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# Tributyltin Aryl Selenides as Efficient Arylselenating Agents. Synthesis of Diaryl and Aryl Organyl Selenides*

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**Abstract**—Tributyltin aryl selenides are highly efficient arylselenating agents in reactions with aryl iodides and aryl triflates under catalysis with Pd and Ni complexes respectively. They also may be used as efficient source of active arylselenolate anion in the presence of fluoride ions in reaction of arylselenation of alkyl halides and activated aryl fluorides.

Compounds with arylseleno group attract attention due to wide possibilities of their application. Amino-substituted diarylselenides are highly efficient antioxidants [1, 2]. Many compounds containing arylselenic and diarylselenic moiety are interesting for pharmacology [3–5]. Polymers based on diaryl selenides are potential electroconducting materials [6–8]. Complexes of arylseleno-substituted tetrathiofulvalene exhibit properties of a semiconductor [9].

Procedures for introducing arylseleno group into organic compound are diverse and contain both electrophilic and nucleophilic arylselenation reactions [10–20]. Therewith the range of organoselenating reagents is sufficiently wide but most of them have various disadvantages, as difficulties in handling, disposition to hydrolysis or oxidation by oxygen. Therefore disregarding the versatility of available organoselenating reagents still remains undying interest to new easy-to-handle compounds that can serve as a source of organoseleno group.

The possibility to apply triorganyltin organochalcogenides as organoselenating agents is poorly studied. Several examples are known of the use of tributyltin organosulfides in the reactions of cross-coupling with aryl and vinyl bromides catalyzed by palladium complexes [21, 2]. However in similar reactions were not used selenium analogs before our studies. Yet the triorganyltin organoselenides are notably easier to handle than analogous selenols for they are more stable against air oxygen, against hydrolysis, and do not stink. We showed that the tributyltin aryl selenides easily prepared by irradiation of a mixture of hexabutyldistannane and the corresponding diaryl selenide are efficient arylselenation reagents in reactions with various substrates, e.g., aryl, benzyl, propargyl, allyl, and alkyl halides, activated aryl fluorides, and also aryl triflates and aryldiazonium salts. (On the use of $Bu_3SnSePh$ as efficient arylselenating reagents was reported in preliminary communications [23–25]).

**Arylselenation of aryl iodides by $Bu_3SnSePh$ catalyzed by palladium complexes.** Aryl halides are among the most widely used substrates for cross-coupling. The preliminary study was carried out by an example of phenylselenation of iodobenzene with $Bu_3SnSePh$ (Scheme 1, Table 1).

The reaction progress was monitored by means of $^{119}Sn$ NMR spectroscopy. The composition and yield of selenium-containing products were controlled by $^{77}Se$ NMR spectroscopy.

We showed that in the absence of the catalyst no diphenyl selenide formed even after heating for 30 h. At the same time the addition of 1.5–5 mol% of $Pd(PPh_3)_4$ resulted in phenylselenation product formed in high yield. The reaction duration depends on the catalyst amount. The activity of the Pd(II) complexes in xylene is considerably lower. Thus in the presence of $PdCl_2(PPh_3)_2$ the reaction time is significantly longer than with $Pd(PPh_3)_4$. Yet in going to more polar solvent, DMF, the rate of reaction catalyzed by $PdCl_2(PPh_3)_2$ notably increases and becomes comparable with that under catalysis with $Pd(PPh_3)_4$. Note that with the latter catalyst the rate

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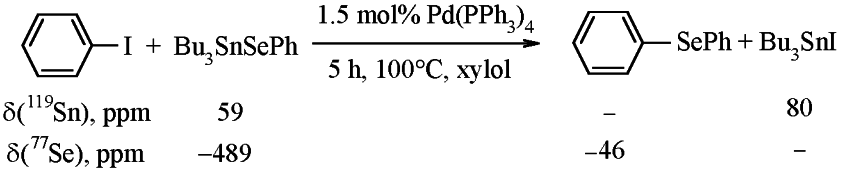
**Scheme 1.**



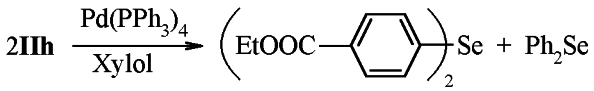

**Scheme 2.**

$$ArI + Bu_3SnSeAr' \xrightarrow[5\ h,\ 100^\circ C]{1.5\ mol\%\ [Pd]} ArSeAr'$$

**Ia–k** **IIa–p**

Method *A*: [Pd] = $Pd(PPh_3)_4$, xylene; method *B*: [Pd] = $PdCl_2(PPh_3)_2$, DMF. **I**), Ar = Ph (**a**), 4-$MeOC_6H_4$ (**b**), 4-$Me_2NC_6H_4$ (**c**), 4-$NO_2C_6H_4$ (**d**), 3-$NO_2C_6H_4$ (**e**), 4-$BrC_6H_4$ (**f**), 4-$IC_6H_4$ (**g**), 4-$AcC_6H_4$ (**h**), 4-$EtOOCC_6H_4$ (**i**), 4-pyridyl (**j**), 1-naphthyl (**k**); **II**, Ar' = Ph: Ar = Ph (**a**), 4-$MeOC_6H_4$ (**b**), 4-$Me_2NC_6H_4$ (**c**), 4-$NO_2C_6H_4$ (**d**), 3-$NO_2C_6H_4$ (**e**), 4-$BrC_6H_4$ (**f**), 4-$PhSeC_6H_4$ (**g**), 4-$AcC_6H_4$ (**h**), 4-$EtOOCC_6H_4$ (**i**), 4-pyridyl (**j**), 1-naphthyl (**k**); Ar' = 4-$FC_6H_4$: Ar = Ph (**l**), 4-$MeOC_6H_4$ (**m**), 4-$NO_2C_6H_4$ (**n**), 4-pyridyl (**o**), 1-naphthyl (**p**).

**Scheme 3.**




Products ratio in the reaction mixture ArSePh : $Ar_2Se$ : $Ph_2Se$ = 2 : 1 : 1.

**Table 1.** Effect of catalyst and reaction conditions on yield of $Ph_2Se$, the product of phenylselenation of iodobenzene with $Bu_3SnSePh$ at 100°C[a]

| Catalyst, mol% | Solvent | Time, h | Conversion $Bu_3SnSePh$,[b] % | Yield,[c] % |
|---|---|---|---|---|
| – | Xylene | 30 | 0 | – |
| $Pd(PPh_3)_4$, 5 | Xylene | 1.5 | 100 | 94 |
| $Pd(PPh_3)_4$, 3 | Xylene | 3 | 100 | 92 |
| $Pd(PPh_3)_4$, 1.5 | Xylene | 5 | 100 | 95 |
| $Pd(PPh_3)_4$, 1.5 | DMF | 5 | 100 | 90 |
| $PdCl_2(PPh_3)_2$, 1.5 | Xylene | 30 | 100 | 93 |
| $PdCl_2(PPh_3)_2$, 1.5 | DMF | 4 | 100 | 98 |
| $PdCl_2(MeCN)_2$, 1.5 | Xylene | 12 | 0 | – |
| $PdCl_2(MeCN)_2$, 1.5 | DMF | 15 | < 10 | – |
| $PdCl_2(PhCN)_2$, 1.5 | Xylene | 12 | 0 | – |
| $PdCl_2(PhCN)_2$, 1.5 | DMF | 16 | < 10 | – |

[a] Reaction conditions: 1 mmol of $Bu_3SnSePh$, 1 mmol of PhI, 2 ml of solvent.

[b] Conversion of $Bu_3SnSePh$ by $^{119}Sn$ NMR data.

[c] Yield of $Ph_2Se$ by $^{77}Se$ NMR data.

