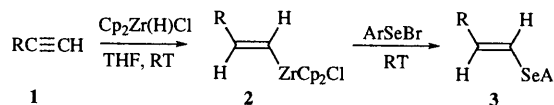


Stereoselective synthesis of (*E*)-vinylic selenides via hydrozirconation of alk-1-yne

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Hydrozirconation of alk-1-yne **1** gives organozirconium(IV) complexes **2**, which are trapped with arylselenenyl bromides to afford (*E*)-vinylic selenides **3** in high yields.



Vinylic selenides have attracted special attention as important intermediates in various synthetic transformations.¹⁻⁴ Direct replacement¹⁻⁵ of selenium-containing groups of (*E*)-vinylic selenides by alkyl or aryl groups affords (*E*)-disubstituted ethenes, which are contained in many natural products.^{6,7} However, no convenient synthesis of (*E*)-vinylic selenides from aryl or alkyl substituted ethynes has been reported in the literature. For example, the addition of arylselenols to monosubstituted ethynes is very slow at room temperature, and the products exhibit predominantly the *Z* configuration.⁸

Bis(cyclopentadienyl)zirconium complexes react with phenylselenenyl bromide to give 1-phenylselenenylbuta-1,3-diene derivatives stereoselectively.⁹ Vinylzirconium complexes react with phenyltellurenyl iodide readily to afford vinylic tellurides.¹⁰ Considering the high electrophilicity of arylselenenyl bromides, we tried treating them with the zirconium complexes **2** produced by hydrozirconation of alk-1-yne. The experimental results showed that the reactions proceeded quite easily to afford (*E*)-vinylic selenides in excellent yields.

$\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ adds to alk-1-yne in THF at room temperature stereospecifically with high regioselectivity¹¹ to yield organozirconium(IV) complexes **2**. The transfer of the vinylic unit from zirconium to selenium is completely stereoselective. Particularly diagnostic for this is the coupling constant between the geminal proton H_A to selenium and the vicinal proton H_B ; typical values of $^3J_{\text{HH}}$ are in the range 15–16 Hz which is consistent¹² with an *E* configuration for the double bond containing the ArSe unit.

Arylselenenyl bromides can be prepared conveniently in solution as needed.¹³ Care must be taken to avoid an excess of bromine and to ensure thorough mixing of the solution during the reaction with diaryldiselenides to prevent formation of ArSeBr_3 .

The present method has advantages of readily available starting materials, simple procedures, mild reaction conditions and excellent yields.

Experimental

¹H NMR spectra were obtained on a Bruker AC-P 200 (200 MHz) spectrometer with $(\text{CH}_3)_4\text{Si}$ as internal standard in CDCl_3 ; *J* values are given in Hz. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyser and IR spectra on a Shimadzu IR-435 instrument. All solvents were dried and distilled prior to use. All reactions were carried out under nitrogen.

General procedure for the synthesis of (*E*)-vinylic selenides **3a–g**

A mixture of $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ (0.8 mmol) and alk-1-yne **1** (0.8 mmol) in THF (4 cm^3) was stirred at room temperature for 20 min. Into the resulting solution was injected ArSeBr (0.8 mmol) in THF (3 cm^3) (prepared *in situ*) and the mixture was stirred at room temperature for 10 min. It was then diluted with light

Table 1 Synthesis of (*E*)-vinylic selenides **3a–g**

Product	R	Ar	mp (T/°C) ^a	Yield (%) ^b
3a	Ph	Ph	oil	84
3b	Ph	4-ClC ₆ H ₄	51–52	88
3c	Ph	4-BrC ₆ H ₄	59–60	85
3d	CH ₃ OCH ₂	Ph	oil	86
3e	CH ₃ OCH ₂	4-ClC ₆ H ₄	oil	87
3f	CH ₃ OCH ₂	4-BrC ₆ H ₄	oil	94
3g	CH ₃ OCH ₂	4-MeC ₆ H ₄	oil	90

^a Uncorrected. ^b Isolated yield.

petroleum and stirred for a further 5 min after which the supernatant was filtered through a short plug of silica gel. After evaporation of the filtrate, the residue was purified by preparative TLC on silica gel [light petroleum as eluent for **3a–c**, diethyl ether–light petroleum (1 : 20) for **3d–g**].

Compound 3a. $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3040, 1640 and 1470; δ_{H} 7.21–7.45 (m, 11 H), 6.80 (d, *J* 15.6, 1 H) (Found: C, 64.7; H, 4.8. Calc. for C₁₄H₁₂Se: C, 64.88; H, 4.67%).

Compound 3b. $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3060, 1630, 1596 and 1088; δ_{H} 7.23 (m, 10 H), 6.81 (d, *J* 15.6, 1 H) (Found: C, 57.3; H, 3.9. Calc. for C₁₄H₁₁ClSe: C, 57.29; H, 3.75%).

Compound 3c. $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3057, 1630, 1480 and 1002; δ_{H} 7.34–7.43 (m, 9 H), 7.29 (d, *J* 15.7, 1 H), 6.98 (d, *J* 15.7, 1 H) (Found: C, 49.8; H, 3.35. Calc. for C₁₄H₁₁BrSe: C, 49.74; H, 3.28%).

Compound 3d. $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2908, 1610, 1575 and 1110; δ_{H} 7.25–7.53 (m, 5 H), 6.70 (d, *J* 15.6, 1 H), 5.99 (m, 1 H), 3.94 (d, *J* 6.0, 2 H), 3.33 (s, 3 H) (Found: C, 53.0; H, 5.6. Calc. for C₁₀H₁₂OSe: C, 52.88; H, 5.33%).

Compound 3e. $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2968, 2812, 1608 and 1472; δ_{H} 7.23–7.44 (m, 4 H), 6.65 (d, *J* 15.7, 1 H), 6.03 (m, 1 H), 3.93 (d, *J* 5.0, 2 H), 3.33 (s, 3 H) (Found: C, 45.95; H, 4.3. Calc. for C₁₀H₁₁ClOSe: C, 45.90; H, 4.21%).

Compound 3f. $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2968, 2810, 1608 and 1480; δ_{H} 7.24–7.42 (m, 4 H), 6.61 (d, *J* 14.9, 1 H), 5.98 (m, 1 H), 3.93 (d, *J* 6.1, 2 H), 3.33 (s, 3 H) (Found: C, 38.9; H, 3.7. Calc. for C₁₀H₁₁BrOSe: C, 39.26; H, 3.60%).

Compound 3g. $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3004, 2815, 1610 and 1487; δ_{H} 7.08–7.42 (m, 4 H), 6.67 (d, *J* 15.5, 1 H), 5.86 (m, 1 H), 3.90 (d, *J* 6.1, 2 H), 3.30 (s, 3 H), 2.32 (s, 3 H) (Found: C, 54.9; H, 6.0. Calc. for C₁₁H₁₄OSe: C, 54.79; H, 5.85%).

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