

# Insertion of selenium into zinc carbon bonds and its application in the synthesis of unsymmetrical diarylselenides<sup>†</sup>

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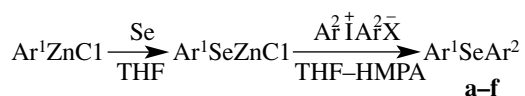
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Selenium inserts into the zinc carbon bond of aryl zinc halides to form the corresponding zinc selenoates; these react in THF-HMPA with diaryliodonium salts to afford unsymmetrical diaryl selenides in good yields.

**Keywords:** selenium, zinc carbon bond, aryl zinc halides

Organoselenium compounds have attracted considerable interest as reagents and intermediates in organic synthesis. There are many reports every year about their preparation and reaction.<sup>1–6</sup> A convenient and general method of introducing a selenium group into organic molecules is the reaction of a metal selenoate with an appropriate electrophile. Recently selenoates or complexes of transition metal such as Ti<sup>7</sup>, Zr<sup>8</sup>, Hf<sup>9</sup>, Sm<sup>10</sup>, Yb<sup>11</sup> and Cd<sup>12</sup> have been used in the synthesis of organoselenium compounds. This is due to their good nucleophilicity in aprotic solvents. Their preparation can be *via* reductive cleavage of Se–Se bonds, but a more convenient and simple method is *via* the insertion reaction of selenium into a carbon metal bond. Zinc is a very abundant, relatively inexpensive and generally nontoxic element. Moreover organic zinc compounds can be readily prepared. This led us to study the insertion of selenium into the zinc carbon bond. In this paper, we describe the reaction and its application in the synthesis of unsymmetrical diarylselenides.

We investigated the insertion of selenium into the zinc carbon bond of aryl zinc halides. The results showed the reaction could be smoothly carried out in THF to give the corresponding zinc aryl selenoates. We then investigated the reaction of the zinc aryl selenoates with some arylating reagents. The results showed that the zinc aryl selenoates did not react with haloarenes, even the active *p*-chloronitrobenzene. Considering that diaryliodonium salts are efficient electrophilic arylating reagents, we further investigated the reaction of zinc aryl selenoates with diaryliodonium salts. The experimental results showed that the reaction could be carried out at 60°C in THF–HMPA and gave unsymmetrical diaryl selenides in good yields (Table 1).



Unsymmetrical diaryl selenides are important compounds. There are several other methods for their preparation.<sup>13–17</sup> However, some of these suffer from disadvantages such as the use of expensive or less easily available reagents or harsh reaction conditions. The present method provides a new path for the synthesis of unsymmetrical diaryl selenides, Moreover it uses available starting materials and gives good yields as well as involving only simple manipulations.

**Table 1** Yields and melting points of unsymmetrical diarylselenides.

Product	Ar <sup>1</sup>	Ar <sup>2</sup>	m.p.(Lit)	Yield/%
a <sup>13</sup>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Ph	Oil	71
b <sup>13</sup>	<i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Ph	Oil	75
c <sup>13</sup>	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	Ph	Oil	68
d <sup>13</sup>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	ph	Oil	73
e <sup>10</sup>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	71–72(72–73)	67
f <sup>10</sup>	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	77–79(80–81)	69

## Experimental

Spectra data of <sup>1</sup>H NMR were recorded on a PMX-60 spectrometer. IR spectra were determined on a PE-683 spectrometer. Tetrahydrofuran was distilled from sodium benzophenoneketyl. Commercial HMPA was dried over calcium hydride, distilled *in vacuo* and stored over molecular sieves. All reactions were carried out under nitrogen.

The representative procedure for the synthesis of unsymmetrical diarylselenides is as follows: To a solution of Ar<sup>1</sup>MgBr (2.0 mmol) in THF (5 ml) was added anhydrous ZnCl<sub>2</sub> (2.0 mmol) and THF (10 ml) at 0°C. The mixture was stirred at r.t. for 30 minutes, then finely ground selenium (2.0 mmol) was added to the solution, which was stirred at reflux in THF until the selenium was consumed. The diaryliodonium salt (2.0 mmol) and HMPA (5ml) were added to the solution. The mixture was stirred at 60°C for 12h and then the reaction mixture was diluted with ether (60 ml). The organic phase was separated, washed with brine and dried with MgSO<sub>4</sub>. The solvent was evaporated. The crude product was subjected to preparative TLC on silica gel using light petroleum-ether as eluent (30:1). Spectroscopic data are as follows:

a: δ<sub>H</sub> (CDCl<sub>3</sub>) 2.28 (s, 3H), 7.10–7.51 (m, 9H). ν<sub>max</sub>(neat) 3080 (w), 2930 (m), 1580 (m), 1480 (s), 1025 (Ar–Se, m).

b: δ<sub>H</sub> (CDCl<sub>3</sub>) 2.30 (s, 3H), 7.07–7.60 (m, 9H). ν<sub>max</sub> (neat) 30759 (w), 2930 (m), 1580 (m), 1480 (s), 1445 (m). 1028(Ar–Se, m).

c: δ<sub>H</sub> (CDCl<sub>3</sub>) 3.73 (s, 3H), 7.13–7.42 (m, 5H), 7.55(m, 2H), 6.88 (m, 2H). ν<sub>max</sub> (neat) 3085(w), 2885 (m), 1605 (m), 1495 (s), 1250 (m), 1066 (Ar–Se, m).

d: δ<sub>H</sub> (CDCl<sub>3</sub>) 7.12–7.61 (m). ν<sub>max</sub> (neat) 3080 w), 1580 (m), 1480 (s), 1440 (m), 1090 (w), 1021 (Ar–Se, m).

e: δ<sub>H</sub> (CDCl<sub>3</sub>) 2.29 (s, 3H), 7.05–7.45 (m, 8H). ν<sub>max</sub>(KBr) 3080 (w), 2930 (m), 1495 (s), 1475 (m), 1010 (Ar–Se, m).

f: δ<sub>H</sub> (CDCl<sub>3</sub>) 2.28 (s, 3H), 6.91–7.30 (m, 8H). ν<sub>max</sub>(KBr) 3080 (w), 2930 (m), 1495 (m), 1390 (m), 1030 (Ar–Se, m).

The spectroscopic data agreed with these in the literature.<sup>10,13</sup>

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<sup>†</sup> This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

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