**Table 2.** Yields of products obtained by arylselenation of aryl iodides ArI with tributyltin aryl selenides $Bu_3SnSeAr'$ at 100°C in the presence of palladium catalysts

| Compd. no. | ArSeAr' | | Method[a] | Yield,[b] % |
|---|---|---|---|---|
| | Ar | Ar' | | |
| **IIa** | Ph | Ph | *A* | 92 (87) |
| **IIa** | | | *B* | 98 (93) |
| **IIl** | | 4-$FC_6H_4$ | *B* | 96 (94) |
| **IIb** | 4-$MeOC_6H_4$ | Ph | *A* | 93 (88) |
| **IIm** | | 4-$FC_6H_4$ | *B* | 90 (87) |
| **IIc** | 4-$Me_2NC_6H_4$ | Ph | *A* | 63 (60)[c], |
| **IIc** | | Ph | *B* | 15[d] |
| **IId** | 4-$NO_2C_6H_4$ | Ph | *A* | 87 (83) |
| **IIn** | | 4-$FC_6H_4$ | *B* | 89 (82) |
| **IIe** | 4-$NO_2C_6H_4$ | Ph | *A* | 93 (85) |
| **IIf** | 4-$BrC_6H_4$ | Ph | *A* | 84 (80) |
| **IIg** | 4-$IC_6H_4$[e] | Ph | *A* | 95 (93) |
| **IIh** | 4-$AcC_6H_4$ | Ph | *A* | 87 (79) |
| **IIh** | | | *B* | 93 (96) |
| **IIi** | 4-$EtO_2CC_6H_4$ | Ph | *A* | 54 (50) |
| **IIi** | | | *B* | 98 (94) |
| **IIj** | 4-Py | Ph | *A* | 90 (81) |
| **IIj** | | | *B* | 96 (92) |
| **IIo** | | 4-$FC_6H_4$ | *B* | 94 (89) |
| **IIk** | 1-$C_{10}H_7$ | Ph | *A* | 92 (86) |
| **IIp** | 1-$C_{10}H_7$ | 4-$FC_6H_4$ | *B* | 90 (83) |
| **IIg** | 4-$PhSeC_6H_4$[e] | Ph | *B* | 98 (95) |

[a] Method *A*: 1 mmol of $Bu_3SnSePh$, 1 mmol of ArI, 1.5 mol% of $Pd(PPh_3)_4$, 2 ml of xylene, 5 h; Method *B*: 1 mmol of $Bu_3SnSePh$, 1 mmol of ArI, 1.5 mol% of $PdCl_2(PPh_3)_2$, 2 ml of DMF, 4 h.

[b] Yield according to $^{77}Se$ NMR data. Preparative yield is given in parentheses.

[c] Reaction time 12 h.

[d] Reaction time 14 h.

[e] Two equiv of $Bu_3SnSePh$ were used.

[f] This aryliodide was synthesized from $Bu_3SnSePh$ and $(4\text{-}IC_6H_4N_2)_2ZnCl_4$ (Table 4).

of reaction does not change in going to DMF solvent. Acetonitrile and benzonitrile palladium(II) complexes are inactive both in xylene and DMF.

Thus the cross-coupling of iodobenzene and $Bu_3SnSePh$ is efficiently catalyzed by complex $Pd(PPh_3)_4$ in xylene or $PdCl_2(PPh_3)_2$ in DMF.

Under the given conditions we studied the effect on the reaction of the substituents in the aryl iodide. It was established that at the use of both methods (Scheme 2) were obtained similar results, and diaryl selenide was formed in high yield (Table 2).

An exception concerned only the reactions of aryl iodides with strong electron-donor substituents, e.g. with dimethylamino group. In this case the Pd(II) complex is of low efficiency. Diaryl selenide **IIb** was obtained only with catalysis by $Pd(PPh_3)_4$ in moderate yield. In reaction with ethyl 4-iodobenzoate (**Ii**) the catalysis by $Pd(PPh_3)_4$ resulted in the disproportionation of the formed diaryl selenide **IIi** (Scheme 3) that reduced the yield of reaction products. Yet in the presence of $PdCl_2(PPh_3)_2$ no disproportionation occurred.

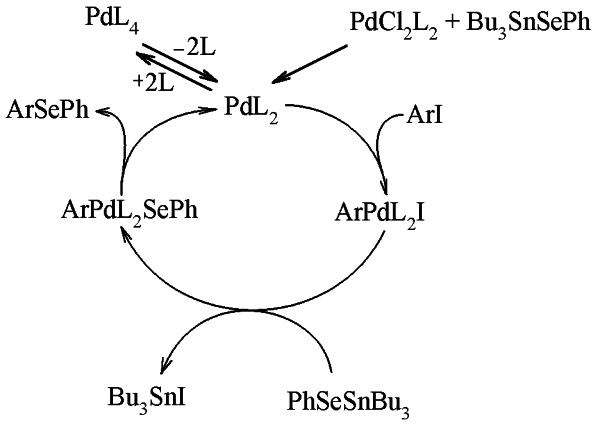
This reaction was extended to derivatives of naphthalene and pyridine. With 4-iodopyridine the Pd(II) catalyst also provided a possibility to obtain 4-(phenylseleno)pyridine in higher yield than with Pd(O) complex in xylene due to reduced amount of side products. 4-Bromoiodobenzene reacts selectively with only iodine substitution.*

With 1,4-diiodobenzene are easily substituted both iodine atoms to furnish diaryl selenide **IIg**.

The monitoring of reaction progress we commonly used was not suitable for reactions performed in DMF. The coordination with solvent apparently accelerated the exchange of anionoide rests, and in the $^{119}Sn$ NMR spectra occurred strong broadening of $Bu_3SnSePh$ and BuSnI signals. Reaction monitoring with the use of $^{77}Se$ NMR spectra is inconvenient due to long time of spectra registering. Therefore we applied to reaction monitoring $^{19}F$ NMR spectroscopy. To this end we synthesized tributyltin aryl selenide containing fluorine label in the *para*-position of the benzene ring. With the use of this compound we obtained by cross-coupling a number of fluorine-substituted diaryl selenides. Their synthesis was carried out by reaction with aryl iodides in the presence of $PdCl_2(PPh_3)_2$ affording diaryl selenides in high yield.

The most probably this reaction follows the common cross-coupling mechanism [27] (Scheme 4).

**Scheme 4.**




**$^{77}Se$ NMR spectra of compounds of ArSePh type.** Compounds of ArSePh type synthesized in this study are a convenient object for investigation on effect of substituents in aryl ligand on the chemical shifts of $^{77}Se$ nuclei. It was established that the $^{77}Se$ chemical shifts (Table 3) measured for 10 model compounds correlated well with Hammett's $\sigma$ constants of the substituted aryl radicals, and the slope of the plot had a positive value: $\delta(^{77}Se) = (26.6 \pm 4.7)\sigma - 49.1$; $r$ 0.981, $s$ 3.6.

This fact evidence that on the shielding of $^{77}Se$ nuclei prevailing influence has the paramagnetic component of the shielding constant. This conclusion is consistent with the common interpretation of the chemical shifts in organoselenium compounds [28, 29]. It should be noted that recently were measured the chemical shifts $^{77}Se$ for 7 compounds [30]. Correlation treatment of these data provided a notably worse correlation factor ($r$ 0.934).

* Recently appeared information [26] on cross-coupling of $Bu_3SnSePh$ with bromo- and even chlorobenzene catalyzed with $Pd(PPh_3)_4$ that was in disagreement with our results. We repeated the described experiments and did not observe the diphenyl selenide formation along cross-coupling reaction. This product formed only by disproportionation of the initial compound along the equation $2Bu_3SnSePh \rightarrow (Bu_3Sn)_2Se + Ph_2Se$. Therefore the yield of reaction product could not be over 50% (in [26] was indicated yield of 60% for reaction with PhCl). Our data obtained by means of $^{119}Sn$ and $^{77}Se$ NMR showed that in reaction of $Bu_3SnSePh$ with chlorobenzene in the presence of $Pd(PPh_3)_4$ formed no $Bu_3SnCl$ but appeared only $(Bu_3Sn)_2Se$ as was confirmed by comparison with spectra of an authentic sample. The reaction monitoring in [26] was performed by GLC that obviously did not allow revealing the above situation.

