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Stereoselective synthesis of (E)-vinylic selenides by palladium catalyzed cross-coupling reactions

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Abstract

Hydrozirconation of arylselenoethynes gives zirconium (IV) complexes **3**, which are cross-coupled with aryl halides in the presence of tetrakis (triphenylphosphine) palladium catalyst to afford (E)-vinylic selenides **5** in high yield.

Keywords: Selenium; Palladium; Zirconium

1. Introduction

Vinylic selenides are promising synthetic intermediates [1], but only a few methods for the synthesis of (E)-vinylic selenides are available. The reaction of selenoacetylenes with $LiAlH_4$ in refluxing THF afforded (E)-vinylic selenides [2]. Hydroboration of 1-alkynes yielded (E)-alkenylboronic acids, which were treated with NaOH followed by PhSeBr stereoselectively to give (E)-vinylic selenides [3]. It is worth noting that there is no carbon–carbon bond formation in these reactions. However, the method described in this paper involves carbon–carbon bond formation.

Hydrozirconation [4] has emerged as a unique hydrometalation with some attractive features, such as the facile formation of terminally Zr-substituted derivatives from internal alkenes [5] and high regioselectivity observed with alkynes [6] and dienes [7]. Moreover, the reaction can tolerate certain functional groups, in particular oxyfunctional groups which are incompatible with hydroalumination [8].

The (E)-alkenylzirconium complexes, obtained by hydrozirconation of 1-alkynes, can be cross-coupled with aryl halides in the presence of a catalytic amount of $Pd(PPh_3)_4$ or $Ni(PPh_3)_4$ to form arylated alkenes [9].

2. Results and discussion

In this paper we will report a facile stereoselective synthesis of (E)-vinylic selenides **5** involving carbon–carbon bond formation by cross-coupling reaction of aryl halides **4** with selenium-containing alkenyl zirconium (IV) complexes **3**, which are produced by hydrozirconation [10] of arylselenoethynes **1** [11], in the presence of $Pd(PPh_3)_4$ catalyst. The experimental results are summarized in Table 1.

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

We found that the optimum molar ratio of **2** to **1** was 1 : 1. When **2** was excess, a side reaction occurred, the undesired yellow diarydiselenides being formed as depicted in Scheme 2.

The yields of (E)-alkenylzirconium derivatives obtained by reaction of $Cp_2Zr(H)Cl$ with alkynes in a 1 : 1 molar ratio have typically been in the range 75–90% by ^1H NMR [12]. Thus, it was necessary to use modest excess of **1** and **2** for the complete conversion of aryl halides into desired cross-coupled products.

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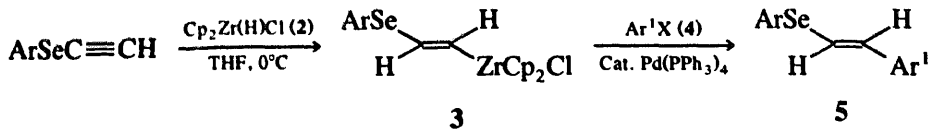


1	a	b	c
Ar	Ph	4-MeC_6H_4	4-BrC_6H_4

4	a	b	c	d
X	I	Br	I	I
Ar^1	Ph	Ph	4-ClC_6H_4	4-BrC_6H_4

Scheme 1.

The stereochemistry of products **5** was easily established, since ^1H NMR spectra of products **5a–f** give rise to a doublet at δ 6.6–7.0 with a coupling constant of 15–16 Hz, typical of trans positioned protons [13].

3. Experimental details

Solvent THF was distilled from $LiAlH_4$. All reactions were carried out under a nitrogen atmosphere. ^1H NMR spectra were recorded on a Bruker AC-P200 (200 MHz) spectrometer with TMS as internal standard in $CDCl_3$. IR spectra were taken on a Shimadzu IR-435 spectrometer. MS spectra were obtained on a HP 5890A mass spectrometer and microanalyses were measured using a Yanaco MT-3 CHN microelemental analyser.

