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Preparation of α-Heteroatom Substituted Allylic Alcohols by Reaction of (*E*)-α-Selanylvinylzirconiums or (*E*)-α-Trimethylsilylvinylzirconiums with Aldehydes†

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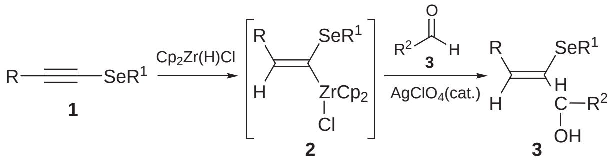
Both (*E*)-α-selanylvinylzirconium and (*E*)-α-trimethylsilylvinylzirconium complexes undergo AgClO$_4$-catalyzed reactions with aldehydes to give α-seleno- or α-trimethylsilyl-substituted allylic alcohols, respectively.

Functionality-bearing allylic alcohols are often vital structural units of biologically active compounds.[1] A number of methods for the preparation of allylic alcohols have been previously reported, the most general method being Barbier reactions.[2] However, to date only the synthesis of α-trimethylsilyl substituted allylic alcohols has been studied to any extent,[3] the synthesis of other α-heteroatom substituted allylic alcohols has been little studied, and the synthesis of α-selanyl substituted allylic alcohols has not been reported. Vinylic selenides[4] are very important intermediates in organic synthesis and we thus attempt to develop a convenient method for synthesis of α-selanyl substituted allylic alcohols.

(*E*)-α-Selanylvinylzirconium complexes can be synthesized stereoselectively by hydrozirconation of internal acetylenic selenides and we have studied the intermediates.[5] Suzuki and coworkers[6] previously reported the addition of vinylzirconocenes to aldehydes in the presence of a catalytic amount of AgClO$_4$ to give allylic alcohols as an extension to our studies, we were interested in using this intermediate to develop new synthetic routes toward α-selanyl substituted allylic alcohols.

The results indicated that **2** can react with aldehydes **3** rapidly in CH$_2$Cl$_2$ at room temperature in the presence of 5 mmol% AgClO$_4$ (Scheme 1), to afford α-selanylallylic alcohols in good yields (Table 1).



Scheme 1

α-Trimethylsilylallylic alcohols have been synthesized previously,[3] but the reported method required low temperature and a number of steps, we report a simple method for synthesizing α-trimethylsilylallylic alcohols. Intermediates **6** can be obtained by hydrozirconation of 1-trimethylsilylalk-1-ynes **5**, which can also react with aldehydes in the presence of 5 mmol% AgClO$_4$ to provide α-trimethylsilylallylic alcohols (Scheme 2). Results are listed in Table 2.

Table 1 Preparation of α-selanylallylic alcohols **4a–d**

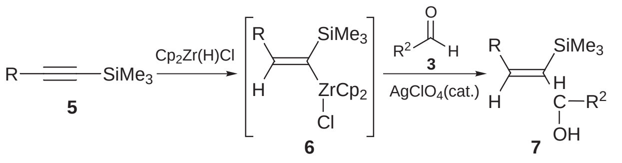
Entry	R	R^1	R^2	Product	Yield[a] (%)
1	CH$_3$OCH$_2$	Et	Pr^n	**4a**	75
2	Bu^n	Et	Pr^n	**4b**	80
3	CH$_3$OCH$_3$	Et	Ph	**4c**	68
4	Bu^n	Et	Ph	**4d**	78

[a] Isolated yield.

Table 2 Preparation of α-trimethylsilylallylic alcohols **7a–d**

Entry	R	R^2	Product	Yield[a] (%)
1	MeOCH$_2$	Pr^n	**7a**	70
2	OCH$_2$	Ph	**7b**	68
3	MeBu^n	Pr^n	**7c**	76
4	Bu^n	Ph	**7d**	72

[a] Isolated yield.



Scheme 2

In summary, we have developed a novel route to the synthesis of α-heteroatom-substituted allylic alcohols, applications of these α-heteroatom substituted allylic alcohols are currently being examined.

Experimental

^{1}H NMR were recorded in CDCl$_3$ on an AZ-300 spectrometer with TMS as internal standard. Mass spectra were obtained using a Finigan 8230 mass spectrometer. The reactions were carried out in pre-dried glassware (150 °C, 4 h) and cooled under a stream of dry nitrogen. All solvents were dried, deoxygenated are redistilled before use.