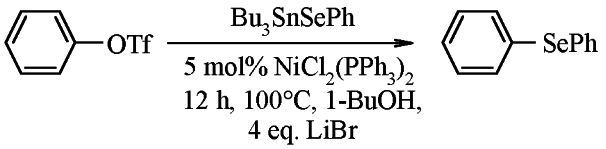
**Table 3.** Chemical shifts in $^{77}Se$ NMR spectra (xylene, ppm) and Hammett's σ constants for a series of synthesized diaryl selenides

| Ar | δ($^{77}Se$) | σ [31] |
|---|---|---|
| 4-$Me_2NC_6H_4$ | –68.6 | –0.83 |
| 4-$H_2NC_6H_4$[a] | –65.4 | –0.66 |
| 4-$CH_3OC_6H_4$ | –61.9 | –0.268 |
| Ph | –46.5 | 0.0 |
| 4-$BrC_6H_4$ | –46.1 | 0.232 |
| 4-Py | –39.3 | 0.44 [32] |
| 4-$AcC_6H_4$ | –36.5 | 0.502 |
| 4-$EtCOOC_6H_4$ | –36.5 | 0.45 |
| 3-$NO_2COC_6H_4$ | –28.3 | 0.71 |
| 4-$NO_2COC_6H_4$ | –25.7 | 0.778 |

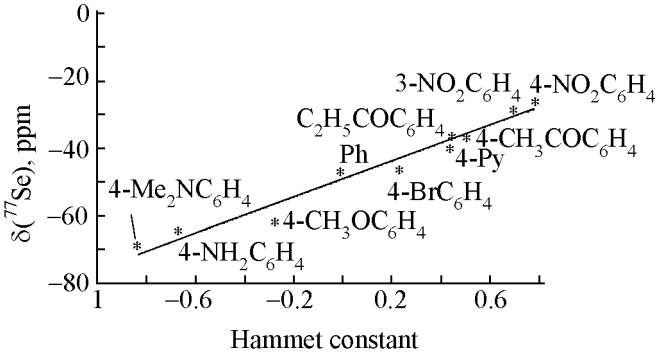
[a] This diaryl selenide was obtained in low yield and characterized only with $^{77}Se$ NMR spectrum.

**Phenylselenation of aryl triflates with the use of $Bu_3SnSePh$ under catalysis with transition metal complexes.** Aryl triflates are interesting substrates due to the availability of the initial phenols. However before our study [23] reactions of aryl triflates with selenium-centered nucleophiles were not known.

**Scheme 5.**




As model compound we selected phenyl triflate as the most accessible compound. It was found that phenylselenation of PhOTf occurred readily in butanol in the presence of $NiCl_2(PPh_3)_2$ with LiBr as additive; the reaction afforded diphenyl selenide in high yield (Table 4). With no LiBr the main reaction product was PhSeSePh. Under these conditions reacted also 1-naphthyl triflate to furnish in good yield 1-naphthyl phenyl selenide (Table 4). In this reaction catalysis by palladium is less efficient. Although on addition of LiBr the yield of diphenyl selenide increased, it still remained lower than at catalysis on nickel complexes.




Correlation between $^{77}Se$ NMR chemical shift and Hammett's σ constant for aryl phenyl selenides (II).

**Phenylselenation of aryldiazonium salts with the use of $Bu_3SnSePh$.** Aromatic amines also can be involved into the cross-coupling reaction via transformation thereof into diazonium salts. The common procedures applying water solutions of diazonium salts and alkaline solutions of selenophenols are inconvenient and afford diaryl selenides in moderate yield [13, 14, 33, 34]. Reaction of ArSeNa with aryldiazonium tosilates in nonaqueous medium gave similar results [35].

We studied reactions of tin selenide with stable aryldiazonium salts, fluoborates and tetrachlorozincates. Both phenyldiazonium fluoborate and the corresponding double salt with zinc chloride readily react with $Bu_3SnSePh$ at room temperature in polar

**Table 4.** Conditions of reaction between $Bu_3SnSePh$ and aryl triflates in the presence of palladium or nickel catalyst at 100°C, and yields of reaction products[a]

| Ar | Catalyst | Additive | Solvent | Time, h | Conversion, %[b] | Yield,[c] % |
|---|---|---|---|---|---|---|
| Ph | $PdCl_2(PPh_3)_2$ | – | DMF | 10 | 0 | 0 |
| Ph | | LiBr[d] | DMF | 17 | 100 | 60 |
| Ph | | LiBr[d] | Dioxane | 35 | 62 | 56 |
| Ph | $Pd(PPh_3)_4$ | – | Xylene | 20 | 20 | 10 |
| Ph | $NiCl_2(PPh_3)_2$ | – | Dioxane | 17 | 25 | 20 |
| Ph | | – | *i*-PrOH | 5[e] | 100 | 26[f] |
| Ph | | LiBr[d] | BuOH | 12 | 100 | 80 (78) |
| 1-$C_{10}H_8$ | | LiBr[d] | BuOH | 12 | 100 | 78 (75) |

[a] Reaction conditions: 1 mmol of ArOTf, 1 mmol of $Bu_3SnSePh$, 2 ml of solvent.

[b] Conversion of $Bu_3SnSePh$ was determined from $^{119}Sn$ NMR spectra.

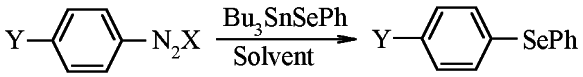
[c] Yield of ArSePh was determined from $^{77}Se$ NMR spectra. Preparative yield is given in parentheses.

[d] 4 equiv of LiBr.

[e] Temperature 82°C. [f] Alongside diphenyl selenide formed diphenyl diselenide (60%).

solvents affording diphenyl selenide in high yield (Table 5). Reaction is very fast and does not require a catalyst. The reaction is of general character and occurs with aryldiazonium salts containing both electron-donor and electron-withdrawing substituents, and also with derivatives of 1-naphthyl and 1,4-phenylenediazonium. In the latter case the reaction with two equiv of $Bu_3SnSePh$ gave rise to a product of double substitution. Reaction with a double mercury salt of phenyldiazonium (**IIc**) resulted in an intractable mixture of products with insignificant content of diphenyl selenide.

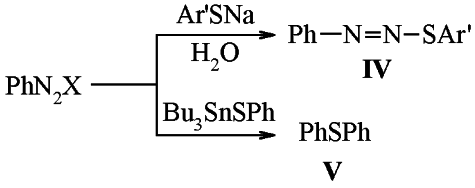
**Scheme 6.**




**IIIa–i** **IIa, b, d, g, q**

Solvent = DMF, acetone, $CH_3CN$, $CH_3OH$. **II**, Y = H (**a**), 4-MeO (**b**), 4-$NO_2$ (**d**), 4-PhSe (**g**), 4-**I** (**q**); YPh = 1-$C_{10}H_7$ (**k**). **III**, Y = H: X = $BF_4^-$ (**a**), X = $ZnCl_4^{2-}$ (**b**), X = $HgCl_3^-$ (**c**); Y = 4-$NO_2$: X = $BF_4^-$ (**d**), X = $ZnCl_4^{2-}$ (**e**); Y = 4-$CH_3O$: X = $BF_4^-$ (**f**), X = $ZnCl_4^{2-}$ (**g**); Y = 4-**I**: X = $ZnCl_4^{2-}$ (**h**), **YPh = 1-$C_{10}H_7$, X = $BF_4^-$** (**i**); Y = $N_2^+$, X = $BF_4^-$ (**j**).

