Note

Hypervalent Iodine in Synthesis 64: Syntheses of Diaryl Selenides and Alkyl Aryl Selenides by Palladium-Catalyzed Arylation of Areneselenyl or Alkaneselenyl Magnesium Bromide with Diaryliodonium Salt†

WANG, Li[b,c](王莉) **CHEN, Zhen-Chu***[,a,b](陈振初) **ZHENG, Qin-Guo**[d](郑钦国)

[a] *Ningbo Institute of Technology, Zhejiang University, Ningbo, Zhejiang 315104, China*

[b] *Department of Chemistry, Zhejiang University (Xixi Campus), Hangzhou, Zhejiang 310028, China*

[c] *Department of Chemistry, Zhejiang Educational Institute, Hangzhou, Zhejiang 310012, China*

[d] *Pharmaceutical Sciences Research Institute, Aston University, Aston Triangle, Birmingham B4 7ET, UK*

Areneselenyl or alkaneselenyl magnesium bromide reacts rapidly with diaryliodonium salt to give the corresponding diaryl or alkyl aryl selenide in the presence of catalytic amounts of Pd(PPh$_3$)$_4$ in good yield.

Keywords diaryliodonium salt, arylation, palladium catalyst, selenide

The chemistry of organoselenium compounds has been growing in recent years, because of the many synthetic applications of organoselenium compounds.[1] A lot of methods for the synthesis of selenides have been reported,[2a-i] such as the reaction of lithium methyl selenide with unactivated aryl halides,[2a] the reaction of diazonium salts with a potassium alkaneselenolate,[2b] the reaction of diselenide with a Grignard reagent,[2c] the reaction of an arylselenium monobromide with a mercurydiaryl,[2c] the reaction of aryllithium compounds with arylselenocyanates,[2d] the arylation of sodium benzeneselenolate with an aryl halide catalyzed by nickel(II) complex,[2e] the photostimulated reaction of iodobenzene with selenide ion in liquid ammonia,[2f] the direct selenation of electron-rich aromatic compounds with (phenylseleno) dimethyl sulfonium tetrafluoroborate,[2g] the reaction of diaryl diselenides with activated halides in the presence of aminoiminomethanesulfinic acid,[2h] alkylation of diaryl diselenides with alkyl halides via Sm/BiCl$_3$[2i] and the palladium-catalyzed reaction of phenyltributylstannyl selenide (PhSeSnBu$_3$) with aryl halides.[2j] However, some of these methods implicate toxic and hazardous reagents,[2c,2j] low yields, long time,[2g] uncommon starting materials,[2d] expensive metallic selenium reagents[2a] or stoichiometric catalysts,[2i] thus limiting a general effective access to selenides. As an alternative to aryl halides, we have reported the palladium-catalyzed reactions of hypervalent iodonium salts with some of nucleophilic substrates.[3] It showed that diaryliodonium salts are efficient electrophilic arylating agents and prompted us to extend the palladium-catalyzed arylation to areneselenyl or alkaneselenyl magnesium bromide prepared from powdered gray selenium and aryl or alkyl Grignard reagent for an efficient synthesis method of aryl selenides. Here we wish to report the palladium-catalyzed cross-coupling of diaryliodonium salts with areneselenyl or alkaneselenyl magnesium bromide (Scheme 1).

Scheme 1

$$RSeMgBr + Ar_2I^+ BF_4^- \xrightarrow[THF,\ r.t.]{Pd(PPh_3)_4} RSeAr$$

It has been found that the palladium-catalyzed cross-coupling of diaryliodonium salts with areneselenyl or alka-

* E-mail: zhenchuc@mail.hz.zj.cn

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neselenyl magnesium bromide took place smoothly, reaching completion within 30 min at room temperature in THF. In the absence of palladium catalyst, the reaction did not proceed, so palladium catalyst is essential for this reaction. The results are summarized in Table 1. All products gave satisfactory m.p., IR and ^{1}H NMR spectra. The reaction was found to be general and applicable to aliphatic or aromatic selenyl magnesium bromide. Several diaryliodonium salts containing various substituents, such as methoxy, methyl, chloro, were successfully reacted. The present method is not only suitable for synthesis of symmetric aryl selenides but also for synthesis of unsymmetric aryl selenides.

In conclusion, we have provide a simple efficient synthesis method of aryl selenides by palladium-catalyzed cross-coupling of diaryliodonium salts with areneselenyl or alkaneselenyl magnesium bromide. It has some advantages over previous methods, such as mild reaction conditions, fast reaction rates and good yields. Furthermore, the method now described can give a contribution to growing applications of organoselenium compounds.

Experimental

General

^{1}H NMR spectra were recorded on a PMX-60 spectrometer, using CCl_4 as the solvent with TMS as an internal standard. IR spectra were determined on a PE-683 spectrophotometer. Melting points were uncorrected.

General procedure for syntheses of aryl selenides

To a stirred solution of diaryliodonium tetrafluoroborate (1.2 mmol), $Pd(PPh_3)_4$(58 mg, 5 mol%) and anhydrous THF (5 mL) under nitrogen atmosphere was added areneselenyl magnesium bromide (1 mmol easily prepared from powdered gray selenium and aryl Grignard reagent) at room temperature. The mixture was stirred at room temperature for half an hour. The solvent was evaporated off. To the residue, a saturated NH_4Cl solution (5 mL) was added and then extracted with ether (2 × 10 mL). The organic layer was dried over anhydrous sodium sulfate and evaporated *in vacuo*. The crude product was separated by preparative thin layer chromatography on silica gel with hexane as a developer to afford the desired product, aryl selenide.

