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Stereoselective synthesis of (*Z*,*E*)-2-phenylselenobutadienes by palladium-catalyzed cross-coupling reaction

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Abstract

Hydrozirconation of 1-alkynes gives (*E*)-alkenylzirconium complexes **3**, which are cross-coupled with (*E*)-α-phenylselenovinyl bromides (**4**) in the presence of tetrakis (triphenylphosphine) palladium catalyst to afford (*Z*,*E*)-2-phenylselenobutadienes (**5**) in good yields.

Keywords: Selenium; Palladium; Zirconium; Hydrozirconation; Cross-coupling reaction

1. Introduction

The stereocontrolled synthesis of conjugated dienes is of considerable interest in organic synthesis since such dienes are often encountered in natural compounds, such as Achillea amide [1], and are also valuable intermediates in the synthesis of more complex targets via Diels–Alder reaction [2]. Conjugated dienes are usually prepared by utilizing either a Wittig type approach [3] or coupling reactions of stereodefined vinyl halides with vinyl organometallic compounds catalyzed by transition metals [4]. The synthesis of 1,3-dienes containing functional groups is also of considerable interest in recent years. The stereoselective synthesis of (*E*,*E*)-1-trimethylsilylbutadienes [5,6], (*E*,*E*)-1-phenylthio-butadienes [7] has already been described in the literature. Dienyl selenides serve as valuable versatile intermediates since vinyl selenides are synthetically equivalent to carbonyls and can be stereospecifically converted to alkenes by nickel-catalyzed coupling reactions with Grignard reagents [8]. In the literature, we found the stereoselective synthesis of (*E*,*E*)-1-arylselenobutadienes [9] and polysubstituted dienyl selenides [10,11]. However, the synthesis of (*Z*,*E*)-2-arylselenobutadienes has been rarely reported [11].

The (*E*)-alkenylzirconium complexes, obtained by hydrozirconation of 1-alkynes, can be cross-coupled with alkenyl halides in the presence of catalytic amount of $Pd(PPh_3)_4$ or $Ni(PPh_3)_4$ to form 1,3-butadienes [12,13]. We now wish to report that (*Z*,*E*)-2-phenylselenobutadienes could be synthesized by cross-coupling reaction of (*E*)-alkenylzirconium complexes with (*E*)-α-phenylselenovinyl bromides in the presence of a catalytic amount of $Pd(PPh_3)_4$.

2. Results and discussion

(*E*)-α-Phenylselenovinyl bromides (**4**) were conveniently synthesized in good yields with high stereoselectivity by the addition of hydrogen bromide to alkynyl phenyl selenides [14]. Hydrozirconation of 1-alkynes **1** at room temperature (r.t.) in THF gave (*E*)-alkenylzirconium complexes **3**, which were cross-coupled with (*E*)-α-phenylselenovinyl bromides (**4**) in the presence of $Pd(PPh_3)_4$ catalyst to afford (*Z*,*E*)-2-phenylselenobutadienes (**5**) in good yields (Scheme 1). The experimental results are summarized in Table 1.

It is well documented that the cross-coupling reaction of alkenylzirconium complexes with alkenyl halides in the presence of a palladium catalyst occurs with retention of configuration [12,13]. The *E*-configuration of the compounds **5** has been proved by their ^{1}H-NMR

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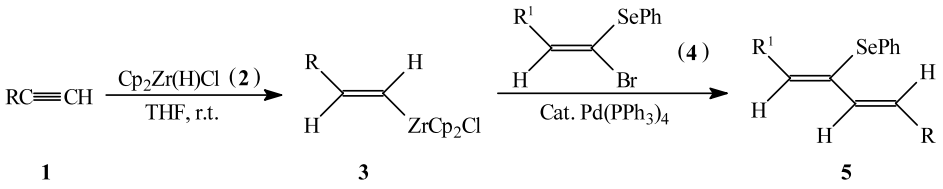


Scheme 1.