**Scheme 7.**




**Reaction of $Bu_3SnSePh$ with activated aryl fluorides.** Polyfluoroaromatic compounds are attractive substrates for arylselenation since the expected polyfluorodiaryl selenides are hard to prepare and poorly studied. Their preparation methods are limited

**Table 5.** Yields of phenylselenation products from aryldiazonium salts $ArN_2X$ and $Bu_3SnSePh$[a]

| $ArN_2X$ | | | Solvent | Ar in ArSePh | Yield,[b] % |
|---|---|---|---|---|---|
| Compd. no. | Ar | X | | | |
| **IIIa** | Ph | $BF_4^-$ | DMF | Ph | 94 |
| | | | $CH_3OH$ | | 93 (89) |
| | | | Acetone | | 90 (85) |
| | | | THF | | 91 |
| **IIIb** | | $ZnCl4_2^-$ | Acetone | | 95 (91) |
| | | | DMF | | 96 |
| | | | $CH_3OH$ | | 99 (96) |
| | | | THF | | 95 |
| | | | $CH_3CN$ | | 96 |
| **IIIc** | | $HgCl_3^-$ | DMF | | 10 |
| **IIId** | 4-$NO_2C_6H_4$ | $BF_4^-$ | Acetone | 4-$NO_2C_6H_4$ | – (90) |
| | | | $CH_3OH$ | | – (95) |
| **IIIe** | | $ZnCl_4^{2-}$ | Acetone | | – (91) |
| | | | $CH_3OH$ | | – (96) |
| **IIIf** | 4-$MeOC_6H_4$ | $BF_4^-$ | $CH_3OH$ | 4-$MeOC_6H_4$ | – (92) |
| **IIIg** | | $ZnCl_4^{2-}$ | $CH_3OH$ | | – (97) |
| **IIIh** | 4-$IC_6H_4$ | $ZnCl4_2^-$ | $CH_3OH$ | 4-$IC_6H_4$ | – (94) |
| **IIIi** | 1-Naphthyl | $BF_4^-$ | $CH_3OH$ | 1-Naphthyl | – (93) |
| **IIIj**[c] | 4-$N_2^+C_6H_4$ | $BF_4^-$ | $CH_3OH$ | 4-$PhSeC_6H_4$ | – (98) |

[a] Reaction conditions: 1 mmol of $Bu_3SnSePh$, 1 mmol of $ArN_2X$, 2 ml of solvent.

[b] Yield from $^{77}Se$ NMR data. Preparative yield is given in parentheses.

[c] Reaction with two equiv of $Bu_3SnSePh$.

**Table 6.** Effect of catalyst and solvent on product yield in reaction of $Bu_3SnSePh$ with octafluorotoluene[a]

| Solvent | Additive | Temperature, °C | Time, h | Yield, % |
|---|---|---|---|---|
| $CHCl_3$ | – | 61 | 8 | 0 |
| $CHCl_3$ | 10% KF | 61 | 14 | 10 |
| $CHCl_3$ | 10% KF + 10 mol% BTEAC | 61 | 12 | 78 |
| $CHCl_3$ | 10% CsF + 10 mol% BTEAC | 61 | 12 | 81 (75) |
| $CHCl_3$ | 10% KF + 10 mol% dibenzo-18-crown-6 | 61 | 12 | 79 |
| $CHCl_3$ | 10% CsF + 10 mol% dibenzo-18-crown-6 | 61 | 12 | 82 |
| DMF | – | 25 | 2 | 97 (95) |

[a] Reaction conditions: 1 mmol of $Bu_3SnSePh$, 1 mmol of $C_6F_5CF_3$, 2 ml of solvent.

in number [37–39] and require stringent conditions. At the same time including a polufluoroaryl substituent into a molecule of diaryl selenide may be interesting from the viewpoint of biological activity.

We found that $Bu_3SnSePh$ reacted with activated fluoroaromatic compounds in the presence of catalytic amounts of inorganic fluorides providing the corresponding diaryl selenides in good yield. Note that nucleophilic assistance of fluoride ion is well known for reactions of organotin compounds, in particular, of tin selenides [40–44].

The reaction conditions were selected by an example of octafluorotoluene. The reaction monitoring was performed by $^{19}F$ NMR spectroscopy. The conversion was evaluated from the ratio of signals belonging to the original octafluorotoluene and the reaction products. The reaction was carried on till the fluorine signals from the original fluoroarene disappeared. The reaction product purity was also checked by $^{77}Se$ NMR spectroscopy.

In Table 6 are presented the results of $Bu_3SnSeAr$ reaction with octafluorotoluene in the presence of various inorganic fluorides and phase-transfer catalysts. Practically no aryl phenyl selenide formed in the absence of fluoride ions and phase-transfer catalysts. In the presence of benzyltriethylammonium chloride or dibenzo-18-crown-6 the character of inorganic cation hardly affected the yield of the phenylselenation product although with potassium fluoride the yield was commonly a little lower.The reaction between $Bu_3SnSeAr$ and octafluorotoluene in the more polar DMF does not require for its initiation an addition of the fluoride catalyst and is complete at room temperature within 2 h. The yield of aryl phenyl selenide is here virtually quantitative. In this connection the published data on low activity of lead arylselenolates under the same conditions were quite unexpected [37].

**Schema 8.**

$$ArF + Bu_3SnSeAr' \rightarrow ArSeAr' + Bu_3SnF$$

**VIa–d** **VIIa–e**

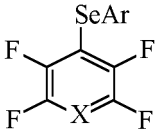
**VI**, Ar = tetrafluoro-4-pyridyl (**a**), 4-$CF_3C_6F_4$ (**b**), $C_6F_5$ (**c**), 4-$NO_2C_6H_4$ (**d**), 4-$AcC_6H_4$ (**e**), 4-$EtO_2CC_6H_4$ (**f**); **VII**, Ar' = Ph: Ar = tetrafluoro-4-pyridyl (**a**), 4-$CF_3C_6F_4$ (**b**), $C_6F_5$ (**c**); Ar' = 4-$FC_6H_4$: Ar = tetrafluoro-4-pyridyl (**d**), 4-$CF_3C_6F_4$ (**e**).

Under the selected conditions the reaction was carried out also with some other fluoroarenes (Scheme 8). The results of reaction between $Bu_3SnSePh$ and various aryl fluorides in chloroform in the presence of fluoride ions or DMF are presented in Table 7. The reaction of pentafluoropyridine with $Bu_3SnSePh$ in the boiling chloroform goes faster and affords higher yield of diaryl selenide **VIIa** than the similar reaction with octafluorotoluene. In DMF the difference disappears, and the yields of the phenylselenation products obtained from octafluorotoluene and pentafluoropyridine are virtually equal. Hexafluorobenzene fails to be phenylselenated under the described conditions. Thus after heating in DMF to 100°C for 15 h formed only negligible amount of diaryl selenide **VIIc**. With 4-nitro-1-fluorobenzene reaction in chloroform provided 4-nitrodiphenyl selenide in a low yield. The main product in this case was diphenyl selenide formed by oxidation of PhSe– anion. However in DMF at 100°C the yield of 4-nitrodiphenyl selenide sharply increased and attained 98%. Yet aryl fluorides with less electron-withdrawing substituents, 4-fluoro-1-acetophenone and ethyl 4-fluorobenzoate, failed to react with $Bu_3SnSePh$ under the given conditions. The monitoring of phenylselenation of monofluoro-substituted arenes by means of $^{19}F$ NMR was performed with the use of fluorobenzene as internal reference inert under the given conditions.

As a result of reactions carried out in the similar way between activated fluorides **VIa, b, d** and 4-$FC_6H_4SeSnBu_3$ were obtained in high yield arylselenation products **IIn** and **VIId, e** (Table 7).

The phenylselenation of perfluoroaromatic compounds occurs with high selectivity: exclusively

forms the product of fluorine atom substitution in the *para*-position with respect to the substituent present in the ring. The structure of products and regioselectivity of the reaction were proved by $^{19}F$ and $^{77}Se$ NMR spectra. No substitution of two or more fluorine atoms in the presence of excess phenylselenating agent was observed.



X = N, C-$CF_3$.

