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Tributylstannyl Aryl Selenides as Efficient Arylselenating Agents in the Synthesis of Seleno Esters*

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Abstract—Tributyltin aryl selenides are convenient and highly efficient arylselenating agents in reactions with acyl chlorides. The activity of acetic anhydride is considerably lower but it can be involved into the arylselenation reaction in the presence of $PdCl_2(PPh_3)_2$ or boron trifluoride etherate as catalysts.

Selenoesters are interesting due to extensive opportunities to apply them as synthetic intermediates. They can be used as building blocks in preparation of oxazoles [1] and polyfunctional alkenes [2]. The lability of the Se–O bond is utilized in their application as precursors of acyl radicals [3–10].

The preparation procedures for selenoesters are based on reactions between acyl chlorides and acid anhydrides or esters with nucleophilic organoselenating reagents, as organoselenols in the presence of bases, mercury bisarylselenolates, samarium and aluminum organoselenolates [11–15]. The carboxylic acids also can be converted into the corresponding selenoesters through reaction with aryl selenocyanates and tributylphosphine [16].

In the most of these methods are used highly toxic compounds, unstable against oxygen and moisture, and often difficult in handling. Therefore new stable, easy to handle and efficient organoselenating reagents are of obvious interest.

In the present report we describe a method for selenoesters synthesis based on stable against moisture and air tributyltin arylselenolates that are used as a source of the arylseleno group (preliminary communication see [17]).

Aryselenation of acyl chlorides with the use of $Bu_3SnSeAr$. We performed reactions of tributyltin aryl selenides $Bu_3SnSeAr$ (Ar = Ph, 4-FC_6H_4) with a series of acyl chlorides.

Scheme 1.

$$\underset{\textbf{Ia–j}}{RCOCl} + \underset{\textbf{IIa, b}}{ArSeSnBu_3} \longrightarrow \underset{\textbf{IIIa–u}}{RCOSeAr} + Bu_2SnCl$$

The arylselenation of benzoyl chloride readily occurs at room temperature both with and without palladium catalyst affording the corresponding selenoester in nearly quantitative yield. The reaction is of general character, and this synthetic procedure can be extended to preparation of selenoesters of aromatic, aliphatic, and α,β-unsaturated acids (Table 1). In the most cases the yield of selenoesters **IIIa–u** is virtually quantitative; however with acyl chloride it decreases presumably due to the enhanced hydrolytic ability. The reaction progress was monitored by ^{119}Sn NMR spectroscopy. However the time of spectrum recording was close to that of the reaction, and therefore we used as arylselenating agent also tributyltin 4-fluorophenyl selenide (**IIb**). This provided a possibility to check the reaction time for various acyl chlorides (Table 1) and to evaluate their relative reactivity. Note that the activity of $Bu_3SnSePh$ and its fluorinated analog with respect to acyl chlorides was virtually the same as was shown by an example of 4-fluorobenzoyl chloride arylselenation. The electron-withdrawing substituents in the acyl chloride molecule accelerate the reaction. This effect is especially pronounced with the nitro group. In reactions with 4-nitrobenzoyl chloride (**Ie**) and (*E*)-4-nitrophenyl-2-propenoyl chloride (**Ij**) the formation of selenoesters **IIIi** and **IIIt** was complete within several minutes after mixing the reagents. Yet the acyl chlorides with electron-donor substituents, as 4-methoxybenzoyl chloride (**Ih**) react notably shower

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Table 1. Reaction time and yields of arylselenation products from acyl chlorides RCOCl and tributyltin aryl selenides $Bu_3SnSeAr$