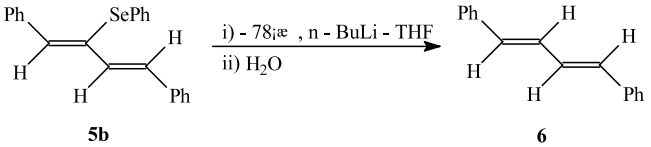
Table 1
Synthesis of (*Z*,*E*)-2-phenylselenobutadienes **5a**–**5i**

R in **1**	R^1 in **4**	Product **5**	Yield [a](%)
n-C_4H_9	Ph	**5a**	85
Ph	Ph	**5b**	72
CH_3OCH_2	Ph	**5c**	67
n-C_4H_9	n-C_4H_9	**5d**	82
Ph	n-C_4H_9	**5e**	77
CH_3OCH_2	n-C_4H_9	**5f**	74
n-C_4H_9	n-C_6H_{13}	**5g**	83
Ph	n-C_6H_{13}	**5h**	76
CH_3OCH_2	n-C_6H_{13}	**5i**	65

[a] Isolated yield based on compound **4**.

spectra, which show a doublet at $\delta = 6.0$–6.8 ppm with a coupling constant of 15–16 Hz, and this is also the evidence of the retention of the *E*-configuration of the starting compounds **3**. In addition, the configuration of the dienyl selenide **5b** could be confirmed from compound **6** which was obtained by treatment of **5b** with *n*-butyllithium in THF followed by hydrolysis, a reaction which occurs stereoselectively (Scheme 2). The stereochemistry of compound **6** was easily established, since ^{1}H-NMR spectrum (500 MHz) of **6** gives rise to a doublet–doublet at $d = 6.97$ ppm with coupling constants of 14.7 and 9.1 Hz and a doublet–doublet at $d =$ 6.68 ppm with coupling constants of 14.6 and 9.0 Hz, which is consistent with an (*E*,*E*)-configuration. The melting point of compound **6** was determined to be 147–148 °C which is also consistent with an (*E*,*E*)-configuration [15].

In conclusion, we have developed a novel route to the synthesis of (*Z*,*E*)-2-phenylselenobutadienes via palladium-catalyzed cross-coupling reaction. The major advantages of this coupling reaction are the preparation convenience of (*E*)-α-phenylselenovinyl bromides (**4**) via the addition of hydrogen bromide to alkynyl phenyl selenides and the configuration retention of both the starting alkenylzirconium complexes and the alkenyl bromides. Investigations into the synthetic applications of (*Z*,*E*)-2-phenylselenobutadienes (**5**) are currently in progress.



Scheme 2.

3. Experimental details

$Cp_2Zr(H)Cl$ was prepared according to literature [16]. Solvent THF was distilled from sodium–benzophenone ketyl before use. ^{1}H-NMR spectra were recorded on a Bruker AC-P200 (200 MHz) or Bruker AC-P500 (500 MHz) spectrometer with TMS as internal standard in $CDCl_3$. IR spectra were determined on an FTS-185 instrument as neat films. Mass spectra were obtained on a Finigan 8239 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyser.

3.1. General procedure for the synthesis of *5a*–*5i*

A dry 25 ml round-bottomed flask was charged with **2** (1.5 mmol). THF (8 ml) was injected, followed by addition of **1** (1.5 mmol) at r.t. The mixture was stirred at r.t. for 30 min under nitrogen to yield a clear solution. It was then added with **4** (1.0 mmol) and $Pd(PPh_3)_4$ ($1.0 \times 5\%$ mmol) and stirred at r.t. for 5 h. The mixture was diluted with diethyl ether (30 ml) and the mixture was filtered through a short plug of silica gel and concentrated to give a residue. The residue was purified by flash chromatography on silica gel eluting with light petroleum ether.