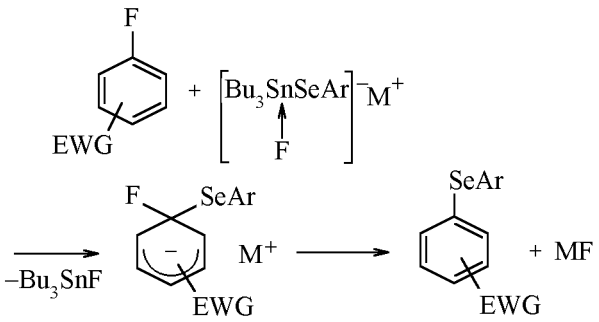
Although the detailed investigation of mechanism was not performed the most probable is the classical aromatic nucleophilic substitution with the nucleophilic assistance of a fluoride ion (Scheme 9).

In the dimethylformamide with no additives the nucleophilic assistance is provided by the solvent (Scheme 10).

**Reaction of $Bu_3SnSeAr$ with alkyl, allyl, benzyl, and propargyl halides.** The usual synthesis of alkyl aryl selenides consists on arylselenation of alkyl halides with arylselenols in the presence of bases or by arylselenolates of alkali metals [45–47]. As organoselenating reagents were also proposed thallium arylselenolates [48]. Yet the difficulties in handling selenols and toxicity of thallium compounds call for a search of new more convenient in handling arylselenating reagents. It was previously shown that fluorodestannylation $(R_3SN)_2Se$ could serve as a convenient procedure for generation of an active selenide dianion [40].

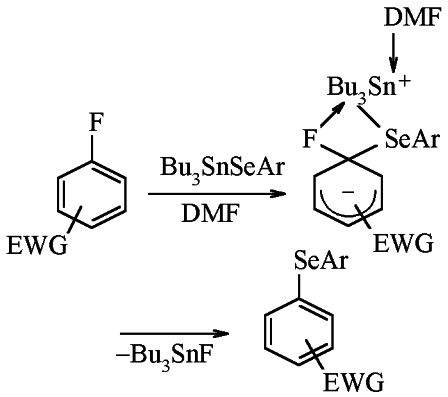
We demonstrated that tributyltin aryl selenides readily react with alkyl, allyl, benzyl, and propargyl halides in the presence of fluoride ions affording the corresponding aryl organyl selenides in high yield.

**Scheme 9.**



EWG = $F_5$, 2,3,5,6-$F_4$-4-$CF_3$, 4-$NO_2$, 2,3,5,6-$F_4$-4-N.

**Scheme 10.**



EWG = 2,3,5,6-$F_4$-4-$CF_3$, 2,3,5,6-$F_4$-4-N.

**Table 7.** Reaction conditions and yields of arylselenation products from activated aryl fluorides and $Bu_3SnSeAr'$[a]

| ArSeAr' | | Compd. | Method[b] | Time, h | Yield,[c] % |
|---|---|---|---|---|---|
| Ar | Ar' | no. | | | |
| 4-$C_5F_4N$ | Ph | **VIIa** | *A* | 5 | 98 (95) |
| | | | *B* | 2 | 97 (92) |
| | 4-$FC_6H_4$ | **VIId** | *B* | 2 | 97 (93) |
| 4-$CF_3C_6F_4$ | Ph | **VIIb** | *A* | 12 | 82 (75) |
| | | | *B* | 2 | 97 (95) |
| | 4-$FC_6H_4$ | **VIIe** | *B* | 2 | 96 (92) |
| $C_6F_5$ | Ph | **VIIc** | *A* | 10 | 0 |
| | | | *C* | 15 | 7 |
| 4-$NO_2C_6H_4$ | Ph | **IId** | *A* | 10 | 20 |
| | | | *C* | 5 | 98 (92) |
| | 4-$FC_6H_4$ | **IIn** | *C* | 5 | 97 (93) |
| 4-$AcC_6H_4$ | Ph | **IIh** | *C* | 12 | 0 |
| 4-$EtO_2CC_6H_4$ | Ph | **IIi** | *C* | 12 | 0 |

[a] Reaction conditions: 1 mmol of ArF, 1 mmol of $Bu_3SnSeAr$, 2 ml of solvent.

[b] Method *A*: 10% CsF + 10% BTEAC, $CHCl_3$, 61°C; Method *B*: DMF, 25°C; Method *C*: 10% CsF, DMF, 100°C.

[c] Yield from $^{77}Se$ NMR data. Preparative yield is given in parentheses.

**Scheme 11.**

$$RHlg + ArSeSnBu_3 \xrightarrow{KF} RSeAr + Bu_3SnF$$

**VIIIa–e** **IXa–f**

**VIII**, R = $PhCH_2$ (**a**), 2-$CH_3C_6H_4CH_2$ (**b**), Et (**c**), $H_2C{=}CHCH_2$ (**d**), $HC{\equiv}CCH_2$ (**e**); **IX**, Ar = Ph: R = $PhCH_2$ (**a**); Ar = 4-$FC_6H_4$: R = $PhCH_2$ (**b**), 2-$CH_3C_6H_4CH_2$ (**c**), Et (**d**), $H_2C{=}CHCH_2$ (**e**), $HC{\equiv}CCH_2$ (**f**).

**Table 8.** Arylselenation conditions with 4-$FC_6H_4SeSnBu_3$ of benzyl bromide, and yield of benzyl 4-fluorophenyl selenide[a]

| Solvent | Additives | Temperature, °C | Time, h | Yield,[b] % |
|---|---|---|---|---|
| $CHCl_3$ | – | 61 | 19 | 96 (92) |
| | 2 equiv KF + 10 mol% BTEAC | 25 | 2 | 96 (90) |
| | 2 equiv KF + 10 mol% BTEAC | 61 | 0.5 | 99 (95) |
| DMF | – | 25 | 11 | 95 (90) |
| DMF | 2 equiv. KF | 25 | 0.5 | 99 (96) |

[a] Reaction conditions: 1 mmol of 4-$FC_6H_4SeSnBu_3$, 1 mmol of $PhCH_2Br$, 2 ml of solvent.

[b] Yield from $^{19}F$ NMR data. Preparative yield is given in parentheses.

**Table 9.** Arylselenation conditions with $Bu_3SnSeAr$ of benzyl, alkyl, allyl, and propargyl halides RHlg, and yield of reaction products[a]

| RSeAr | | Compd. no. | Method[b] | Time, h | Yield,[c] % |
|---|---|---|---|---|---|
| R | Ar | | | | |
| $PhCH_2$ | Ph | **IXa** | *A* | 2 | 97 (94) |
| | | | *B* | 0.5 | 98 (93) |
| | 4-$FC_6H_4$ | **IXb** | *A* | 2 | 99 (95) |
| | | | *B* | 0.5 | 99 (94) |
| 2-$CH_3C_6H_4CH_2$ | 4-$FC_6H_4$ | **IXc** | *A* | 4 | 91 (82) |
| Et | 4-$FC_6H_4$ | **IXd** | *B* | 2 | 93 (81) |
| $H_2C$= $CHCH_2$ | 4-$FC_6H_4$ | **IXe** | *A* | 4 | 82 (78) |
| | | | *B* | 1 | 93 (84) |
| HC=$CCH_2$ | 4-$FC_6H_4$ | **IXf** | *A* | 3 | 90 (81) |
| | | | *B* | 1 | 97 (89) |

[a] Reaction conditions: 1 mmol of 4-$FC_6H_4SeSnBu_3$, 1 mmol of RHlg, 2 ml of solvent.

[b] Method *A*: 2 equiv of KF + 10 mol% BTEAC, $CHCl_3$, 25°C; method *B*: 2 equiv of KF, DMF, 25°C.

[c] Yield from $^{19}F$ NMR data. Preparative yield is given in parentheses.

