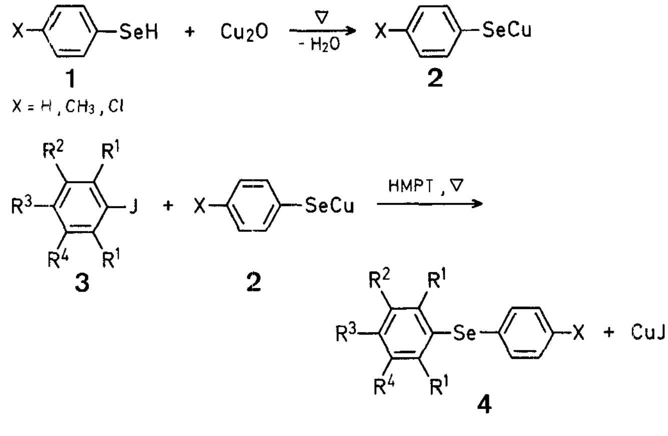
A Simple Synthesis of Unsymmetrical Diaryl Selenides from Copper(I) Areneselenolates and Aryl Iodides

Atsuhiro Osuka*, Nobuko Ohmasa, Hitomi Suzuki*

Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790, Japan

Among the useful and general methods for the preparation of unsymmetrical diaryl selenides[1], we can cite those involving the use of Grignard reagents, aryllithium reagents, diarylmercury compounds, diazonium salts, and photostimulated $S_{RN}1$ conditions[2]. However, these methods often suffer from disadvantages such as the use of expensive or less easily available reagents, incompatibility with the presence of functional groups, or laborious manipulation.

In a previous study, we have shown that copper(I) iodide is able to promote the arylation of areneselenolates by aryl iodides in hexamethylphosphoric triamide (HMPT) in which the *in situ* formed copper(I) areneselenolate is assumed to be a reactive species[3]. We have now found that copper(I) areneselenolates (**2**) can be conveniently prepared from copper(I) oxide and areneselenols (**1**) as insoluble solids and that compounds **2** are efficient reagents for converting aryl iodides into diaryl selenides under mild conditions. Compounds **2** have long been known but have received little attention in organic synthesis. The procedure involves simple heating a suspension of equimolecular amounts of **2** and an aryl iodide **3** in HMPT at 120 °C. The reaction mixture gradually turns to a light brown homogeneous solution. Dilution of the reaction mixture with water, followed by extraction of the precipitate with hexane affords the diaryl selenide **4** in good yield.



The reaction is easy, clean, and mild, and little tarry materials are formed. The method is particularly useful for the preparation of polymethylated diaryl selenides. The order of reactivity of aryl halides toward **2** is ArJ > ArBr ≫ ArCl, which is in accordance with copper(I) assisted nucleophilic aromatic substitutions[4]. Thus, when the mixed aryl halides **3h** and **3i** are treated with a copper(I) areneselenolate (**2**) the products **4** obtained are those arising from the preferential replacement of iodine.

Table 1. Unsymmetrical Diaryl Selenides (**4**) prepared

4	R^1	R^2	R^3	R^4	X	Yield[a] [%]	m.p. [°C]	Molecular formula[b]
a	H	H	CH_3	H	H	90	oil (136–137°)[c]	$C_{13}H_{12}Se$ (247.2)
b	CH_3	H	CH_3	H	H	94	oil	$C_{15}H_{16}Se$ (275.2)
c	CH_3	CH_3	H	CH_3	CH_3	91	101–102°	$C_{17}H_{20}Se$ (303.3)
d	CH_3	CH_3	CH_3	CH_3	H	93	97–99°	$C_{17}H_{20}Se$ (303.3)
e	CH_3	CH_3	CH_3	CH_3	CH_3	75	98–100°	$C_{18}H_{22}Se$ (317.3)
f	CH_3	CH_3	H	CH_3	Cl	84	93–94°	$C_{16}H_{17}ClSe$ (323.7)
g	CH_3	CH_3	CH_3	CH_3	Cl	88	92–93°	$C_{17}H_{19}ClSe$ (337.7)
h	CH_3	Br	CH_3	CH_3	H	66	97–101°	$C_{16}H_{17}BrSe$ (368.2)
i	CH_3	Cl	CH_3	CH_3	CH_3	70	87–90°	$C_{17}H_{19}ClSe$ (337.7)

[a] Yield of isolated product.