3.1.1. (1*Z*,3*E*)-1-Phenyl-2-phenylseleno-1,3-octadiene (*5a*)

IR (film): ν (cm^{-1}) 3056, 3021, 2955, 2926, 1634, 1597, 1491, 1476, 735, 690. ^{1}H-NMR: d 7.13–7.56 (m, 11H), 6.23 (m, 2H), 2.40 (m, 2H), 1.22–1.45 (m, 4H), 0.90 (t, $J = 6.5$ Hz, 3H) ppm. MS: *m*/*z* 341 ([M^+], 12), 178 (100). Anal. Found: C, 70.22; H, 6.28. Calc. for $C_{20}H_{22}Se$: C, 70.38; H, 6.45%.

3.1.2. (1*Z*,3*E*)-1,4-Diphenyl-2-phenylseleno-1,3-butadiene (*5b*)

IR (film): ν (cm^{-1}) 3057, 3024, 1596, 1576, 1493, 736, 690. ^{1}H-NMR: d 7.02–7.62 (m, 18H) ppm. MS: *m*/*z* 362 ([M^+], 16), 77 (100). Anal. Found: C, 73.25; H, 4.84. Calc. for $C_{22}H_{18}Se$: C, 73.13; H, 4.99%.

*3.1.3. (1Z,3E)-1-Phenyl-2-phenylseleno-5-methoxy-1,3-pentadiene (**5c**)*

IR (film): ν (cm^{-1}) 3056, 3020, 2924, 1639, 1577, 1491, 1122, 735, 690. ^{1}H-NMR: d 7.15–7.54 (m, 10H), 7.09 (s, 1H), 6.45 (d, $J = 16.0$ Hz, 1H), 6.32 (m, 1H), 3.99 (d, $J = 6.0$ Hz, 2H), 3.30 (s, 3H) ppm. MS: m/z 330 ([M^+], 17), 115 (100). Anal. Found: C, 65.47; H, 5.41. Calc. for $C_{18}H_{18}OSe$: C, 65.65; H, 5.47%.

*3.1.4. (5Z,7E)-6-Phenylseleno-5,7-dodecadiene (**5d**)*

IR (film): ν (cm^{-1}) 3058, 3015, 2942, 1578, 1476, 1438, 734, 689. ^{1}H-NMR: d 7.15–7.54 (m, 5H), 6.53 (t, $J = 7.0$ Hz, 1H), 6.09 (m, 2H), 2.05–2.45 (m, 4H), 1.18–1.52 (m, 8H), 0.69–1.08 (m, 6H) ppm. MS: m/z 322 ([M^+], 28), 81 (100). Anal. Found: C, 67.13; H, 8.04. Calc. for $C_{18}H_{26}Se$: C, 67.29; H, 8.10%.

*3.1.5. (1E,3Z)-1-Phenyl-3-phenylseleno-1,3-octadiene (**5e**)*

IR (film): ν (cm^{-1}) 3058, 3024, 2956, 2870, 1623, 1578, 1493, 1476, 734, 689. ^{1}H-NMR: d 7.14–7.47 (m, 11H), 6.83 (d, $J = 16.0$ Hz, 1H), 6.37 (t, $J = 7.0$ Hz, 1H), 2.43 (m, 2H), 1.27–1.49 (m, 4H), 0.90 (t, $J = 6.5$ Hz, 3H) ppm. MS: m/z 342 ([M^+], 10), 129 (100). Anal. Found: C, 70.51; H, 6.39. Calc. for $C_{20}H_{22}Se$: C, 70.38; H, 6.45%.

*3.1.6. (2E,4Z)-1-Methoxy-4-phenylseleno-2,4-nonadiene (**5f**)*

IR (film): ν (cm^{-1}) 3057, 3038, 2924, 1644, 1578, 1476, 1438, 1123, 734, 689. ^{1}H-NMR: d 7.14–7.39 (m, 5H), 6.31 (d, $J = 15.2$ Hz, 1H), 6.24 (t, $J = 7.0$ Hz, 1H), 6.13 (m, 1H), 3.94 (d, $J = 5.8$ Hz, 2H), 3.30 (s, 3H), 2.42 (m, 2H), 1.26–1.42 (m, 4H), 0.88 (t, $J = 7.0$ Hz, 3H) ppm. MS: m/z 310 ([M^+], 41), 45 (100). Anal. Found: C, 62.30; H, 7.21. Calc. for $C_{16}H_{22}OSe$: C, 62.14; H, 7.12%.

