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New approaches to the synthesis of unsymmetrical diaryl selenides

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Abstract

Unsymmetrical diaryl selenides PhSeAr were obtained by the palladium catalysed reactions of aryl (heteroaryl) iodide or triflate with $Bu_3SnSePh$ in high yields. The same compounds can be obtained by the non-catalytic reactions of $Bu_3SnSePh$ with ArN_2BF_4 or $(ArN_2)_2ZnCl_4$. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Diaryl selenide; Aryl iodide; Aryl triflate; Aryldiazonium salts; Trialkyltin arylselenide

1. Introduction

Organotin compounds are widely used in cross-coupling reactions with the formation of C–C, C–N, C–P, C–S, C–Sn bonds as nucleophiles [1]. Although these reactions with tin derivatives proceed easier than those of corresponding anions, they have a number of disadvantages such as high toxicity of organotin compounds and their tedious synthesis. Thus the use of free amines, phosphines and thiols in the presence of base is more convenient [1]. Another situation is observed in the case of selenium derivatives, where starting selenols are foul-smelling, inconvenient to handle compounds. At the same time corresponding trialkyltin derivatives are easier to handle in comparison with selenols and they can be simply obtained in situ by irradiation of the mixture of Alk_6Sn_2 and R_2Se_2 [2].

The preparation of diaryl selenides has attracted considerable effort due to the fact that these compounds have widespread applications. Diaryl selenides, containing aminogroups, have useful antioxidative properties [3], some biologically active molecules include diarylselenium moiety [4], such polymers as poly(*p*-phenyleneselenide) and poly-(2,5 thienyleneselenide) [5] have evoked recent interest.

Most of the known methods of ArSeAr′ synthesis are based on one of two types of reactions. The first is the electrophylic substitution by RSeX (X = Hal, CN, SeR) in aryllithium, aryl Grignard reagents, diarylmercurials [6], or in anilines and phenols [7]. Diaryldiselenides can be used instead of ArSeCl that leads to the loss of one ArSe group. Another way is the nucleophilic reaction of $ArSe^-$ with aryl halogenides [8] or aryl diazonium salts [9]. In the case of aryl halides conditions of the reaction are rather drastic but this difficulty can be overcome by using nickel catalysis [10] or by activating the C–Hal bond by complexation of aryl halide with $Cr(CO)_3$, $CpFe^+$ or $Mn(CO)_3^+$ [11].

It has been shown recently that triarylbismuth reacts with diaryldiselenides to form corresponding diarylselenium compounds [12].

Most of these methods have the essential disadvantages. Methods of formation of starting selenolates are rather not effective. For example, excessive amounts of reducing agent is required in the synthesis based on diselenides. The use of selenols involves working with foul-smelling reagents. The synthesis of diaryl selenides requires an excess of selenolate that makes it difficult to separate the product. The product yield usually does not exceed 50–60%. Thus the simple and convenient general methods of synthesis of diaryl selenides are still of great interest. In the present paper we propose the convenient methods of synthesis of arylphenylselenides by the reaction of $Bu_3SnSePh$ with aryl iodides or with

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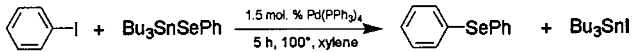
aryl triflates catalysed by palladium or nickel complexes or by the noncatalytic reaction of $Bu_3SnSePh$ with aryl diazonium salts.

2. Results and discussion

2.1. Reaction of $Bu_3SnSePh$ with aryl iodides

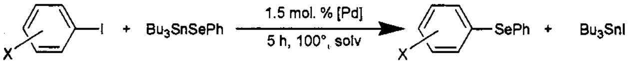
Aryl halogenides are the most widely used substrates for the cross-coupling reactions. The initial study of the reaction was done on the phenylation of $Bu_3SnSePh$ by iodobenzene (Table 1). We have found that the $Pd(PPh_3)_4$ catalysed reaction gives an excellent yield of diphenyl selenide (Eq. (1)).