RCOCl	RCOSeAr		Compd. no.	Time, min[a]	Yield, %[b]
	R	Ar			
Ia	Ph	Ph	**IIIa**	60[c]	99 (96)
	Ph	4-FC_6H_4	**IIIb**	45[d]	98 (94)
Ib	4-FC_6H_4	Ph	**IIIc**	35	99 (97)
	4-FC_6H_4	4-FC_6H_4	**IIId**	37	99 (96)
Ic	4-ClC_6H_4	Ph	**IIIe**	60[c]	98 (96)
	4-ClC_6H_4	4-FC_6H_4	**IIIf**	33	97 (93)
Id	4-BrC_6H_4	Ph	**IIIg**	60[c]	99 (97)
	4-BrC_6H_4	4-FC_6H_4	**IIIh**	37	98 (96)
Ie	4-$NO_2C_6H_4$	4-FC_6H_4	**IIIi**	5	96 (92)
If	4-(PhSeCO)C_6H_4	Ph	**IIIj**	60[c]	95 (93)
	4-(4-FC_6H_4COSe)C_6H_4	4-FC_6H_4	**IIIk**	27	98 (92)
If	4-(ClCO)C_6H_4	Ph	**IIIl**	60[c]	92 (89)
IIIl	4-(PhSeCO)C_6H_4	Ph	**IIIj**	60[c]	99
	4-(PhSeCO)C_6H_4	4-FC_6H_4	**IIIm**	48	99 (94)
Ig	2-(4-FC_6H_4COSe)C_6H_4	4-FC_6H_4	**IIIn**	35	92 (86)
	2-(ClCO)C_6H_4	4-FC_6H_4	**IIIo**	39	87 (80)
Ih	4-$MeOC_6H_4$	4-FC_6H_4	**IIIp**	63	95 (90)
Ii	(*E*)-PhCH=CH	Ph	**IIIq**	60[c]	97 (94)
	(*E*)-PhCH=CH	4-FC_6H_4	**IIIr**	38	98 (93)
Ij	(*E*)-4-$NO_2C_6H_4$CH= CH	Ph	**IIIs**	15[e]	(96)
Ik	Me	Ph	**IIIt**	60[c]	97 (90)
	Me	4-FC_6H_4	**IIIu**	15	96 (85)

[a] Time of reaction between acyl chlorides and 4-$FC_6H_4SeSnBu_3$ according to ^{19}F NMR data.

[b] Yield according to ^{19}F and ^{77}Se spectra. The preparative yield is given in parentheses.

[c] After the indicated time according to ^{119}Sn NMR data in the reaction mixture the signals of the initial $Bu_3SnSePh$ were lacking.

[d] In the presence of 1.0 mol% $Pd(PPh_3)_4$ the reaction took 20 min.

[e] Selenoester formed in virtually quantitative yield.

It was shown that in the presence of a palladium catalyst the reaction rate somewhat increased. Addition of 1 mol% of $Pd(PPh_3)_4$ reduced the reaction time for benzoyl chloride with 4-$FC_6H_4SeSnBu_3$ from 45 to 20 min.

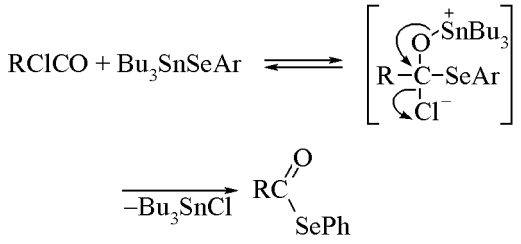
The reactivity of COCl group in the terephthaloyl chloride (**If**) and in monoselenoester **IIIl** with respect to tributyltin aryl selenides is sufficiently different to provide a possibility to substitute a single halogen at the equimolar reagents ratio (Scheme 2). Addition of the second equiv of $Bu_3SnSePh$ gives rise to diselenoester **IIIj**. Using in the second stage the fluoro-substituted tin selenide **IIb** afforded in a good yield asymmetrical diselenoester **IIIm**. This reaction can be performed without isolation of the intermediate monoselenated product **IIIl**.

A selective substitution of one chlorine in phthaloyl chloride (**Ig**) is performed at deficit of arylselenating agent **II** (0.85 equiv) for the reaction at equimolar ratio of reagents affords considerable amount (up to 10–15%) of bis-arylselenated product **IIIo**.