*3.1.7. (5E,7Z)-7-Phenylseleno-5,7-tetradecadiene (**5g**)*

IR (film): ν (cm^{-1}) 3058, 3016, 2925, 2855, 1638, 1578, 1476, 1438, 733, 688. ^{1}H-NMR: d 7.15–7.55 (m, 5H), 6.53 (t, $J = 7.0$ Hz, 1H), 6.08 (m, 2H), 2.06–2.45 (m, 4H), 1.18–1.58 (m, 12H), 0.72–1.02 (m, 6H) ppm. MS: m/z 349 ([M^+], 13), 109 (100). Anal. Found: C, 68.59; H, 8.51. Calc. for $C_{20}H_{30}Se$: C, 68.77; H, 8.60%.

*3.1.8. (1E,3Z)-1-Phenyl-3-phenylseleno-1,3-decadiene (**5h**)*

IR (film): ν (cm^{-1}) 3057, 3024, 1623, 1578, 1493, 1476, 1437, 733, 689. ^{1}H-NMR: d 7.14–7.54 (m, 11H), 6.81 (d, $J = 16.0$ Hz, 1H), 6.37 (t, $J = 7.0$ Hz, 1H), 2.45 (m, 2H), 1.14–1.55 (m, 8H), 0.88 (t, $J = 6.5$ Hz, 3H). MS: m/z 370 ([M^+], 10), 43 (100). Anal. Found: C, 71.37; H, 6.95. Calc. for $C_{22}H_{26}Se$: C, 71.54; H, 7.05%.

*3.1.9. (2E,4Z)-1-Methoxy-4-phenylseleno-2,4-undecadiene (**5i**)*

IR (film): ν (cm^{-1}) 3058, 3039, 2924, 2854, 1645, 1578, 1476, 1438, 1123, 734, 689. ^{1}H-NMR: d 7.13–7.33 (m, 5H), 6.32 (d, $J = 15.2$ Hz, 1H), 6.24 (t, $J = 7.0$ Hz, 1H), 6.13 (m, 1H), 3.94 (d, $J = 5.8$ Hz, 2H), 3.23 (s, 3H), 2.45 (m, 2H), 1.25–1.42 (m, 8H), 0.87 (t, $J = 6.5$ Hz, 3H). MS: m/z 338 ([M^+], 14), 45 (100). Anal. Found: C, 64.15; H, 7.81. Calc. for $C_{18}H_{26}OSe$: C, 64.09; H, 7.72%.

*3.2. Synthesis of (1E,3E)-1,4-diphenyl-1,3-butadiene (**6**)*

n-BuLi (1.6 M hexane solution, 1.1 mmol) was added to a THF (5.0 ml) solution of **5b** (0.361 g, 1.0 mmol) at −78 °C. After stirring for 30 min, the mixture was hydrolyzed with saturated aqueous NH_4Cl and extracted with CH_2Cl_2 (2×10 ml). The organic extract was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by column chromatography over silica gel using light petroleum ether as eluent to give **6** (0.166 g, 81%). m.p. 147–148 °C, literature [15] m.p. 149–150 °C. IR (KBr): ν (cm^{-1}) 3054, 3015, 1635, 1593, 1490, 992, 739, 690. ^{1}H-NMR (500 MHz, $CDCl_3$): d 7.45 (d, $J = 7.5$ Hz, 4H), 7.22–7.35 (m, 6H), 6.97 (dd, $J = 14.7$, 9.1 Hz, 2H), 6.68 (dd, $J = 14.6$, 9.0 Hz, 2H).

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