Phenyl methyl selenide (Entry 1) oil;[2a] ^{1}H NMR δ: 7.40—7.00 (m, 5H), 2.25 (s, 3H); IR (film) ν: 3050, 2940, 2870, 1575, 1470, 1370, 1058, 1000, 1023, 1018, 685 cm^{-1}.

p-Chlorophenyl methyl selenide (Entry 2) M.p. 26—27 ℃ (lit.[2e] 28—28.5 ℃); ^{1}H NMR δ: 7.30—7.05 (m, 4H), 2.33 (s, 3H); IR (KBr) ν: 3080,

Table 1 Syntheses of selenides[a]

Entry	RSeMgBr R	$Ar_2I^+ BF_4^-$ Ar	Product	Yield (%)	
				This work[b]	Lit.[c]
1	CH_3	Ph	CH_3SePh	60	45[2a]
2	CH_3	*p*-ClC_6H_4	$CH_3SeC_6H_4Cl$-*p*	65	/
3	$C_6H_5CH_2$	Ph	$C_6H_5CH_2SePh$	87	72[2b]
4	$C_6H_5CH_2$	*p*-ClC_6H_4	$C_6H_5CH_2SeC_6H_4Cl$-*p*	92	96[2h]
5	*p*-$CH_3C_6H_4$	Ph	*p*-$CH_3C_6H_4SePh$	82	73[2d]
6	*p*-$CH_3C_6H_4$	*p*-ClC_6H_4	*p*-$CH_3C_6H_4SeC_6H_4Cl$-*p*	76	68[2d]
7	*p*-ClC_6H_4	Ph	*p*-ClC_6H_4SePh	86	74[2e]
8	*p*-ClC_6H_4	*p*-$CH_3C_6H_4$	*p*-$ClC_6H_4SeC_6H_4CH_3$-*p*	77	68[2d]
9	Ph	Ph	PhSePh	85	12[2f]
10	Ph	*p*-$CH_3C_6H_4$	$PhSeC_6H_4CH_3$-*p*	84	73[2d]
11	Ph	*p*-ClC_6H_4	$PhSeC_6H_4Cl$-*p*	87	68[2d]
12	Ph	*p*-$CH_3OC_6H_4$	$PhSeC_6H_4OCH_3$-*p*	81	44[2e]

[a] Reagent and conditions: 1.2 mmol of iodonium salt, 5 mol% $Pd(PPh_3)_4$ and 1 mmol of areneselenyl or alkaneselenyl magnesium bromide, in 5 mL of THF at room temperature under nitrogen atmosphere. [b] Isolated yields based on areneselenyl or alkaneselenyl magnesium bromide. [c] Yields reported in literature.

2930, 2865, 1575, 1475, 1380, 1060, 1015, 810, 730, 680 cm^{-1}.

Benzyl phenyl selenide (Entry 3) oil;[2b] ^1H NMR δ: 7.5—7.0 (m, 10H), 3.97 (s, 2H); IR (film) ν: 3080, 3040, 2950, 1610, 1585, 1505, 1485, 1465, 1440, 1310, 1220, 1180, 1160, 1065, 1020, 1000, 905, 867, 690 cm^{-1}.

Benzyl p-chlorophenyl selenide (Entry 4) M.p. 42—44 ℃ (lit.[2h] 43—45 ℃); ^1H NMR δ: 7.45—6.90 (m, 9H), 3.95 (s, 2H); IR (KBr) ν: 3105, 3070, 3040, 2940, 1600, 1500, 1480, 1455, 1390, 1220, 1185, 1090, 1073, 1030, 1010, 905, 690 cm^{-1}.

4-*Methylphenyl phenyl selenide* (Entries 5 and 10) oil;[2e] ^1H NMR δ: 7.45—7.00 (m, 9H), 2.30 (s, 3H); IR (film) ν: 3080, 2930, 1573, 1475, 1440, 1062, 1020, 800, 730, 682 cm^{-1}.

4-*Chlorophenyl* 4-*methylphenyl selenide* (Entries 6 and 8) M. p. 72—74 ℃ (lit.[2d] 72—73 ℃); ^1H NMR δ: 7.45—6.95 (m, 8H), 2.30 (s, 3H); IR (KBr) ν: 3080, 2930, 1490, 1480, 1390, 1250, 1090, 1065, 1015, 870, 810, 685 cm^{-1}.

4-*Chlorophenyl phenyl selenide* (Entries 7 and 11) oil;[2e] ^1H NMR δ: 7.70—7.10 (m, 9H); IR (film) ν: 3080, 2930, 1575, 1475, 1390, 1065, 1020, 810, 730, 685, 665 cm^{-1}.

Diphenyl selenide (Entry 9) oil;[2e] ^1H NMR δ: 7.55—7.10 (m, 10H); IR (film) ν: 3050, 1575, 1470, 1058, 1000, 1023, 1018, 680 cm^{-1}.

4-*Methoxyphenyl phenyl selenide* (Entry 12) M. p. 43—45 ℃ (lit.[2d] 45—46 ℃); ^1H NMR δ: 7.55—7.00 (m, 9H), 3.80 (s, 3H); IR (KBr) ν: 3080, 2950, 1605, 1500, 1250, 1060, 1028, 1004, 870, 820, 770, 680 cm^{-1}.

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