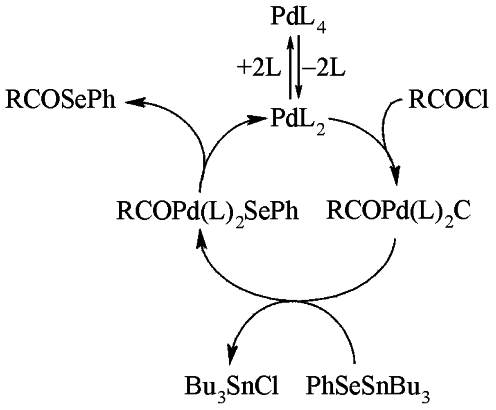
Although we have not studied in detail the reaction mechanism we regard as the most probable that presented in Scheme 3.

The addition of palladium catalyst changes the reaction path, and the mechanism apparently becomes

Scheme 3.



Scheme 4.



similar to that commonly accepted for the cross-coupling reaction (Scheme 4).

Arylselenation of acetic anhydride with the use of $Bu_3SnSeAr$. We used as acylating reagents also acid anhydrides. They have some advantages over acyl chlorides for they are cheeper and less aggressive although considerably less reactive toward nucleophiles.

The analysis of published data showed that acid anhydrides are commonly used in reactions with active nucleophiles, as samarium organoselenolates in HMPA [18] or titanocene organoselenolates [19]. Yet the more active acyl chlorides react with much less reactive mercury arylselenolates [14] and free selenols [20]. In the latter case the reaction is assisted by the presence of a base [11, 13].

The conditions of reactions were selected using as a model arylselenation of acetic anhydride (Table 2). The reaction progress was monitored by ^{19}F NMR spectroscopy.

Scheme 5.

$$(CH_3CO)_2O + 4\text{-}FC_6H_4SeSnBu_3 \longrightarrow 4FC_6H_4SeCOCH_3$$

	IIb	**IIIu**
δ_F, ppm	2.57	0.37

At room temperature both in chloroform and DMF product **IIIu** was not detected even after 24 h. The heating to 100°C resulted in selenoester **IIIu** formation although the reaction rate was still slow.

We succeeded in considerable acceleration of the reaction by applying as a catalyst $PdCl_2(PPh_3)_2$ in DMF. Under the chosen conditions the arylselenation of acetic anhydride provided selenoester **IIIu** in good yield within 4 h.

Table 2. Conditions of reaction between acetic anhydride and $4\text{-}FC_6H_4SeSnBu_3$, and yield of the selenoester

Solvent vent	Additive	Temperature, °C	Time, h	Yield, %[a]
$CHCl_3$	–	25	24	–
DMF	–	25	24	–
DMF	–	100	14	95
DMF	1 mol% $PdCl_2(PPh_3)_2$	100	4	97
$CHCl_3$	2 equiv KF + 5 mol% BTEAC	25	24	–
DMF	2 equiv CsF	25	24	–
DMF	2 equiv CsF	100	20	92
THF + +EtOH[b]	–	66	4	77[c]
DMF	10 mol% BF_3-Et_2O	25	7	96

[a] As arylselenating agent was used arylselenolate anion obtained by reduction of an appropriate diaryl selenide with $NaBH_4$.

[b] Yield according to ^{19}F NMR data.

[c] Preparative yield 70%.

Another approach to initiation of this reaction may consist in nucleophilic activation of $4\text{-}FC_6H_4SeSnBu_3$. The activation of organotin derivatives with the use of nucleophilic assistance by fluoride ion is well known [21–26]. However in our case the presence of the fluoride ions in the reaction mixture even decelerated the process. For instance, the reaction time at 100°C in the presence of CsF was 1.5 times longer than when the reaction occurred without F^-. This fact evidences that the coordination of anhydride oxygen to tin atom is a significant factor for this reaction (Scheme 5). It is an indirect indication that no free RSe anion forms in the reaction in the presence of fluoride ion as has been earlier presumed [21].