(1)

The time of reaction depends on the amount of added catalyst (Table 1, entries 1–3). The activity of $PdCl_2(PPh_3)_2$ in xylene is less that of $Pd(PPh_3)_4$. The reaction time increases from 5 to 30 h (Table 1, entry 4). At the same time this complex is significantly more effective in DMF, the reaction needs 4 h to be completed (Table 1, entry 5). Complexes without phosphine ligands $PdCl_2(PhCN)_2$ and $PdCl_2(MeCN)_2$ are not efficient in xylene and exhibit very low efficiency in DMF (entries 7–10).

We used both procedures ($Pd(PPh_3)_4$–xylene (A) and $PdCl_2(PPh_3)_2$–DMF (B)) (Eq. (2)) to obtain a variety of ArSePh (Table 2).

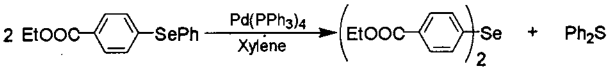


Procedure A [Pd] = $Pd(PPh_3)_4$, Solv = Xylene

Procedure B [Pd] = $PdCl_2(PPh_3)_2$, Solv = DMF

X = H, 4-Br, 4-NO_2, 3-NO_2, 4-CO_2Et, 4-MeO, 4-Me_2N, 4-I, 4-Ac, 4-SePh (2)

The results are better with $Pd(PPh_3)_4$ in xylene for the aryl iodides bearing very strong electron-donating groups such as dimetylamino-group (Table 2, entries 4 and 5) and with $PdCl_2(PPh_3)_2$ for the aryl iodides containing electron-withdrawing groups (Table 2, entries 10 and 13). In the case of ethyl ester of 4-iodobenzoic acid, the use of $Pd(PPh_3)_4$ drastically decreases the yield of the product due to disproportion of obtained arylphenylselenide (Eq. (3)) (Table 2, entry 9).



ArSePh : Ar_2Se : Ph_2Se = 2:1:1

(3)

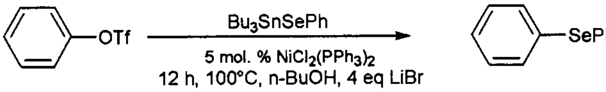
Disproportion has not been observed in the presence of $PdCl_2(PPh_3)_2$ (Table 2, entry 10). No reaction of $Bu_3SnSePh$ occurs with 4-iodoaniline. Reactions with 4-iodopyridine and 1-iodonaphtalene (Table 2, entries 14–16) give excellent yields of corresponding selenides. 4-Bromoiodobenzene reacts with substitution of only the iodine atom even in excess of $Bu_3SnSePh$. In the case of 1,4-diiodobenzene both iodine atoms can be readily replaced by phenylseleno-group.

The reaction with aryl bromides does not proceed under these conditions [13].

The catalytic cycle, which is usually proposed for cross-coupling reactions [14], may be suggested and for given reaction (Scheme 1).

2.2. Reaction of $Bu_3SnSePh$ with aryl triflates

To the best of our knowledge the substitution in aryl triflates have never been used for formation of diaryl selenides. This synthetic pathway is very attractive due to the availability of starting phenols. We have found that the reaction of PhOTf with $Bu_3SnSePh$ when it is catalysed by $NiCl_2(PPh_3)_2$ in the presence of LiBr leads to the Ph_2Se in a good yield (Eq. (4)) (Table 3, entry 7).



(4)

In the presence of $NiCl_2(PPh_3)_2$ in butanol reaction proceeds with a low yield of diphenylselenide (Table 3, entry 6). According to the ^{77}Se-NMR data, the main

Table 1
Effect of varying catalyst and reaction conditions on the yield of the coupling reaction of PhI with $Bu_3SnSePh$

N	Catalyst	Mol%	Solvent	Time (h)	Conversion of $Bu_3SnSePh$% [a]
1	$Pd(PPh_3)_4$	5	Xylene	1.5	100 (94)
2	$Pd(PPh_3)_4$	3	Xylene	3	100 (92)
3	$Pd(PPh_3)_4$	1.5	Xylene	5	100 (92)
4	$PdCl_2(PPh_3)_2$	1.5	Xylene	30	100 (93)
5	$PdCl_2(PPh_3)_2$	1.5	DMF	4	100 (98)
7	$PdCl_2(MeCN)_2$	1.5	Xylene	12	0
8	$PdCl_2(MeCN)_2$	1.5	DMF	15	<10
9	$PdCl_2(PhCN)_2$	1.5	Xylene	12	0
10	$PdCl_2(PhCN)_2$	1.5	DMF	16	<10

[a] Conversion of $Bu_3SnSePh$ according to the ^{119}Sn-NMR spectra. The yield of Ph_2Se according to the ^{77}Se-NMR spectra is given in parentheses.