[b] The microanalyses were in good agreement with the calculated values: C, ±0.25; H, ±0.17.

[c] m.p. of dibromide (Ref.[5], m.p. 138–139 °C).

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Table 2. Spectral Data of Compounds **4**

4	I.R. (KBr) ν [cm^{-1}]	^{1}H-N.M.R. (60 MHz, CCl$_4$/TMS$_{int}$) δ [ppm]
a	690, 730, 850, 1020, 1070, 1295, 1375, 1440, 1475	2.23 (s, 3H); 6.6–7.5 (m, 9H)
b	690, 730, 850, 1020, 1070, 1290, 1370, 1435, 1470, 1570	2.23 (s, 3H); 2.40 (s, 6H); 6.7–7.0 (m, 7H)
c	795, 870, 1015, 1070, 1385, 1460, 1485, 1495	2.05 (s, 3H); 2.24 (s, 6H); 2.40 (s, 6H); 6.8 (s, 5H)
d	670, 690, 1010, 1085, 1380, 1440, 1480, 1580	2.27 (s, 9H); 2.50 (s, 6H); 7.00 (s, 5H)
e	800, 1020, 1070, 1305, 1490	2.21 (s, 12H); 2.47 (s, 6H); 6.8 (s, 4H)
f	720, 805, 875, 1005, 1060, 1085, 1090, 1375, 1385, 1460, 1470	2.23 (s, 6H); 2.38 (s, 6H); 6.7–7.2 (m, 5H)
g	730, 820, 1010, 1070, 1095, 1380	2.22 (s, 9H); 2.46 (s, 6H); 6.6–7.2 (m, 4H)
h	690, 735, 895, 920, 980, 1020, 1070, 1440, 1475, 1575	2.38 (s, 3H); 2.47 (s, 6H); 2.70 (s, 3H); 7.0 (m, 5H)
i	795, 925, 1015, 1065, 1300, 1485	2.22 (s, 6H); 2.37 (s, 3H); 2.47 (s, 3H); 2.60 (s, 3H); 6.8 (m, 4H)

Copper(I) areneselenolates (**2**) are neither water- nor air-sensitive and may be stored without loss of reactivity under a nitrogen atmosphere at −10 °C, at least for several months. They are also odorless, unlikely to be toxic, and easy to handle.

The structures of all new products were established by analytical data and ^{1}H-N.M.R. and I.R. spectra. All melting points are uncorrected.

Copper(I) 4-Methylbenzeneselenolate (2, X = CH$_3$); Typical Procedure:

A mixture of red copper(I) oxide (3 g, 21 mmol), 4-methylbenzeneselenol (7 g, 41 mmol; freshly distilled, b.p. 97–98 °C/22 torr), and ethanol (10 ml) is refluxed under nitrogen with stirring for 10 h, by which time the red suspension has turned to a thick salmon-pink suspension. Vacuum filtration, several washings with ethanol, and drying in vacuo give *copper(I) 4-methylbenzeneselenolate*; yield: 9.3 g (97%).

Copper(I) benzeneselenolate (**2**, X = H) and *copper(I) 4-chlorobenzeneselenolate* (**2**, X = Cl) are similarly prepared from copper(I) oxide and the corresponding benzeneselenols **1** in 94 and 89% yields, respectively.

2,3,4,4′,5,6-Hexamethyldiphenyl Selenide (4e); Typical Procedure:

A mixture of pentamethyliodobenzene (1.4 mmol), copper(I) 4-methylbenzeneselenolate (**2**, X = CH$_3$; 1.4 mmol), and HMPT (7 ml) is heated with stirring under nitrogen at 120 °C for 90 min, and is then poured into water (300 ml). The milky solution gradually separates a light brown precipitate which is filtered off, washed with water, sucked as dry as possible, placed in a filter thimble, and extracted with hexane using a Soxhlet extractor. The solvent is removed from the extract using a rotary evaporator and the residue is chromatographed on a silica gel column using hexane as eluent to give **4e** as a crystalline solid which is recrystallized from ethanol; yield: 333 mg (75%); m.p. 98–100 °C.

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* Address for correspondence.

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