A simpler version of this reaction is treating with acetic anhydride of arylselanolate anion obtained by reduction of diaryl selenide with sodium tetrahydroborate (Scheme 6). Yet the selenoester yield in this case is notably lower than in reactions with $Bu_3SnSeAr$.

Acid anhydrides can be activated for the nucleophilic attack by complexing with the Lewis acids. We applied BF_3 etherate since it had been shown before that it had efficiently catalyzed reaction of $Bu_3SnSePh$ with epoxides [27]. With the acetic anhydride $BF_3 \cdot Et_2O$ also turned out to be very active. In contrast to catalysis with palladium complexes that requires heating the reaction in the presence of $BF_3 \cdot Et_2O$

Table 3. ^{1}H and ^{13}C NMR spectra ($CDCl_3$) of selenoesters **IIIa**–**u**

Compd. no.	^{1}H NMR spectrum, δ, ppm	^{13}C NMR spectrum, δ_C, ppm
IIIa	7.39 m (3H), 7.61 m (4H), 7.75 (1H), 8.01 (2H)	125.4 (C), 125.8 (CH), 127.58 (C), 127.67 (CH), 130.64 (CH), 132.98 (CH), 133.60 (CH), 135.88 (CH), 193.5 (CO)
IIIb	7.17 pseudo-*t* (2H), 7.54 d.d [2H, ^{3}J 8.72, $^{2}J(^{1}H–^{19}F)$ 5.13 Hz], 7.61 m (3H), 7.94 m (2H)	117.45 (CH), 124.29 (C), 125.80 (CH), 132.98 (CH), 133.46 (CH), 134.85 (C), 135.88 (CH), 161.08 (C), 193.05 (CO)
IIIc	7.17 pseudo-*t* (2H), 7.44 m (3H), 7.60 m (2H), 7.96 d.d [2H, ^{3}J 8.72, $^{2}J(^{1}H–^{19}F)$ 4.98 Hz]	116.11 d [$C^{3,5}$, 4-FC_6H_4, $^{2}J(^{13}C–^{19}F)$ 22.1 Hz], 125.52 (C^{1}, Ph), 129.17 (C^{4}, Ph), 129.41 (Ph), 129.90 d [$C^{2,6}$, 4-FC_6H_4, $^{3}J(^{13}C–^{19}F)$ 9.6 Hz], 134.85 d [C^{1}, 4-FC_6H_4, $^{4}J(^{13}C–^{19}F)$ 2.8 Hz], 136.30 (Ph), 166.12 d [C^{4}, 4-FC_6H_4, $^{1}J(^{13}C–^{19}F)$ 255.8 Hz], 191.79 (CO)
IIId	7.14 pseudo- (2H), 7.49 m (4H), 8.11 d.d [2H, ^{3}J 8.72, $^{2}J(^{1}H–^{19}F)$ 5.08 Hz]	114.77 (CH), 117.26 (CH), 122.11 (C), 124.29 (C), 133.46 (CH), 138.53 (CH), 161.08 (C), 168.56 (C), 193.67 (CO)
IIIe	7.14 m (3H), 7.56 m (2H), 7.59 d (2H, *J* 8.73 Hz), 7.77 d (2H, *J* 8.73 Hz)	125.79 (C), 128.46 (CH), 128.87 (CH), 128.96 (CH), 129.22 (CH), 136.31 (CH), 136.83 (C), 139.73 (C), 190.63 (CO)
IIIf	7.17 pseudo-t (2H), 7.62 d (2H, *J* 8.73 Hz), 7.76 d (2H, *J* 8.73 Hz) 7.96 d.d [2H, ^{3}J 8.72, $^{2}J(^{1}H–^{19}F)$ 5.01 Hz]	117.45 d [$C^{3,5}$, 4-FC_6H_4, $^{2}J(^{13}C–^{19}F)$ 22.0 Hz], 124.82 (C^{1}, 4-ClC_6H_4), 129.17 (C^{4}, 4-ClC_6H_4), 129.41 (4-ClC_6H_4), 129.62 d.d [$C^{2,6}$, 4-FC_6H_4, $^{3}J(^{13}C–^{19}F)$ 9.6 Hz], 134.89 d [C^{1}, 4-FC_6H_4, $^{4}J(^{13}C–^{19}F)$ 3.0 Hz], 140.30 (4-ClC_6H_4), 166.16 d [C^{4}, 4-FC_6H_4, $^{1}J(^{13}C–^{19}F)$ 255.4 Hz], 192.19 (CO)