Table 2
The results of reaction of ArI with $Bu_3SnSePh$ at 100°C in the presence of palladium catalysts

N	ArI	Procedure [a]	Product	Yield (%) [b]
1	PhI	A	PhSePh	92 (87)
2	PhI	B	PhSePh	98 (93)
3	4-MeOC_6H_4I	A	4-MeOC_6H_4SePh	93 (88)
4	$4\text{-Me}_2NC_6H_4I$	A	$4\text{-Me}_2NC_6H_4SePh$	63 (60) [c]
5	$4\text{-Me}_2NC_6H_4I$	B	$4\text{-Me}_2NC_6H_4SePh$	15 [d]
6	$3\text{-NO}_2C_6H_4I$	A	$3\text{-NO}_2C_6H_4SePh$	93 (85)
7	4-BrC_6H_4I	A	4-BrC_6H_4SePh	84 (80)
8	$4\text{-NO}_2C_6H_4I$	A	$4\text{-NO}_2C_6H_4SePh$	87 (83)
9	$4\text{-EtO}_2CC_6H_4I$	A	$4\text{-EtO}_2CC_6H_4SePh$	54 (50)
10	$4\text{-EtO}_2CC_6H_4I$	B	$4\text{-EtO}_2CC_6H_4SePh$	98 (94)
11	$1,4\text{-C}_6H_4I_2$ [e]	A	$1,4\text{-(PhSe)}_2C_6H_4$	95 (93)
12	4-AcC_6H_4I	A	4-AcC_6H_4SePh	87 (79)
13	4-AcC_6H_4I	B	4-AcC_6H_4SePh	93 (86)
14	$1\text{-C}_{10}H_7I$	A	$1\text{-PhSeC}_{10}H_7$	92 (86)
15	4-PyI	A	4-PhSePy	90 (81)
16	4-PyI	B	4-PhSePy	96 (92)
17	4-PhSeC_6H_4I [f]	B	$1,4\text{-(PhSe)}_2C_6H_4$	98 (95)

[a] Procedure A, 1.5 mol% $Pd(PPh_3)_4$, xylene, 5 h; procedure B 1.5 mol% $PdCl_2(PPh_3)_2$, DMF, 4 h.

[b] The yield according to the ^{77}Se-NMR spectra. The yields of isolated pure compounds are given in parentheses.

[c] Reaction time is 12 h.

[d] Reaction time is 14 h.

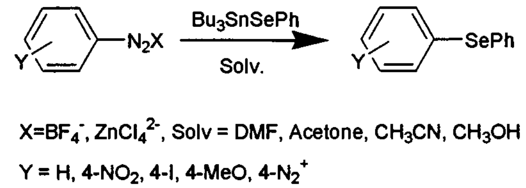
[e] Two equivalents of $Bu_3SnSePh$ are used.

[f] This aryl iodide is synthesised by reaction of $Bu_3SnSePh$ with $(4\text{-IC}_6H_4N_2)_2ZnCl_4$ (Table 4, entry 18).

product formed under these conditions is diphenyldiselenide. However, the addition of LiBr drastically changes the reaction pathway, and the yield of diphenylselenide increases up to 80% (Table 3, entry 7). Reaction under these conditions can successfully be applied to the substitution in 1-naphtyltriflate to give 1-(phenylseleno)naphthalene with a good yield (Table 3, entry 8). Both $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$ are not efficient in these reactions (Table 3, entries 1 and 4). Although the addition of LiBr increases the yield of diphenylselenide in the palladium catalysed reaction, it remains lower than in the case of the nickel catalysis.