The preliminary experiments were carried out by the example of arylselenation of benzyl bromide with tributyltin 4-fluorophenyl selenide. In the absence of fluoride ions the reaction rate is low, and complete conversion in boiling chloroform is reached in 19 h. The addition of 2 equiv of KF and 10 mol% of benzyltriethylammonium chloride strongly facilitates the reaction, and it completes in 2 h at room temperature. In boiling chloroform the reaction time is reduced to 0.5 h.

It should be notes that the course of the reaction is considerably affected by the mode of reagents mixing. In case tributyltin aryl selenide is added to the mixture of RHlg and KF, the reaction rate sharply decreases, and the yield of arylselenation product is notably lower than if potassium fluoride is added to the mixture of $Bu_3SnSeAr$ and RHlg.

In going to more polar DMF the rate of benzyl bromide arylselenation significantly grows. For instance, without fluoride ions at room temperature reaction completes in 11 h against 19 h in boiling chloroform. The reaction rate sharply increases after addition of potassium fluoride, and the complete conversion of $Bu_3SnSeAr$ is attained already in 0.5 h. In all cases the yield of 4-fluorophenyl benzyl selenide was close to quantitative.

Thus the reaction between $Bu_3SnSeAr$ and alkyl halides easily goes in the presence of KF at room temperature in DMF or in boiling chloroform with addition of a phase-transfer catalyst.

In reaction with benzyl bromide was also used as organoselenating agent $Bu_3SnSePh$ whose reactivity was on the same level as that of 4-$FC_6H_4SeSnBu_3$.

Into reaction with tributyltin aryl selenides was also involved a number of the other organyl halides (Table 9). Among all the bromides studied (**VIIIa, c–d**) the most active was benzyl bromide. Reactivity of propargyl bromide was somewhat higher than that of allyl bromide; however in the more polar DMF the difference is levelled. The least active was ethyl bromide: the reaction in DMF took 2 h against 0.5–1 h in the other cases. Also chloromethyl-2-methylbenzene was involved into the reaction; however, here the yield of diorganyl selenide **IXc** was somewhat lower than with unsubstituted benzyl bromide, probably due to steric hindrances.

Hence tributyltin aryl selenides are highly efficient arylselenating reagents in reactions with aryl iodides and aryl triflates under catalysis with complexes of Pd and Ni respectively, and also in reactions with the stable aryldiazonium salts. They can be used also as efficient source of active arylselenolate anion in the presence of fluoride ions in arylselenation reactions of alkyl halides and activated alkyl fluorides.

## EXPERIMENTAL

All reactions save those with aryldiazonium salts were carried out under inert nitrogen atmosphere.

The workup of reaction mixtures and separation of reaction products does not require inert atmosphere. The solvents were dried by standard methods [31] and distilled under nitrogen just before use. The NMR monitoring of reactions was performed by carrying out the process in sealed NMR tubes. Aryl triflates [49], aryldiazonium salts [50], $Pd(PPh_3)_4$ [51], $PdCl_2(PPh_3)_2$ [52], $NiCl_2(PPh_3)_2$ [53] were synthesized along described procedures. Tributyltin aryl selenides were obtained by reaction of $Bu_6Sn_2$ with ArSeSeAr in benzene under irradiation with daylight [54].

$^{77}Se$ and $^{199}Sn$ NMR spectra were recorded on spectrometer Bruker WP-200 SY at operating frequencies 38.19 and 74.6 MHz respectively from solutions in benzene or chloroform. $^{19}F$ NMR spectra were registered on spectrometers Bruker WP-200 SY and Bruker AMX-400 at operating frequencies 188.3 and 376.5 MHz respectively from solutions in chloroform or DMF. The stabilization was performed from external $D_2O$ sample. As external references were used $Me_4Sn$ ($^{119}Sn$), $Ph_2Se_2$ ($^{77}Se$), and trifluoroacetic acid ($^{19}F$). $^1H$ and $^{13}C$ NMR spectra were measured on Bruker AMX-400 instrument at operating frequencies 400.13 and 100.5 MHz respectively from solutions in acetone-$d_6$ or $CDCl_3$. Mass spectra were measured on Kratos MS 890 spectrometer.

**Reaction of aryl iodides with $Bu_3SnSePh$.** Method *A*. To a solution of 1 mmol of ArI and 0.015 mmol of $Pd(PPh_3)_4$ (1.5 mol%, 17 mg) in 1 ml of anhydrous toluene in a Schlenk vessel under argon atmosphere was added 1 mmol of $Bu_3SnSeAr$ in 1 ml of anhydrous toluene. The arising brown-red mixture was heated to 100°C for 5 h. On evaporating the solution the residue was dissolved in acetone and poured into water solution of KF. After treating with toluene the organic layer was filtered and dried with $Na_2SO_4$. The solvent was removed in a vacuum, diaryl selenide was purified by column chromatography on silica gel [eluent hexane (**IIa, b, f, h, k, l, m, p**), hexane + 5% of chloroform (**IIc, d, e, i, j, n, o**)] or by recrystallization from hexane (**IIg**). The spectral data of compounds obtained are presented in Tables 10 and 11.

Method *B*. To a solution of 1 mmol of ArI and 0.015 mmol of $PdCl_2(PPh_3)_2$ (1.5 mol%, 11 mg) in 1 ml of anhydrous DMF in a Schlenk vessel under argon atmosphere was added 1 mmol (0.446 g) of $Bu_3SnSeAr$ in 1 ml of anhydrous DMF. The arising brown-red mixture was heated to 100°C for 5 h. On finishing the heating the reaction mixture was poured into water. Further workup was carried out as in method *A*.

**Table 10.** $^1H$ and $^{13}C$ NMR spectra of diaryl selenides **IIa–q** (acetone-$d_6$)

| Compd. no. | $^1H$ NMR spectrum, δ, ppm | $^{13}C$ NMR spectrum, $\delta_C$, ppm |
|---|---|---|
| **IIa** | 7.32–7.41 m (6H), 7.49–7.57 m (4H) | 127.13, 127.79, 127.93, 130.24 |
| **IIb** | 3.57 s (3H), 6.89 d (2H, *J* 8.72 Hz), 7.15–7.22 m (3H), 7.28–7.31 m (2H), 7.48 d (2H, *J* 8.72 Hz) | 56.05, 116.47, 120.62, 127.72, 130.47, 130.71, 131.95, 134.1, 137.81 |
| **IIc** | 2.9 s (6H), 6.6 d (2H, *J* 10 Hz), 7.01–7.18 m (3H), 7.21–7.24 m (2H), 7.42 d (2H, *J* 10 Hz) | 40.77, 114.41, 127.05, 130.02, 130.29, 132.37, 135.91, 138.05, 152.03 |
| **IId** | 7.44 d (2H, *J* 8.76 Hz), 7.4–7.47 m (3H), 7.62–7.65 m (2H), 8.02 d (2H, *J* 8.76 Hz) | 125.1, 128.57, 130.53, 131.22, 131.32, 136.84, 144.59, 147.62 |
| **IIe** | 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 |
| **IIf** | 7.30–7.33 m (3H), 7.32 d (2H, *J* 8.72 Hz), 7.44 d (2H, *J* 8.72 Hz), 7.43–7.48 m (2H) | 122.24, 129.19, 130.9, 131.18, 131.83, 133.64, 134.63, 135.41 |
| **IIg** | 7.33 s (6H), 7.37 m (4H), 7.54 m (6H) | 127.54, 129.33, 130.38, 130.53, 133.17, 133.30 |
| **IIh** | 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* 8.23 Hz) | 26.64, 128.56, 128.69, 128.89, 129.70, 130.50, 135.02, 135.39, 140.12, 197.03 |
| **IIi** | 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 |
| **IIj** | 7.02 d (2H, *J* 4.8 Hz), 7.3–7.4 m (3H), 7.55–6 m (2H), 8.2 br.s (2H) | 123.45, 127.13, 127.79, 128.77, 131.86, 132.87, 146.65 |
| **IIk** | 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 |
| **IIl** | 7.29–7.39 m (3H), 7.51–7.59 m (2H), 7.46 d.d [2H, $^3J$ 8.56, $^3J(^1H–^{19}F)$ 5.60 Hz], 6.99 pseudo-t (2H) | 114.76, 124.6, 127.13, 127.79, 129.70, 130.24, 161.10 |