IIIg	7.44 m (3H), 7.58 m (2H), 7.63 d (2H, *J* 8.72 Hz), 7.79 d (2H, *J* 8.72 Hz)	125.35 (C), 128.67 (CH), 128.96 (C), 129.22 (CH), 129.43 (CH), 132.22 (CH), 136.25 (CH), 137.25 (C), 192.50 (CO)
IIIh	7.17 pseudo-*t* (2H), 7.62 d (2H, *J* 8.73 Hz), 7.76 d (2H, *J* 8.73 Hz) 7.96 d.d [2H, ^{3}J 8.72, $^{2}J(^{1}H–^{19}F)$ 5.01 Hz]	117.49 d [$C^{3,5}$, 4-FC_6H_4, $^{2}J(^{13}C–^{19}F)$ 22.0 Hz], 124.81 (C^{1}, 4-BrC_6H_4), 128.56 (C^{4}, 4-BrC_6H_4), 129.41 (4-BrC_6H_4), 129.62 d.d [$C^{2,6}$, 4-FC_6H_4, $^{3}J(^{13}C–^{19}F)$ 9.6 Hz], 134.89 d [C^{1}, 4-FC_6H_4, $^{4}J(^{13}C–^{19}F)$ 3.0 Hz], 138.30 (4-BrC_6H_4), 166.21 d [C^{4}, 4-FC_6H_4, $^{1}J(^{13}C–^{19}F)$ 256.0 Hz], 192.19 (CO)
IIIi	7.14 pseudo-*t* (2H), 7.54 d.d [2H, ^{3}J 8.72, $^{2}J(^{1}H–^{19}F)$ 5.23 Hz], 8.05 d (2H, *J* 8.72 Hz), 8.31 d (2H, *J* 8.72 Hz)	117.45 (CH), 122.38 (CH), 124.29 (C), 131.37 (C), 133.46 (CH), 133.71 (CH), 150.73 (C), 161.01 (C), 193.56 (CO)
IIIj	7.45 m (6H), 7.61 m (4H), 8.03 s (4H)	125.42 (C), 127.71 (CH), 129.28 (CH), 129.46 (CH), 136.12 (CH), 142.32 (C), 189.11 (CO)
IIIk	7.14 pseudo-*t* (4H), 7.55 d.d [4H, ^{3}J 8.72, $^{2}J(^{1}H–^{19}F)$ 5.29 Hz], 8.01 s (4H)	117.45 (CH), 125.26 (C), 131.39 (C), 133.45 (CH), 136.11 (CH), 161.08 (C), 189.51 (CO)
IIIl	7.46 m (3H), 7.63 m (2H), 7.89 d (2H, *J* 8.72 Hz), 8.23 d (2H, *J* 8.72 Hz)	127.56 (CH), 127.67 (CH), 130.64 (CH), 132.89 (C), 133.60 (CH), 138.59 (CH), 140.11 (C), 167.30 (COCl), 183.24 (COSe) 117.45 (CH), 124.29 (C), 127.58 (C), 127.67 (CH), 130.64 (CH), 131.91 (C), 133.46 (CH), 133.6 (CH), 134.62 161.08 (C), 191.34 (CO)
IIIm	7.14 pseudo-*t* (2H), 7.45 m (3H), 7.55 d.d [2H, ^{3}J 8.72, $^{2}J(^{1}H–^{19}F)$ 5.21 Hz], 7.64 m (2H), 8.02 s (4H)	
IIIn	7.12 pseudo-*t* (4H), 7.49 d.d [4H, ^{3}J 8.72, $^{2}J(^{1}H–^{19}F)$ 5.11 Hz], 8.11 m (2H), 8.23 m (2H)	116.29 (CH), 123.76 (C), 130.24 (CH), 134.68 (CH), 142.63 (C), 161.43 (C), 188.73 (CO)
IIIo	7.16 pseudo-*t* (4H), 7.52 d.d [4H, ^{3}J 8.72, $^{2}J(^{1}H–^{19}F)$ 5.15 Hz], 7.78–8.12 m (4H)	
IIIp	3.81 s (CH_3), 7.01 d (2H, *J* 8.72 Hz), 7.14 pseudo-*t* (4H), 7.49 d.d [4H, ^{3}J 8.72, $^{2}J(^{1}H–^{19}F)$ 5.11 Hz], 7.89 d (2H, *J* 8.72 Hz)	55.67 (CH_3), 112.56 (CH), 117.21 (CH), 120.45 (C), 124.46 (C), 133.46 (CH), 136.49 (CH), 161.13 (C), 165.97 (C), 193.5 (CO)
IIIq	6.85 d (1H, =C<u>H</u>CO, *J* 15.57 Hz), 7.46 m (6H), 7.57 m (2H), 7.65 m (2H), 7.67 d (2H, PhC<u>H</u>=, *J* 15.57 Hz)	126.00 (CH), 126.06 (C), 128.46 (CH), 128.84 (C), 128.88 (CH), 129.23 (CH), 130.77 (CH), 133.61 (CH), 135.71 (CH), 140.91 (CH), 190.52 (CO)