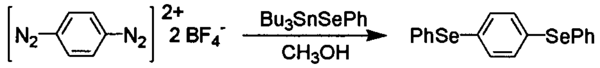
2.3. Reaction of $Bu_3SnSePh$ with aryldiazonium salts

Arylamines can be also involved in the cross-coupling reactions as arylating agents after being converted into diazonium salts. We have studied the reaction of stable aryldiazonium salts ArN_2BF_4 and so called 'double diazonium salts' [15] $(ArN_2)_2ZnCl_4$ (Eq. (5)). Both phenyldiazonium borofluoride and the corresponding double zinc salt readily react with $Bu_3SnSePh$ at room temperature in polar solvents such as DMF, acetonitrile, acetone, methanol, THF without any catalysis to give an excellent yield of diphenylselenide (Table 4).



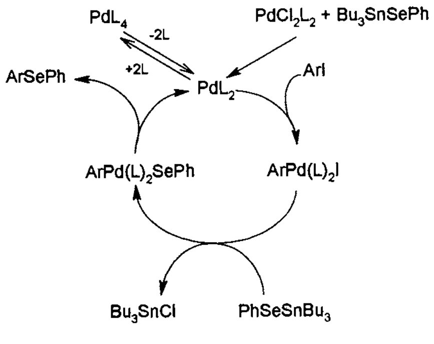
(5)

Under these conditions, the reaction completes in 10 min (Table 4, entries 2–10). The substituted phenyldiazonium salts with both electron-donating and electron-withdrawing substituents react with $Bu_3SnSePh$ to give good yields of ArSePh (Table 4, entries 12–20). It has been previously shown that the reaction of $4\text{-IC}_6H_4N_2Ts$ with an excess of PhSeNa gives only traces of 4-IC_6H_4SePh and the main product is 1,4-bis-(phenylseleno)benzene [9c]. We have found that the diazo-group can be selectively substituted in $(4\text{-IC}_6H_4N_2)_2ZnCl_4$ for PhSe group by the reaction of $Bu_3SnSePh$ (Table 4, entry 18). The iodine atom can be further substituted then in the Pd-catalysed reaction by any other group (Table 2, entry 17). In the case of 1,4-benzenebisdiazonium salt (Table 4, entry 20) both diazo groups can react with $Bu_3SnSePh$ in the ratio 1:2 to give $1,4\text{-(PhSe)}_2C_6H_4$ (Eq. (6)).



(6)

When PhN_2HgCl_3 is used in the reaction with $Bu_3SnSePh$ in DMF, the mixture of unidentified compounds containing less then 10% of Ph_2Se is formed (Table 4, entry 11). The reaction of ArN_2BF_4 with $Bu_3SnSePh$ in non-polar xylene in the presence of $Pd(PPh_3)_4$ produces the mixture of diphenylselenide and diphenyldiselenide in 1:1 ratio with 80% conversion after 6 h (Table 4, entry 1).



Scheme 1. The catalytic cycle for the cross-coupling reaction of $Bu_3SnSePh$ with ArI.

Table 3
The results of the reaction of aryl triflates with $Bu_3SnSePh$ in the presence of palladium or nickel catalysts

N	Ar	Catalyst	Addition	Solvent	Time (h)	*T* (°C)	Conversion (%) [a]	Yield (%) [a]
1	Ph	$PdCl_2(PPh_3)_2$		DMF	10	100	0	0
2	Ph	$PdCl_2(PPh_3)_2$	LiBr [b]	DMF	17	100	100	60
3	Ph	$PdCl_2(PPh_3)_2$	LiBr [b]	Dioxane	35	100	62	56
4	Ph	$Pd(PPh_3)_4$		Xylene	20	100	20	10
5	Ph	$NiCl_2(PPh_3)_2$		Dioxane	17	100	25	20
6	Ph	$NiCl_2(PPh_3)_2$		^{i}PrOH	5	82	100	26
7	Ph	$NiCl_2(PPh_3)_2$	LiBr [b]	BuOH	12	100	100	80 (78)
8	1-$C_{10}H_8$	$NiCl_2(PPh_3)_2$	LiBr [b]	BuOH	12	100	100	78 (75)

[a] Conversion of $Bu_3SnSePh$ is determined by the ^{119}Sn-NMR spectra. The yield of ArSePh is determined by the ^{77}Se-NMR spectra. The yields of pure isolated compounds are given in parentheses.

