hz, 6 H), 0.14 (s, 9 H).  
MS: \(m/z = 326\) (M\(^+\)).  
Anal. Calcd for \(\text{C}_{16}\text{H}_{32}\text{SiSe}\): C, 59.00; H, 7.79. Found: C, 58.79; H, 7.62.
4e  
IR (film): 3073, 2954, 2870, 1628, 1578, 1471, 1385, 1366, 1249, 838, 756 cm⁻¹.  
¹H NMR (CDCl₃): δ = 7.37–6.92 (m, 4 H), 6.46 (t, J = 7.0 Hz, 1 H), 2.48–2.00 (m, 2 H), 1.72–1.12 (m, 3 H), 0.90 (d, J = 6.7 Hz, 6 H), 0.15 (s, 9 H).  
MS: m/z = 360 (M⁺).  

4f  
IR (film): 3069, 3016, 2952, 2869, 1631, 1577, 1488, 1384, 1366, 1249, 860, 839, 800 cm⁻¹.  
¹H NMR (CDCl₃): δ = 7.28–6.79 (m, 4 H), 6.38 (t, J = 7.0 Hz, 1 H), 2.45–1.95 (m, 5 H), 1.70–1.10 (m, 3 H), 0.89 (d, J = 6.7 Hz, 6 H), 0.15 (s, 9 H).  
MS: m/z = 340 (M⁺).  
Anal. Calcd for C₁₇H₂₈SiSe: C, 60.10; H, 8.25. Found: C, 60.31; H, 8.40.

4g  
IR (film): 3070, 2960, 2855, 1590, 1485, 1250, 840, 740, 690 cm⁻¹.  
¹H NMR (CDCl₃): δ = 7.51–7.07 (m, 5 H), 6.59 (t, J = 6.9 Hz, 1 H), 2.45–2.18 (m, 2 H), 1.60–1.13 (m, 8 H), 0.88 (t, J = 5.3 Hz, 3 H), 0.05 (s, 9 H).  
MS: m/z = 340 (M⁺).  
Anal. Calcd for C₁₇H₂₇ClSiSe: C, 60.10; H, 8.25. Found: C, 60.36; H, 8.39.

4h  
IR (film): 3069, 3016, 2958, 2860, 1587, 1490, 1248, 839, 756 cm⁻¹.  
¹H NMR (CDCl₃): δ = 7.41–7.12 (m, 4 H), 6.68 (t, J = 7.0 Hz, 1 H), 2.44–2.17 (m, 2 H), 1.50–1.17 (m, 8 H), 0.89 (t, J = 5.3 Hz, 3 H), 0.15 (s, 9 H).  
MS: m/z = 374 (M⁺).  
Anal. Calcd for C₁₇H₂₈SiSe: C, 60.56; H, 7.22. Found: C, 56.27; H, 7.03.

4i  
IR (film): 3070, 2956, 2855, 1589, 1488, 1247, 838, 800, 753 cm⁻¹.  
¹H NMR (CDCl₃): δ = 7.31–6.93 (m, 4 H), 6.56 (t, J = 7.0 Hz, 1 H), 2.48–2.33 (m, 2 H), 2.29 (s, 3 H), 1.51–1.19 (m, 8 H), 0.91 (t, J = 5.4 Hz, 3 H), 0.05 (s, 9 H).  
MS: m/z = 354 (M⁺).  

4j  
IR (film): 3060, 3027, 2953, 2852, 1576, 1494, 1248, 839, 736, 691 cm⁻¹.  
¹H NMR (CDCl₃): δ = 7.50–7.04 (m, 10 H), 6.58 (t, J = 7.0 Hz, 1 H), 3.53 (d, J = 7.2 Hz, 2 H), 0.11 (s, 9 H).  
MS: m/z = 346 (M⁺).  

4k  
IR (film): 3061, 3027, 2954, 2853, 1601, 1575, 1494, 1249, 844, 700 cm⁻¹.  
¹H NMR (CDCl₃): δ = 7.55–7.03 (m, 9 H), 6.61 (t, J = 7.0 Hz, 1 H), 3.57 (d, J = 7.3 Hz, 2 H), 0.15 (s, 9 H).  
MS: m/z = 380 (M⁺).  

(E)-Vinyl Selenides 5a–f; General Procedure  
To a solution of (E)-α-Selenenylvinylsilanes 4 (0.5 mmol) in benzene (1 mL) was addedaq 57% HI (0.04 mL). The mixture was stirred at r.t. for 1 h, quenched with sat. aq NaHCO₃ (10 mL) and extracted with Et₂O (2 × 15 mL). The ethereal solution was washed with H₂O (3 × 20 mL), dried (MgSO₄) and concentrated under reduced pressure. The oily residue was purified by flash column chromatography on silica gel using light petroleum (bp 30–60 °C) as eluent to give 5a–f as oils.
Anal. Calcd for C$_{14}$H$_{20}$Se: C, 62.92; H, 7.49. Found: C, 63.17; H, 7.72.

**5f**
IR (film): 3070, 3018, 2960, 2862, 1598, 1489, 880, 758, 690 cm$^{-1}$.
$^1$H NMR (CDCl$_3$): $\delta$ = 7.64–7.12 (m, 4 H), 6.42 (d, $J$ = 15 Hz, 1 H), 6.03 (dt, $J$ = 15, 6 Hz, 1 H), 2.42–2.13 (m, 2 H), 1.63–1.18 (m, 8 H), 0.89 (t, $J$ = 5.4 Hz, 3 H).
Anal. Calcd for C$_{14}$H$_{19}$ClSe: C, 55.72; H, 6.30. Found: C, 55.51; H, 6.10.

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**References**