Table 3. ^{1}H and ^{13}C NMR spectra($CDCl_3$) of selenoesters **IIIa**–**u**

Compd. no.	^{1}H NMR spectrum, δ, ppm	^{13}C NMR spectrum, δ_C, ppm
IIIr	6.78 d (1H, =CHCO, *J* 15.57 Hz), 7.11 pseudo-t (2H), 7.41 m (3H), 7.54 m (4H), 7.63 d (2H, PhCH=, *J* 15.57 Hz)	117.27 (CH), 123.92 (C), 128.34 (CH), 128.47 (CH), 133.01 (CH), 135.71 (CH), 152.52 (CH), 161.33 (C), 192.17 (CO)
IIIs	6.88 d (1H, CH=CHCO, *J* 15.8 Hz), 7.45 m (3H, Ph), 7.57 m (2H, Ph), 7.61 d (1H, CH=CHCO, *J* 15.8 Hz), 7.71 d (2H, 4-$NO_2C_6H_4$, *J* 8.4 Hz), 8.25 d (2H, 4-$NO_2C_6H_4$, *J* 8.4 Hz)	124.01 (CH), 125.47 (C), 128.86 (CH), 129.06 (CH), 129.29 (CH), 129.54 (CH), 135.48 (CH), 137.18 (CH), 139.80 (C), 148.38 (C), 190.43 (CO)
IIIt	2.26 s (3H, CH_3), 7.31 m (3H), 7.61 m (2H)	31.18 (CH_3), 127.75 (C), 127.91 (CH), 130.17 (CH), 133.03 (CH), 198.52 (CO)
IIIu	2.23 s (3H, CH_3), 7.16 pseudo t-(2H), 7.54 d.d [4H, ^{3}J 8.72, $^{2}J(^{1}H-^{19}F)$ 5.40 Hz]	31.18 (CH_3), 116.98 d [$C^{3,5}$, 4-FC_6H_4, $^{2}J(^{13}C-^{19}F)$ 22.1 Hz], 132.89 d [$C^{2,6}$, 4-FC_6H_4, $^{3}J(^{13}C-^{19}F)$ 9.6 Hz], 133.45 d [C^{1}, 4-FC_6H_4, $^{4}J(^{13}C-^{19}F)$ 2.8 Hz], 166.02 d [C^{4}, 4-FC_6H_4, $^{1}J(^{13}C-^{19}F)$ 255.8 Hz], 198.79 (CO)