[b] Four equivalents of LiBr are used.

3. Experimental

3.1. General procedures

All reactions except the reactions with diazonium salts were carried out under an inert atmosphere of N_2 that however was not necessary for the workup of reaction mixture. For NMR monitoring, the reactions were performed in NMR tubes sealed in vacuum. All solvents were distilled under nitrogen atmosphere. Aryl triflates [16], aryldiazonium salts [15], $Pd(PPh_3)_4$ [17], $PdCl_2(PPh_3)_2$ [18], $NiCl_2(PPh_3)_2$ [19] were synthesised using standard procedures. $Bu_3SnSePh$ was synthesised by the reaction of Bu_6Sn_2 with PhSeSePh in benzene under daylight [2]. ^{77}Se- and ^{119}Sn-NMR spectra were recorded on a Bruker WP-200 SY spectrometer in benzene solution. The operating frequencies were 38.19 and 74.6 MHz, respectively. The stabilisation of the resonance conditions was performed using external D_2O. The ^{119}Sn chemical shifts were measured relative to external Me_4Sn. The ^{77}Se chemical shifts were measured relative to external diphenyl diselenide. The ^{1}H- and ^{13}C-NMR spectra were recorded on the Bruker AMX-400 in the d_6 acetone solutions. The operating frequencies were 400.13 and 100.5 MHz, respectively. Mass spectra were recorded on the spectrometer Kratos MS 890.

3.2. The reaction of aryl iodides with $Bu_3SnSePh$

3.2.1. Reaction using Schlenk technique

$Bu_3SnSePh$ (1.0 mmol 0.446 g) was added to a solution of ArI (1.0 mmol) and $Pd(PPh_3)_4$ (method A) or $PdCl_2(PPh_3)_2$ (method B) (1.5 mol%, 17.3 or 10.5 mg, respectively) in xylene or DMF (1.0 ml) in a Schlenk tube. The deep-red mixture was stirred at 100°C within 5 h, diluted with ether (40 ml) and poured into the aqueous KF solution. After the filtering organic layer was dried (Na_2SO_4) and the solvent was removed on a rotary evaporator. The crude product was chromatographed on silica gel (eluant–hexane for cases 1 and 2 (Table 5) or hexane–chloroform for cases 3, 5–12 (Table 5)) or recrystallized from hexane (Table 5, case 4).

3.2.2. Reaction in a sealed NMR tube

$Bu_3SnSePh$ (0.5 mmol, 0.223 g) was added to a solution of ArI (0.5 mmol) and $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$ (1.5 mol%, 8.7 or 5.3 mg, respectively) in xylene or DMF (0.5 ml) in a NMR tube. The tube was sealed and heated at 100°C. (The temperature in the blank experiment was 98–99°C). The NMR spectra were recorded at room temperature.

Table 4
The results of the reaction of aryldiazonium salts with $Bu_3SnSePh$

N	ArN_2X	ArSePh	Solvent	Yield (%) [a]
1	PhN_2BF_4	PhSePh	Xylene	40 [b]
2	PhN_2BF_4	PhSePh	DMF	94
3	PhN_2BF_4	PhSePh	CH_3OH	93 (89)
4	PhN_2BF_4	PhSePh	Acetone	90 (85)
5	PhN_2BF_4	PhSePh	THF	91
6	$(PhN_2)_2ZnCl_4$	PhSePh	Acetone	95 (91)
7	$(PhN_2)_2ZnCl_4$	PhSePh	DMF	96
8	$(PhN_2)_2ZnCl_4$	PhSePh	CH_3OH	99 (96)
9	$(PhN_2)_2ZnCl_4$	PhSePh	THF	95
10	$(PhN_2)_2ZnCl_4$	PhSePh	CH_3CN	96
11	$(PhN_2)HgCl_3$	PhSePh	DMF	10
12	4-$NO_2C_6H_4N_2BF_4$	4-$NO_2C_6H_4$SePh	Acetone	– (90)
13	4-$NO_2C_6H_4N_2BF_4$	4-$NO_2C_6H_4$SePh	CH_3OH	– (95)
14	$(4\text{-}NO_2C_6H_4N_2)_2ZnCl_4$	4-$NO_2C_6H_4$SePh	Acetone	– (91)
15	$(4\text{-}NO_2C_6H_4N_2)_2ZnCl_4$	4-$NO_2C_6H_4$SePh	CH_3OH	– (96)
16	$(4\text{-}MeOC_6H_4N_2)_2ZnCl_4$	4-$MeOC_6H_4$SePh	CH_3OH	– (97)
17	4-$MeOC_6H_4N_2BF_4$	4-$MeOC_6H_4$SePh	CH_3OH	– (92)
18	$(4\text{-}IC_6H_4N_2)_2ZnCl_4$	4-IC_6H_4SePh	CH_3OH	– (94)
19	1-$C_{10}H_7N_2BF_4$	1-$C_{10}H_7$SePh	CH_3OH	– (93)
20	1,4-$C_6H_4(N_2BF_4)_2$	1,4-$(PhSe)_2C_6H_4$	CH_3OH	– (98)