3.1. General procedure for the synthesis of 5a–e

A dry 10 ml round-bottomed flask was charged with **2** (0.8 mmol). THF (4 ml) was injected, followed by addition of **1** (0.8 mmol) at 0°C. The mixture was stirred at 0°C for 40 min to yield a clear solution. It was then added with **4** (0.6 mmol) and $Pd(PPh_3)_4$ (0.6 × 5% mmol) and stirred at room temperature for 4 h. The mixture was diluted with diethyl ether (15 ml) and the mixture was filtered through a short plug of silica gel and concentrated to give a residue. The residue was purified by preparative TLC on silica gel eluting with light petroleum ether.

Table 1
Synthesis of (E)-vinylic selenides **5a–e**

1	4	Product 5	M.p. (°C) [a]	Yield [b]
1a	4a	5a	oil	85
1a	4b	5a	oil	43
1a	4c	5b	49–50	75
1b	4a	5c	oil	79
1b	4c	5d	90–91	82
1b	4d	5e	83–84	66
1c	4a	5f	59–60	81

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

3.1.1. (E)-1-(Phenylseleno)-2-phenylethene (5a)

IR (film), ν(cm^{-1}) 3040, 1675, 1475, 930, 690. ^1H NMR [14]: δ 7.20–7.45 (m, 11H), 7.0 (d, J = 15.6 Hz, 1H). MS: m/z 260 (M^+, 38.84), 77 (100.00).

3.1.2. (E)-1-(Phenylseleno)-2-(4-chlorophenyl) ethene (5b)

IR (KBr): ν(cm^{-1}) 3041, 1629, 1571, 784, 748. ^1H NMR: δ 7.13–7.34 (m, 10H), 6.62 (d, J = 15.7 Hz, 1H). MS: m/z 293.95, (M^+, 54.30), 178.05 (100.00). Anal. Found: C, 57.46; H, 3.99. $C_{14}H_{11}ClSe$ Calc.: C, 57.27; H, 3.78%.

3.1.3. (E)-1-(4-Methylphenylseleno)-2-phenylethene (5c)

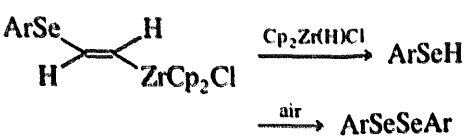
IR film: ν(cm^{-1}) 3044, 1596, 1487, 800, 728. ^1H NMR: δ 7.24–7.60 (m, 10H), 6.92 (d, J = 16.4 Hz, 1H), 2.47 (s, 3H). MS: m/z 274.00 (M^+, 69.06), 194.20 (100.00). Anal. Found: C, 66.53; H, 4.37. $C_{15}H_{14}Se$ Calc.: C, 66.69; H, 4.11%.

3.1.4. (E)-1-(4-Methylphenylseleno)-2-(4-chlorophenyl) ethene (5d)

IR (KBr): ν(cm^{-1}) 3057, 2948, 1634, 1485, 829. ^1H NMR: δ 7.14–7.49 (m, 9H), 6.70 (d, J = 15.6 Hz, 1H), 2.37 (s, 3H). MS: m/z 307.95 (M^+, 55.15), 228.15 (100.00). Anal. Found: C, 58.40; H, 4.60. $C_{15}H_{13}ClSe$ Calc.: C, 58.57; H, 4.26%.

3.1.5. (E)-1-(4-Methylphenylseleno)-2-(4-bromophenyl) ethene (5e)

IR (KBr): ν(cm^{-1}) 2904, 1586, 1481, 956, 835. ^1H NMR: δ 7.14–7.44 (m, 9H), 6.68 (d, J = 15.6 Hz, 1H), 2.37 (s, 3H). MS: m/z 351.95 (M^+, 75.51), 178.15 (100.00). Anal. Found: C, 51.20; H, 3.95. $C_{15}H_{13}BrSe$ Calc.: C, 51.17; H, 3.72%.



Scheme 2.

3.1.6. (E)-1-(4-Bromophenylseleno)-2-phenylethene (5f)

IR (KBr): $\nu(cm^{-1})$ 3055, 1631, 1481, 1394, 809. ^1H NMR: δ 7.33–7.42 (m, 9H), 7.27 (d, $J = 15.7$ Hz, 1H), 6.98 (d, $J = 15.7$ Hz, 1H). MS: m/z 337.90 (M^+, 48.04), 178.00 (100.00). Anal. Found: C, 50.01; H, 3.54. $C_{14}H_{11}BrSe$ Calc.: C, 49.74; H, 3.28%.

Acknowledgements

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