



Diarylation of chalcogen elements using arylboronic acids via copper- or palladium-catalyzed oxidative coupling



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ABSTRACT

Transition metal-catalyzed diarylations of sulfur, selenium and tellurium were achieved using arylboronic acids in air. A copper-catalyzed reaction of sulfur or selenium efficiently yielded numerous symmetrical diaryl sulfides or selenides in the presence of NH_4BF_4 . However, the diarylation of tellurium was not possible using this method, and required a palladium catalyst in the presence of KI and air for the reaction to proceed.

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1. Introduction

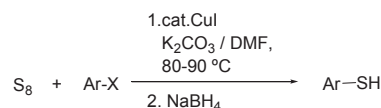
The transition metal-catalyzed formation of carbon–chalcogen bonds is an important reaction in organic syntheses. This method has been extensively researched and utilized to date.^{1,2} Herein produced compounds have been widely employed as convenient intermediates or reagents.³

To synthesize organochalcogenides, chalcogenols or dichalcogenides are often used as a chalcogen source.² Alternatively, procedures using chalcogens are also reported. Among them, Grignard reaction⁴ or coupling reaction of aryl or alkyl halides with sodium chalcogenides⁵ are routinely performed. However, the use of a transition metal-catalyzed synthesis is limited, either because of the formation of stable metal–chalcogen compounds as intermediates or because of the poor reactivity of transition metals with chalcogens.

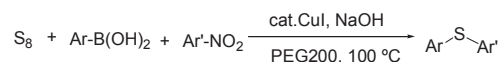
Recently, some methods have been exploited for the arylation of chalcogens. For instance, procedures involving the formation of S_{n+1}^{2-} following a reaction of sulfur with hydroxide were reported. Copper-catalyzed sulfidation of aryl halides using K_2CO_3 followed by NaBH_4 reduction affords aryl thiols (Scheme 1a).^{6a} A three component coupling using $\text{ArB}(\text{OH})_2$, ArNO_2 and sulfur was also performed in the presence of NaOH (Scheme 1b).^{6b} On the other hand, using magnesium as a reductant, diaryl sulfides or selenides were produced from aryl

halides in the presence of CuI catalyst (Scheme 1c).⁷ Furthermore, a CuF_2 -catalyzed reaction using arylboronic acids yields disulfides or monoselenides (Scheme 1d).⁸ The reaction is performed under nitrogen atmosphere, and is necessary for DMSO as an oxidant.

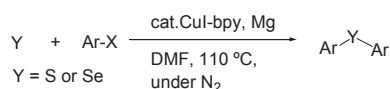
(a) Sulfidation of aryl halides with K_2CO_3



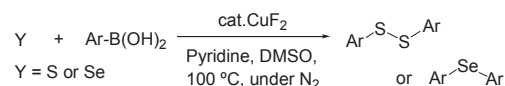
(b) Sulfidation of aryl boronic acid with NaOH



(c) Sulfidation of aryl halides



(d) Sulfidation of arylboronic acids



Scheme 1. Existing synthetic methods for the diarylation of chalcogen elements.

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These abovementioned reactions (Schemes 1a–d) are performed under basic or reductive conditions or require excess reagents and therefore are not efficient methods for synthesizing organochalcogenides involving various functional groups. Selective mono-sulfide synthesis is not easy owing to the generation of disulfides or trisulfides. Moreover, it is not possible to use tellurium in these reactions. Therefore, there is a need to develop of an efficient method for the arylation of chalcogens, including tellurium.

To overcome the aforementioned problems, the labilization of stable metal–chalcogen complexes formed as intermediates is required. It is hypothesized that the oxidation of these complexes is the most efficient method. The arylation of chalcogen elements with arylboronic acids in air was investigated by adopting conditions similar to those of the copper-catalyzed coupling of dichalcogenides with organoboronic acids.^{9,10}

From numerous experiments, the copper-catalyzed arylation of sulfur or selenium was found to occur in air. The reaction involving tellurium smoothly proceeded in the presence of a palladium catalyst, KI, and air. In this article, these developed methodology will be described.

2. Results and discussion

To establish suitable conditions, a combination of sulfur and 4-tolylboronic acid was initially evaluated (Table 1). When the reaction was performed using CuI catalyst, di(4-tolyl) sulfide **3b** was not formed (Entry 1). On the contrary, amine ligands promoted the reaction to a small extent (Entries 2–5). Fortunately, the addition of NH₄PF₆ or NH₄BF₄ improved the production of **3b** to 70 and 79% yield, respectively (Entries 6–7).¹¹ The reactions using other copper salts also gave good results (Entries 8–10). However, it was observed that palladium chloride or nickel chloride catalysts could not stimulate the reaction (Entries 11–12).