[a] The yield was determined according to the ^{77}Se-NMR spectra. The isolated yields are given in the parentheses.

[b] Reaction time 6 h, conversion 80%, 1.5 mol% of $Pd(PPh_3)_4$.

Table 5
The ^{1}H-, ^{13}C-, ^{77}Se-NMR and other analytical data for the synthesised arylphenylselenides

N	ArSePh	^{1}H	^{13}C	^{77}Se	M.p	Literature	MS
1	PhSePh	7.32–7.41 (m, 6H), 7.49–7.57 (m, 4H)	127.13, 127.79, 127.93, 130.24	−46.5			234
2	1-$C_{10}H_7$SePh	7.1–8.4 (12H)	127.45, 127.80, 128.26, 128.34, 128.68, 129.89, 129.96, 130.06, 130.66, 130.72, 132.79, 132.91, 135.26, 135.59	−108.5			284
3	4-(PhSe)Py	7.02 (d, 2H, $J = 4.8$ Hz), 7.3–7.4 (m, 3H), 7.55–7.6 (m, 2H), 8.2 (ws, 2H)	123.45, 127.13, 127.79, 128.77, 131.86, 132.87, 146.65	−39.3			235
4	1,4-$(PhSe)_2C_6H_4$	7.33 (s, 6H), 7.37 (m, 4H), 7.54 (m, 6H)	127.54, 129.33, 130.38, 130.53, 133.17, 133.30	−46.6	102	100–101 [20]	390
5	4-BrC_6H_4SePh	7.30–7.33 (m, 3H), 7.32 (d, 2H, $J = 8.7$ Hz), 7.44 (d, 2H, $J = 8.7$ Hz), 7.43–7.48 (m, 2H)	122.24, 129.19, 130.9, 131.18, 131.83, 133.64, 134.63, 135.41	−46.4	31	32 [6a]	312
6	4-IC_6H_4SePh	7.16 (d, 2H, $J = 7.83$ Hz), 7.27–7.35 (m, 3H), 7.46–7.54 (m, 2H), 7.57 (d, 2H, $J = 7.8$ Hz)	92.88, 127.93, 129.63, 131.6, 133.37, 133.61, 134.34, 138.37	−46.3	43		360
7	3-$NO_2C_6H_4$SePh	7.4–7.7 (m, 6H), 8.0–8.2 (m, 2H), 8.1 (s, 1H)	122.83, 126.41, 130.1, 131.22, 131.58, 135.7, 135.93, 138.21, 155.44, 167.8	−28.3	40	41.5 [21]	279
8	4-$NO_2C_6H_4$SePh	7.44 (d, 2H, $J = 8.7$ Hz), 7.4–7.47 (m, 3H), 7.62–7.65 (m, 2H), 8.02 (d, 2H, $J = 8.7$ Hz)	125.1, 128.57, 130.53, 131.22, 131.32, 136.84, 144.59, 147.62	−25.7	59	58 [8c]	279
9	4-$Me_2NC_6H_4$SePh	2.9 (s, 6H), 6.6 (d, 2H, $J = 10.0$ Hz), 7.01–7.18 (m, 3H), 7.21–7.24 (m, 2H), 7.42 6 (d, 2H, $J = 10.0$ Hz)	40.77, 114.41, 127.05, 130.02, 130.29, 132.37, 135.91, 138.05, 152.03	−68.6	68	67–68 [21]	277
10	4-$MeOC_6H_4$SePh	3.57 (s, 3H), 6.89 (d, 2H, $J = 8.7$ Hz), 7.15–7.22 (m, 3H) 7.28–7.31 (m, 2H), 7.48 (d, 2H, $J = 8.7$ Hz)	56.05, 116.47, 120.62, 127.72, 130.47, 130.71, 131.95, 134.1, 137.81	−61.9	46	46.3 [6a]	264
11	4-AcC_6H_4SePh	2.58 (s, 3H), 7.38–7.42 (m, 3H), 7.43 (d, 2H, $J = 8.23$ Hz), 7.62–7.64 (m, 2H), 7.83 (d, 2H, $J = 8.2$ Hz)	26.64, 128.56, 128.69, 128.89, 129.70, 130.50, 135.02, 135.39, 140.12, 197.03	−36.5		61.2 [10]	276
12	4-$EtO_2CC_6H_4$SePh	1.33 (t, 3H, $J = 6.1$ Hz), 4.31 (q, 2H, $J = 6.1$ Hz), 7.39 (m, 5H), 7.58 (m, 2H), 7.87 (d, 2H, $J = 7.8$ Hz)	14.32, 60.99, 128.96, 129.13, 129.40, 130.19, 130.39, 130.74, 135.17, 139.58, 165.76	−36.5			306

