

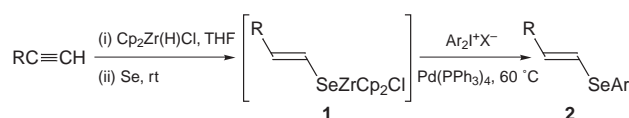
# A Stereoselective Synthesis of (*E*)-Arylvinyl Selenides *via* Coupling of (*E*)-Vinylseleno Zirconocenes and Diaryliodonium Salts†

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(*E*)-Arylvinyl selenides are prepared by coupling of (*E*)-vinylseleno zirconocenes and diaryliodonium salts.

Vinyl selenides are important intermediates in organic synthesis, and their promising potential could be anticipated by the combination of the special reactivity of selenium and the reactivity associated with the carbon–carbon double bond. They are particularly useful in highly stereoselective C–C bond formation processes.<sup>1</sup> Various preparations of these compounds have been reported, however, most of these methods involved the use of highly toxic selenides, such as RSeX, RSeSeR or RSeH, furthermore, many of these methods are not stereocontrolled and give mixtures of isomers.<sup>1</sup> Recently we developed a novel methodology which involved the insertion of elemental selenium into the C(sp<sup>2</sup>)–Zr bond of alkenylchlorozirconocenes derived from hydrozirconation of alkynes, affording vinylseleno zirconocenes **1** as active intermediates. This method has been applied to the stereoselective synthesis of vinylseleno esters.<sup>2</sup> Herein we report a stereoselective synthesis of (*E*)-arylvinyl selenides *via* coupling of (*E*)-vinylseleno zirconocenes **1** and diaryliodonium salts (Scheme 1).



Scheme 1

The insertion of elemental selenium into the C(sp<sup>2</sup>)–Zr bond proceeds smoothly in THF at room temperature and is usually completed within 30 minutes, affording a red solution. The vinylseleno zirconocenes **1** produced were trapped with diaryliodonium salts, giving arylvinyl selenides **2** in moderate yields. Catalytic amounts of Pd(0) can effectively accelerate the reaction. The results are summarized in Table 1. It is noteworthy that arylation of aryl selenides with diaryliodonium salts has been reported.<sup>3</sup>

**Table 1** Synthesis of (*E*)-vinyl selenides from alkynes, elemental selenium and diaryliodonium salts

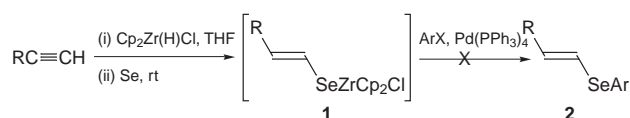
RC≡CH R	Ar <sub>2</sub> I <sup>+</sup> X <sup>-</sup> Ar	Products	Yield <sup>a</sup> (%)
Ph	Ph	<b>2a</b>	66
Ph	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	<b>2b</b>	72
Ph	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	<b>2c</b>	65
MeOCH <sub>2</sub>	Ph	<b>2d</b>	69
MeOCH <sub>2</sub>	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	<b>2e</b>	71
MeOCH <sub>2</sub>	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	<b>2f</b>	62

<sup>a</sup>Isolated yields.

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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)*.

Coupling of aryl halides with a variety of organometallics has long been achieved *via* organopalladium chemistry.<sup>4</sup> Initially we tried the Pd-catalyzed coupling reaction of vinylseleno zirconocenes **1** with aryl bromides and aryl iodides but it failed. (Scheme 2).



Scheme 2

It should be pointed out that besides the alkynes employed in Scheme 1, various internal alkynes can undergo the hydrozirconation reaction smoothly and stereoselectively,<sup>5</sup> moreover, all the reagents used in Scheme 1 are easily available and of low toxicity. As a result, the present method has provided an environmentally friendly, stereoselective route to various arylvinyl selenides.

## Experimental

Cp<sub>2</sub>Zr(H)Cl<sup>6</sup> and diaryliodonium salts<sup>7</sup> were prepared according to literature procedures. THF was freshly distilled from sodium/benzophenone before use. All reactions were carried out under an N<sub>2</sub> atmosphere.