Table 1
Investigation of suitable reaction conditions^a

Entry	Cu-L (mol %)	Add.	3b (%)
1	CuI	None	0
2	CuI-bpy	None	54
3	CuI-TMEDA	None	0
4 ^b	CuI-Phen·H ₂ O	None	38
5	CuI-Phen·H ₂ O	None	50
6	CuI-Phen·H ₂ O	NH ₄ PF ₆	70
7	CuI-Phen·H ₂ O	NH ₄ BF ₄	79
8	CuCl-Phen·H ₂ O	NH ₄ BF ₄	76
9	CuBr-Phen·H ₂ O	NH ₄ BF ₄	75
10	CuCl ₂ -Phen·H ₂ O	NH ₄ BF ₄	73
11	PdCl ₂ -Phen·H ₂ O	NH ₄ BF ₄	0
12	NiCl ₂ -Phen·H ₂ O	NH ₄ BF ₄	0

^a A mixture of **1** S₈ (0.025 mmol), **2** (0.5 mmol), Metal-Phen·H₂O (1:1, 10 mol%) and additive (0.05 mmol) was treated in DMSO (0.2 mL) and H₂O (0.1 mL).

^b Isolated yields after silica gel chromatography.

According to the developed procedure, numerous diarylations of sulfur or selenium were then investigated (Table 2). The procedure afforded expected diaryl monosulfides or selenides in good yields (Entries 1–20). Arylboronic acids involving carbonyl groups were also synthesized (Entries 9–11, 17–18). Regrettably, the reaction using alkylboronic acids could not produce the corresponding

Table 2
Copper-catalyzed diarylation of chalcogen element using arylboronic acids^a

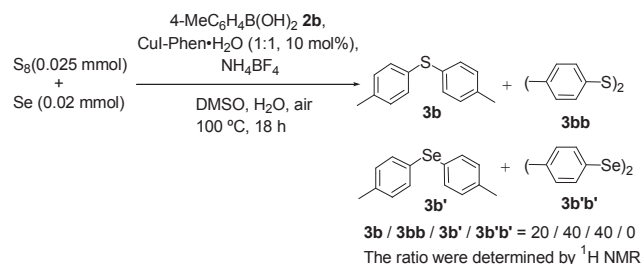
Entry	Y	Ar	Time (h)	3 (%) ^b
1	S ₈	Ph	18	80(3a)
2	Se		36	74(3a')
3	S ₈	4-MeC ₆ H ₄	18	79(3b)
4	Se		36	67(3b')
5	S ₈	4-MeOC ₆ H ₄	18	78(3c)
6	Se		36	73(3c')
7	S ₈	4-ClC ₆ H ₄	36	72(3d)
8	Se		36	74(3d')
9	S ₈	4-OHCC ₆ H ₄	36	87(3e)
10	S ₈	4-MeO ₂ CC ₆ H ₄	36	61(3f)
11	Se		36	72(3f')
12	S ₈	2-MeC ₆ H ₄	18	70(3g)
13	Se		36	78(3g')
14	S ₈	2-MeOC ₆ H ₄	24	82(3h)
15	Se		36	83(3h')
16	S ₈	2-ClC ₆ H ₄	36	85(3i)
17	S ₈	2-OHCC ₆ H ₄	36	73(3j)
18	Se		36	34(3j')
19	S ₈	1-Naphtyl	18	70(3k)
20	Se		36	60(3k')
21	S ₈	PhCH ₂ CH ₂	18	0
22	Te	4-MeC ₆ H ₄	18	0

^a A mixture of **1** S₈ (0.025 mmol) or Se (0.02 mmol), **2** (0.5 mmol), CuI-Phen·H₂O (1:1, 10 mol%) and NH₄BF₄ (0.05 mmol) was treated in DMSO (0.2 mL) and H₂O (0.1 mL).

^b Isolated yields after silica gel chromatography.

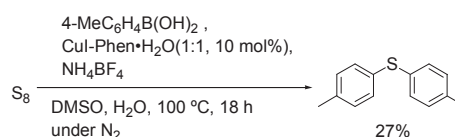
product and complex mixture was obtained (Entry 21). The reaction of tellurium hardly proceeded (Entry 22).

In the procedure, when a competitive reaction in the presence of both sulfur and selenium was performed, a sulfidation of arylboronic acid was predominate (Scheme 2).



Scheme 2. A reactivity of sulfur and selenium.

To elucidate the reaction mechanism, several experiments were carried out. When a mixture of sulfur and 4-tolylboronic acid were then reacted in the absence of oxygen, the corresponding sulfide was obtained in only 27% yield (Scheme 3).



Scheme 3. Diarylation of sulfur in the absence of oxygen.

The reactivity of copper-chalcogenides considered as intermediates was evaluated (Scheme 4). Using CuS or CuSe, the

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