3.2.3. *Reaction with generation of $Bu_3SnSePh$ in situ*

The $Bu_3SnSnBu_3$ (0.5 mmol, 0.290 g) was added to a solution of PhSeSePh (0.5 mmol, 0,156 g), PhI (1.0 mmol, 0.102 g) and $PdCl_2(PPh_3)_2$ (1.5 mol%, 0.0105 g) in DMF (1.0 ml) in a Schlenk tube. The deep-red mixture was exposed to daylight for half an hour and was stirred at 100°C within 5 h, diluted with ether (40 ml) and poured into aqueous KF solution. After filtering, the organic layer was dried (Na_2SO_4) and the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel (eluant hexane). The yield of Ph_2Se was 0.217 g (93%).

3.3. *The reaction of ArOTf with $Bu_3SnSePh$*

$Bu_3SnSePh$ (1.0 mmol, 0.446 g) was added to a solution of ArOTf (1.0 mmol), LiBr (4.0 mmol, 0.348 mg) and $NiCl_2(PPh_3)_2$ (1.5 mol%, 9.8 mg) in *n*-BuOH (2.0 ml) in a Schlenk tube. The reaction mixture was stirred at 100°C for 12 h and diluted with ether (40 ml) and poured into aqueous KF solution. After filtering the organic layer was dried (Na_2SO_4) and the solvent was removed on a rotary evaporator. The chromatography on silica gel (eluant hexane) gives rise to pure ArSePh.

3.4. *The reaction of aryldiazonium salts with $Bu_3SnSePh$*

$Bu_3SnSePh$ (1.0 mmol, 0.446 g) was gradually added to ArN_2BF_4 (1.0 mmol) or $(ArN_2)_2ZnCl_4$ in methanol (2.0 ml) under stirring. The mixture was stirred for 10 min and poured into aqueous KF solution. Then the ether (40 ml) was added. After filtering the organic layer was dried (Na_2SO_4) and the solvent was removed. The crude product was chromatographed on silica gel (eluant hexane).

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[13] In the course of preparing our paper the communication of Japan authors (Y. Nishiyama, K. Tokunaga, N. Sonoda, Org. Lett. 1 (1999) 1725) appeared. They have performed the reaction of $Bu_3SnSePh$ with aryl halides, which is catalyzed by palladium complexes. The results concerning the reaction with aryl iodides are comparable with our data. However, in contrast to our experiments Japan authors carried out this reaction with PhBr as well as even with PhCl using $Pd(PPh_3)_4$ catalysis. Our attempts to reproduce these results failed. Diphenylselenide obtained under these conditions is formed as a result of disproportion of $Bu_3SnSePh$.

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