**General Procedure for the Synthesis of Arylvinyl Selenides (2a–2f).**—To a stirred suspension of Cp<sub>2</sub>Zr(H)Cl (1.2 mmol, 0.308 g) in THF (8 ml) under an N<sub>2</sub> atmosphere was added alkyne (1.0 mmol). The mixture was stirred until the solution became clear and was then transferred *via* syringe into a stirred suspension of selenium powder (1.0 mmol, 0.080 g) in THF (2 ml). The mixture turned gradually from a green suspension into a red solution during 0.5 h. Diaryliodonium salt (1 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.05 mmol) were added and the mixture was left stirring at about 60 °C for 6 h. It was then diluted with light petroleum and filtered through a short plug of silica gel. After evaporation of the filtrate the residue was purified by preparative thin layer chromatography on silica gel (light petroleum as the eluent for **2a–2c**, light petroleum–ethyl acetate (20:1) for **2d–2f**). Compound **2a**:<sup>8</sup> δ<sub>H</sub>(CCl<sub>4</sub>, HMDS) 7.50–6.90 (11H, m), 6.72 (1H, d, *J* 15.6 Hz). IR (film): ν<sub>max</sub>/cm<sup>-1</sup> 3100, 3080, 3050, 1650, 1610, 1590, 1506, 950, 730, 690. Compound **2b**:<sup>9</sup> δ<sub>H</sub>(CCl<sub>4</sub>, HMDS) 7.60–6.90 (10H, m), 6.68 (1H, d, *J* 16.4 Hz), 2.28 (3H, s). IR (film): ν<sub>max</sub>/cm<sup>-1</sup> 3100, 3060, 1610, 1494, 800, 728, 690. Compound **2c**: mp 58–60 °C (lit.<sup>8</sup> 59–60 °C). δ<sub>H</sub>(CCl<sub>4</sub>, HMDS) 7.60–6.90 (10H, m), 6.74 (1H, d, *J* 15.2 Hz), IR (film, CCl<sub>4</sub>): ν<sub>max</sub>/cm<sup>-1</sup> 3042, 1612, 1584, 1508, 950, 690. Compound **2d**:<sup>8</sup> δ<sub>H</sub>(CCl<sub>4</sub>, HMDS) 7.60–6.90 (5H, m), 6.57 (1H, d, *J* 15.6 Hz), 5.86 (1H, dt, *J* 5.6 and 15.6 Hz), 3.82 (2H, d, *J* 5.6 Hz), 3.20 (3H, s). IR (film): ν<sub>max</sub>/cm<sup>-1</sup> 3100, 3020, 1640, 1600, 1495, 960, 745, 700, 675. Compound **2e**:<sup>8</sup> δ<sub>H</sub>(CCl<sub>4</sub>, HMDS) 7.50–7.20 (2H, m), 7.16–6.87 (2H, m), 6.53 (1H, d, *J* 15.4 Hz), 5.80 (1H, dt, *J* 5.4 and 15.4 Hz), 3.80 (2H, d, *J* 5.4 Hz), 3.16 (3H, s), 2.27 (3H, s). IR (film): ν<sub>max</sub>/cm<sup>-1</sup> 3020, 1640, 1505, 950, 810, 755. Compound **2f**:<sup>8</sup> δ<sub>H</sub>(CCl<sub>4</sub>, HMDS) 7.50–7.16 (4H, m), 6.57 (1H, d, *J* 15.8 Hz), 5.86 (1H, dt, *J* 5.2 and 15.8 Hz), 3.84 (2H, d, *J* 5.2 Hz), 3.20 (3H, s). IR (film): ν<sub>max</sub>/cm<sup>-1</sup> 3020, 1640, 1585, 1500, 1490, 960, 920, 820, 715.

This work was supported by the National Natural Science Foundation of China (Projects 29672008 and 29772007).

Received, 1st July 1999; Accepted, 22nd July 1999  
Paper E/9/05291G

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