General Procedure for the Synthesis of **4a**–**d**.—A mixture of Cp$_2$Zr(H)Cl of (2 mmol) and acetylenic selenide **1** (2 mmol) in CH$_2$Cl$_2$ (5 ml) was stirred at room temperature for 20 min. To the resulting solution was added aldehyde **3** (1.8 mmol) in CH$_2$Cl$_2$ (5 ml) followed by AgClO$_4$ (90 μmol, 5 mmol%). The reaction mixture turned dark gradually. After stirring for 15 min, the mixture was poured into sat. NaHCO$_3$ aqueous solutions. Extractive workup (EtOAc) followed by purification with preparative TLC (hexane–EtOAc, 411:1) gave α-seleno substituted allylic alcohols **4a**-**d**:

Compound **4a**. δ_H 6.25 (t, 1 H), 4.12 (t, 1 H), 3.85 (d, 2 H), 3.24 (s, 3 H), 2.58 (q, 2 H), 1.89 (s, 1 H), 0.91–1.57 (m, 10 H). MS, *m/z* 252 (M$^+$ + 1) (Found: C, 47.49; H, 7.62; O, 12.49. C$_{10}$H$_{20}$SeO$_2$ requires C, 47.82; H, 8.03; O, 12.72%).

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† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Compound **4b**. δ_H 6.19 (t, 1 H), 4.10 (t, 1 H), 2.57 (q, 2 H), 1.85–2.29 (m, 3 H), 0.90–1.58 (m, 17 H), MS, *m/z* 263 ($M^+ + 1$) (Found: C, 54.39; H, 8.84; O, 5.79. $C_{12}H_{24}SeO$ requires C, 54.74; H, 9.19; O, 6.07%).

Compound **4c**. δ_H 7.10–7.50 (m, 5 H), 6.23 (t, 1 H), 4.35 (s, 1 H), 3.85 (d, 2 H), 3.25 (s, 3 H), 2.59 (q, 2 H), 2.02 (s, 1 H), 1.50 (t, 3 H). MS, *m/z* 285 ($M^+ + 1$) (Found: C, 54.54; H, 6.12; O, 11.00. $C_{13}H_{18}SeO_2$ requires C, 54.75; H, 6.36; O, 11.21%).

Compound **4d**. δ_H 7.10–7.50 (m, 5 H), 6.20 (t, 1 H), 4.33 (s, 1 H), 2.56 (q, 2 H), 1.80–2.33 (m, 3 H), 0.92–1.60 (m, 10 H). MS, *m/z* 297 ($M^+ + 1$) (Found: C, 60.49; H, 7.28; O, 5.17. $C_{15}H_{22}SeO$ requires C, 60.60; H, 7.46; O, 5.38%).

General Procedure for the Synthesis of **7a–d**.—A mixture of $Cp_2Zr(H)Cl$ (2 mmol) and 1-trimethylsilylalk-1-yne **5** (2 mmol) in CH_2Cl_2 (5 ml) was stirred at room temperature for 1 h. The following steps were the same as for the synthesis of **4a–d**.

Compound **7a**. δ_H 6.25 (t, 1 H), 4.15 (t, 1 H), 3.95 (d, 2 H), 3.45 (s, 3 H), 2.15 (s, 1 H), 1.15–1.61 (m, 7 H), 0.35 (s, 9 H). MS, *m/z* 217 ($M^+ + 1$) (Found: C, 61.38; H, 11.47; O, 14.95. $C_{11}H_{24}SeO_2$ requires C, 61.07; H, 11.18; O, 14.77%).

Compound **7b**. δ_H 7.05–7.46 (m, 5 H), 6.24 (t, 1 H), 4.33 (s, 1 H), 3.90 (d, 2 H), 3.43 (s, 37 H), 2.10 (s, 1 H), 0.35 (s, 9 H). MS, *m/z* 250 ($M^+ + 1$) (Found: C, 67.42; H, 8.94; O, 12.82. $C_{14}H_{22}SeO_2$ requires C, 67.16; H, 8.86; O, 12.76%).

Compound **7c**. δ_H 6.18 (t, 1 H), 4.10 (t, 1 H), 1.86–2.27 (m, 3 H), 1.10–1.59 (m, 14 H), 0.34 (s, 9 H). MS, *m/z* 228 ($M^+ + 1$) (Found: C, 68.53; H, 12.52; O, 7.30. $C_{13}H_{28}SeO$ requires C, 68.35; H, 12.36; O, 7.00%).

Compound **7d**. δ_H 7.10–7.50 (m, 5 H), 6.22 (t, 1 H), 4.31 (s, 1 H), 1.82–2.35 (m, 3 H), 0.92–1.60 (m, 7 H), 0.35 (s, 9 H). MS, *m/z* 262 ($M^+ + 1$) (Found: C, 73.45; H, 12.12; O, 6.43. $C_{16}H_{26}SeO$ requires C, 73.24; H, 9.99; O, 6.09%).

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