**Table 10.** (Contd.)

| Compd. no. | $^1$H NMR spectrum, δ, ppm | $^{13}$C NMR spectrum, $\delta_C$, ppm |
|---|---|---|
| **IIm** | 3.57 s (3H), 6.89 d (2H, *J* 8.72 Hz), 7.05 pseudo-t (2H), 7.46 d.d [2H, $^3J$ 8.51, $^3J(^1H^{-19}F)$ 5.64 Hz], 7.44 d (2H, *J* 8.72 Hz) | 54.50, 113.46, 114.28, 121.17, 124.52, 129.79, 131.09, 161.01 |
| **IIn** | 7.01 pseudo-t (2H), 7.44 d (2H, *J* 8.76 Hz), 7.49 d.d [2H, $^3J$ 8.55 Hz, $^3J(^1H^{-19}F)$ 5.61 Hz], 8.05 d (2H, *J* 8.76 Hz) | 115.06, 122.01, 122.44, 126.34, 129.7, 136.31, 145.54, 161.06 |
| **IIo** | 7.02 d (2H, *J* 4.8 Hz), 7.11 pseudo-t (2H), 7.49 d.d [2H, $^3J$ 8.47, $^3J(^1H^{-19}F)$ 5.54 Hz], 8.2 br.s (2H) | 114.89, 123.45, 125.47, 131.33, 133.58, 146.56, 161.12 |
| **IIp** | 7.01 pseudo-t (2H), 7.1–8.4 (9H) | 116.61, 124.12, 124.43, 125.12, 125.46, 125.72, 126.06, 126.76, 128.30, 129.91, 130.76, 133.15, 161.09 |
| **IIq** | 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* 7.83 Hz) | 92.88, 127.93, 129.63, 131.6, 133.37, 133.61, 134.34, 138.37 |

Method *C*. To a solution of 1 mmol of ArI and 0.015 mmol of $PdCl_2(PPh_3)_2$ (1.5 mol%, 11 mg) in 1 ml of anhydrous DMF in a Schlenk vessel under argon atmosphere was added 0.5 mmol (0.29 g) of $Bu_3SnSnBu_3$ and a solution of 0.5 mmol of PhSeSePh in 1 ml of anhydrous DMF. The solution obtained was kept under light for 1.5 h and then heated for 5 h to 100°C. Further workup was carried out as in method *A*.

**4-Methoxydiphenyl selenide (IIb).** Colorless needles. mp 46°C (from ethanol) [34].

**4-Dimethylaminodiphenyl selenide (IIc).** Light-yellow needles. mp 68°C (from 60% ethanol) [55].

**4-Nitrodiphenyl selenide (IId).** Yellow needles. mp 59°C (from 60% ethanol) [20].

**3-Nitrodiphenyl selenide (IIe).** Yellow crystals. mp 40°C (from 40% ethanol) [55].

**4-Bromodiphenyl selenide (IIf).** Colorless crystals. mp 31°C (from 40% ethanol) [15].

**Table 11.** $^{77}$Se and $^{19}$F NMR spectra and molecular ions of diaryl selenides **IIa**–**q**

| Compd. no. | $^{77}$Se NMR spectrum, $\delta_{Se}$, ppm | $^{19}$F NMR spectrum, $\delta_F$, ppm | $[M]^+$ [a] |
|---|---|---|---|
| **IIa** | –46.5 | – | 234 |
| **IIb** | –61.9 | – | 264 |
| **IIc** | –68.6 | – | 277 |
| **IId** | –25.7 | – | 279 |
| **IIe** | –28.3 | – | 279 |
| **IIf** | –46.4 | – | 312 |
| **IIg** | –46.6 | – | 390 |
| **IIh** | –36.5 | – | 276 |
| **IIi** | –36.5 | – | 306 |
| **IIj** | –39.3 | – | 235 |
| **IIk** | –108.5 | – | 284 |
| **IIl** | –48.1 | 1.06 | 255 |
| **IIm** | –70.2 | 0.45 | 282 |
| **IIn** | –35.7 | 2.39 | 297 |
| **IIo** | –41.2 | 2.25 | 253 |
| **IIp** | –111.6 | 0.22 | 302 |
| **IIq** | –46.3 | – | 360 |

[a] Molecular ion corresponds to diaryl selenide molecule containing the most abundant natural isotope $^{80}$Se.

**1,4-Bis(phenylseleno)benzene (IIg).** Colorless needles. mp 102°C (from hexane) [56].

**4-Phenylselenoacetophenone (IIh).** Light-yellow needles. mp 60°C (from 60% ethanol) [19].

**4-Methoxy-4′-fluorodiphenyl selenide (IIm).** Light-yellow needles. mp 51°C (from hexane).

**4-Nitro-4′-fluorodiphenyl selenide (IIn).** Yellow needles. mp 72°C (from hexane).

**Reaction of aryl triflates with $Bu_3SnSePh$.** General procedure. To a solution of 1 mmol of ArOTf, 4 mmol of LiBr (4 equiv, 0.348 g), and 0.015 mmol of $Ni(PPh_3)_2Cl_2$ (9.8 mg, 1.5% mol) in 2 ml of butanol in a Schlenk vessel equipped with a magnetic stirrer was added under inert atmosphere 1 mmol (0.446 g) of $Bu_3SnSePh$. Purple-colored reaction mixture was heated to 100°C at stirring for 12 h, and then it was poured into a water solution of KF. The mixture obtained was treated with benzene, the water layer was filtered and extracted with benzene. The combined benzene extracts were dried with $MgSO_4$, the solvent was removed under reduced pressure. The diaryl selenide was isolated from the residue by column chromatography on $SiO_2$, eluent hexane.

Reaction of aryldiazonium salts with $Bu_3SnSePh$. General procedure. To a mixture of 1 mmol of aryl-

diazonium fluoborate $ArN_2BF_4$ and 2 ml of solvent was added by portions at stirring 1 mmol (0.446 g) of $Bu_3SnSePh$. The mixture was stirred 10 min till the end of gas evolution and then it was poured into a water solution of KF. Further workup was as described before.

**4-Iododiphenyl selenide (IIq).** Colorless prisms. mp 43°C (from hexane).

**Diphenylsulfide V** was prepared by reaction of 1 mmol (0.192 g) of $PhN_2BF_4$ with 1 mmol (0.399 g) of $Bu_3SnSPh$ in 2 ml of acetone. The reaction mixture was treated as above. Yield of pure diphenyl sulfide 0.187 g (90%). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 7.00 t (1H, $H^4$, *J* 7.34 Hz), 7.06 t (2H, $H^{3,5}$, *J* 8.04 Hz), 7.20 d (2H, $H^{2,6}$, *J* 8.04 Hz).

**Reaction of activated fluoroarenes with $Bu_3SnSePh$.** Method *A*. To a mixture of 15 mg of CsF (10 mol%, 0.1 mmol) and 22.7 mg of benzyltriethylammonium chloride (BTEAC)in a Schlenk vessel under argon atmosphere was added 1 mmol of ArF in 2 ml of anhydrous chloroform and 1 mmol (0.446 g) of $Bu_3SnSePh$. The mixture was heated to boiling. On cooling the reaction mixture was diluted with 25 ml of benzene and filtered. On removing the solvent in a vacuum the diaryl selenide was isolated from the residue by column chromatography.

Method *B*. A mixture of 1 mmol of ArF and 1 mmol of $Bu_3SnSePh$ in 2 ml of anhydrous DMF was stirred at room temperature. On completion of the reaction the reaction mixture was worked up as in method *A*.