Table 4. Melting points, ^{77}Se ($CHCl_3$), ^{19}F ($CHCl_3$) NMR and mass spectra of selenoesters **IIIa**–**u**

Compd. no.	mp, °C	δ_{Se}, ppm	δ_F, ppm	M^+, *m/z*	Formula[a]	Compd. no.	mp, °C	δ_{Se}, ppm	δ_F, ppm	M^+, *m/z*	Formula[a]
IIIa [15]	48	168	–	262	$C_{13}H_{10}OSe$	**IIIk**	112	188	0.78	482	$C_{20}H_{12}F_2O_2Se_2$
						IIIl	39	192	–	324	$C_{14}H_9ClO_2Se$[b]
IIIb	51	172	8.64	280	$C_{13}H_9FOSe$	**IIIm**	110	186	0.76	464	$C_{20}H_{13}FO_2Se_2$
IIIc	52	170	–	280	$C_{13}H_9FOSe$	**IIIn**	–	196	0.64	482	$C_{20}H_{12}F_2O_2Se_2$
IIId	55	173	8.69, 0.56	298	$C_{13}H_8F_2OSe$	**IIIo**	–	201	0.55	342	$C_{14}H_8ClFO_2Se$[b]
						IIIp	38	162	–0.32	310	$C_{14}H_{11}FO_2Se$
IIIe [16]	49	174	–	296	$C_{13}H_9ClOSe$[b]	**IIIq** [31]	42	154	–	288	$C_{15}H_{12}OSe$
IIIf	53	178	0.44	314	$C_{13}H_8ClFOSe$[b]	**IIIr**	44	158	0.12	306	$C_{15}H_{11}FOSe$
IIIg [15]	55	174	–	340	$C_{13}H_9BrOSe$[c]	**IIIs**	84	161	–	333	$C_{15}H_{11}NO_3Se$
						IIIt [32]	–	201	–	200	C_8H_8OSe
IIIh	60	179	0.39	358	$C_{13}H_8BrFOSe$[c]						
IIIi	89	184	1.22	325	$C_{13}H_8FNO_3Se$	**IIIu**	–	204	0.37	218	C_8H_7FOSe
IIIj	106	185	–	446	$C_{20}H_{14}O_2Se_2$						

[a] The molecular ion is given for a molecule containing the most abundant natural isotope ^{80}Se.
[b] The molecular ion is given for a molecule containing the most abundant natural isotope ^{35}Cl.
[c] The molecular ion is given for a molecule containing the most abundant natural isotope ^{79}Br.

affords selenoester within the same time at room temperature.

Thus we considered three possible approaches to the reaction of acetic anhydride with tributyltin arylselenolates: catalysis with palladium complexes, nucleophilic activation of tributyltin aryl selenides with fluoride ion, and electrophilic activation of the acetic anhydride for nucleophilic attack with the Lewis acids (BF_3–Et_2O). The optimal procedure for this reaction consists in the use of boron trifluoride etherate as catalyst. Catalysis with palladium complexes requires more rigid conditions, and the presence in the reaction medium of fluoride ions hampers the reaction course.

EXPERIMENTAL

^{119}Sn and ^{77}Se NMR spectra were registered from chloroform solutions on spectrometer Bruker WP-200 SY at operating frequencies 74.6 and 38.19 MHz

respectively. ^{19}F NMR spectra were recorded from solutions in chloroform, DMF, or THF on Bruker WP-200 SY and Bruker AMX-400 instruments at operating frequencies 188.3 and 376.5 MHz respectively. The resonance stabilization was performed on D_2O as external lock. Chemical shifts of ^{119}Sn, ^{77}Se, and ^{19}F were measured relative to external references Me_4Sn, Ph_2Se_2, and fluorobenzene respectively. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ solutions on spectrometer Bruker AMX-400 at operating frequencies 400.13 and 100.5 MHz respectively. Mass spectra were measured on Kratos MS 890 instrument.