Method *C*. To 15 mg of CsF (10 mol%, 0.1 mmol) in a Schlenk vessel under argon was added 1 mmol of ArF in 2 ml of DMF and 1 mmol (0.446 g) of $Bu_3SnSePh$. The mixture obtained was heated to 100°C on an oil bath at stirring. On completion of the reaction the reaction mixture was poured in water and extracted with benzene (3 × 25 ml). The extracts were dried on $MgSO_4$, and the solvent was removed in a vacuum.

**4-(Phenylseleno)-2,3,5,6-tetrafluoropyridine (VIIa).** Light-yellow oily substance with a specific odor. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 7.35 m (3H), 7.65 m (2H). $^{19}$F NMR spectrum ($CHCl_3$), $\delta_F$, ppm: –13.25 m (2F, $F^{3,5}$), –53.8 m (2F, $F^{2,6}$). $^{77}$Se NMR spectrum ($CHCl_3$), $\delta_{Se}$, ppm: –126. Mass spectrum, *m/z*: 307 $[M]^+$.

**1-Trifluormethyl-4-phenylseleno-2,3,5,6-tetrafluorobenzene (VIIb).** Yellow oily substance. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 7.32 m (3H), 7.52 m (2H). $^{19}$F NMR spectrum ($CHCl_3$), $\delta_F$, ppm: 21.10 t (3F, $CF_3$, *J* 22 Hz), –48.69 m (2F), –62.91 m (2F). $^{77}$Se NMR spectrum ($CHCl_3$), $\delta_{Se}$, ppm: –158. Mass spectrum, *m/z*: 374 $[M]^+$.

**Table 12.** $^1$H and $^{13}$C NMR spectra of aryl organyl selenides **IXa**–**f** (acetone-$d_6$)

| Compd. no. | $^1$H NMR spectrum, δ, ppm | $^{13}$C NMR spectrum, $\delta_C$, ppm |
|---|---|---|
| **IXa** | 4.01 br.s (2H, $CH_2$), 7.15 br.s (5H, $C_6H_5CH_2$), 7.22–7.35 m (3H), 7.52–7.57 m (2H) | 31.77, 126.42, 127.83, 128.80, 128.87, 128.99, 130.76, 132.85, 137.97 |
| **IXb** | 4.1 s (2H, $CH_2$), 6.99 pseudo-t (2H), 7.22 m (3H), 7.29 m (2H), 7.45 d.d [2H, $^3J$ 8.47, $^3J$ ($^1$H–$^{19}$F) 5.60 Hz] | 33.45, 116.13, 127.47, 127.83, 128.8, 128.96, 133.11, 137.97, 160.74 |
| **IXc** | 2.24 s (3H, $CH_3$), 3.99 br.s (2H, $CH_2$), 6.89 pseudo-t (2H), 7.00–7.05 m (1H), 7.19–7.29 m (3H), 7.38 d.d [2H, $^3J$ 8.47, $^3J$($^1$H–$^{19}$F) 5.60 Hz] | 17.63, 28.09, 116.10, 126.48, 126.74, 129.06, 129.2, 129.47, 133.11, 136.43, 136.93, 160.86 |
| **IXd** | 1.39 t (3H, *J* 6.1 Hz), 2.44 q (2H, *J* 6.1 Hz), 6.57 pseudo-t (2H), 7.67 d.d [2H, $^3J$ 8.47, $^3J$($^1$H–$^{19}$F) 5.60 Hz] | 15.41, 20.95, 115.66, 127.64, 132.54, 160.98 |
| **IXe** | 3.52 d (2H, $SeCH_2$, *J* 7.0 Hz), 4.93 d.d (1H, $=CH_2$-*trans*, $^2J$ 2.1, $^3J_{cis}$ 10.61 Hz), 5.28 d.d (1H, $=CH_2$-*trans*, $^2J$ 2.1, $^3J_{cis}$ 17.41 Hz), 5.76 m (1H, CH=), 6.64 pseudo-t (2H), 7.46 d.d [2H, $^3J$ 8.47, $^3J$ ($^1$H–$^{19}$F) 5.60 Hz] | 30.30, 115.95, 116.2, 126.61, 132.8, 134.1, 160.89 |
| **IXf** | 1.84 t (1H, HC≡C, $^4J$ 2.36 Hz), 3.61 d.d (2H, C≡C$CH_2$, $^4J$ 2.36, $^2J$ 12.57 Hz), 6.59 pseudo-t (2H), 7.47 d.d [2H, $^3J$ 8.47, $^3J$ ($^1$H–$^{19}$F) 5.60 Hz] | 18.18, 71.41, 115.76, 127.08, 134.62, 161.00 |

**2,3,5,6-Tetrafluoro-4-(4-fluorophenylseleno)-pyridine (VIId).** Light-yellow oily substance with a specific odor. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 6.87 pseudo-t (2H), 7.46 d.d [2H, $^3J$ 8.47, $^3J$($^1$H-$^{19}$F) 5.60 Hz]. $^{19}$F NMR spectrum ($CHCl_3$), $\delta_F$, ppm:

**Table 13.** $^{77}$Se and $^{19}$F NMR spectra and molecular ions of aryl organyl selenides **IXa**–**f**

| Compd. no. | $^{77}$Se NMR spectrum, $\delta_{Se}$, ppm | $^{19}$F NMR spectrum, $\delta_F$, ppm | $[M]^+$ [a] |
|---|---|---|---|
| **IXa** | –89.6 | – | 248 |
| **IXb** | –85.0 | –36.36 | 266 |
| **IXc** | –92.2 | –37.22 | 280 |
| **IXd** | –125.2 | –34.56 | 204 |
| **IXe** | –94.6 | –37.42 | 216 |
| **IXf** | –92.1 | –35.86 | 214 |

[a] Molecular ion corresponds to diaryl selenide molecule containing the most abundant natural isotope $^{80}$Se.

–19.22 m (2F, $F^{3,5}$), –37.61 s (1F, 4-$FC_6H_4$), –51.42 m (2F, $F^{2,6}$). $^{77}$Se NMR spectrum ($CHCl_3$), $\delta_{Se}$, ppm: –129. Mass spectrum, *m/z*: 325 $[M]^+$.

**1-Trifluoromethyl-2,3,5,6-tetrafluoro-4-(4-fluorophenylseleno)benzene (VIIe).** Yellow oily substance. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 6.96 pseudo-t (2H), 7.52 d.d [2H, $^3J$ 8.42, $^3J(^1H–^{19}F)$ 5.60 Hz]. $^{19}$F NMR spectrum ($CHCl_3$), $\delta_F$, ppm: 19.22 t (3F, $CF_3$, *J* 22 Hz), –37.61 s (1F, 4-$FC_6H_4$), –51.42 m (2F), –65.77 m (2F). $^{77}$Se NMR spectrum ($CHCl_3$), $\delta_{Se}$, ppm: –158. Mass spectrum, *m/z*: 392 $[M]^+$.

**Reaction of organyl halides with $Bu_3SnSeAr$.** Method A. To a solution of 1 mmol of $Bu_3SnSeAr$ and 1 mmol of alkyl halide in 2 ml of chloroform was added 2 mmol (0.116 g) of KF and 10 mol% (0.1 mmol, 0.21 g) of BTEAC. The reaction mixture was stirred at room temperature till the end of the process, diluted with 25 ml of benzene, and the solution obtained was filtered, the solvent was removed in a vacuum, and alkyl aryl selenide was isolated from the residue by column chromatography on silica gel (eluent hexane). The spectral characteristics of compounds obtained are listed in Tables 12 and 13.

Method *B.* To a solution of 1 mmol of $Bu_3SnSeAr$ and 1 mmol of alkyl halide in 2 ml of DMF was added 2 mmol (0.116 g) of KF and 10 mol% (0.1 mmol, 0.21 g) of BTEAC. The reaction mixture was stirred at room temperature till the end of the process and then it was poured into water. After extraction with benzene the combined organic solutions were twice washed with water and dried with $Na_2SO_4$. Further isolation was carried out as in method *A.*

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