All reactions were carried out under inert nitrogen atmosphere. The workup of reaction mixtures did not require inert atmosphere. Chloroform was dried by distillation over P_2O_5, DMF was distilled over CaH_2. All the solvents were distilled under nitrogen just before use. $Pd(PPh_3)_4$ [28] and $PdCl_2(PPh_3)_2$ [29] were prepared by known procedures. Tributyltin aryl selenides were obtained by reaction between Bu_6Sn_2 and ArSeSeAr in benzene under daylight [30].

Reaction of acyl chlorides and $Bu_3SnSeAr$. General procedure for selenoesters synthesis. To a solution of 1 mmol of acyl chloride in 1 ml of anhydrous chloroform in a Schlenk vessel was added 1 mmol (0.85 mmol in reaction with acyl chloride **Ig**) of $Bu_3SnSeAr$ in 1 ml of chloroform. In the synthesis of disubstituted selenoesters **IIIj, k, n** was used a solution of 2 mmol of $Bu_3SnSeAr$ in 2 ml of chloroform. The reaction mixture was stirred for 1.5 h, and the solvent was removed in a vacuum. The residue was diluted with 5 ml of acetone and poured into KF solution. On extraction with benzene the organic layer was filtered, dried with Na_2SO_4, and the solvent was evaporated. The residue was recrystallized from hexane (compounds **IIIa–k, p–s**) or subjected to column chromatography (compounds **IIIn, o, t, u**). Monoselenoester of terephthalic acid **IIIl** was separated by recrystallization of the residue after distillation of the solvent from the reaction mixture. The spectral data and physical constants of compounds obtained are given in Tables 3, 4.

Se^1,Se^4-Diphenylselenoester of 1,4-benzenedicarboxylic acid (IIIj). Found, %: Se 36.21. $C_{20}H_{14}O_2Se_2$. Calculated, %: Se 35.55.

(*Z*)-3-(4-Nitrophenyl)-Se-phenyl-2-propeneselenoate (IIIs). Found, %: Se 22.94. $C_{15}H_{11}NO_3Se$. Calculated, %: Se 23.77.

Reaction of acetic anhydride with $Bu_3SnSeAr$. To a solution of 1 mmol (0.102 g) of acetic anhydride in 1 ml of anhydrous solvent was added 1 mmol (0.464 g) of $4\text{-}FC_6H_4SeSnBu_3$ in 1 ml of anhydrous solvent. The reaction conditions are listed in Table 3. After the end of the reaction the reaction mixture was poured into KF solution and extracted with benzene. The organic extract was filtered, dried on Na_2SO_4, the solvent was removed in a vacuum. The selenoester was purified by column chromatography on SiO_2, eluent hexane + 5% of $CHCl_3$.

Reaction of acetic anhydride with $Bu_3SnSeAr$ catalyzed by $PdCl_2(PPh_3)_2$. To a solution of 1 mmol (0.102 g) of acetic anhydride in 1 ml of anhydrous DMF and 1 mol% (0.01 mmol, 0.007 g) of $PdCl_2(PPh_3)_2$ in a Schlenk vessel equipped with a magnetic stirrer in an argon flow was added 1 mmol (0.464 g) of $4\text{-}FC_6H_4SeSnBu_3$ in 1 ml of anhydrous DMF. The reaction mixture was stirred for 4 h at 100°C. Further workup was performed as in the previous experiment. The yield of selenoester **IIIu** 0.196 g (90%).

Reaction of acetic anhydride with $Bu_3SnSeAr$ in the presence of inorganic fluorides. To a solution of 1 mmol (0.102 g) of acetic anhydride in 1 ml of anhydrous solvent and 2 mmol (0.304 g) of CsF [or 2 mmol (0.116 g) of KF and 10 mol% (0.1 mmol, 0.0228 g) of benzyltriethylammonium chloride] in a Schlenk vessel equipped with a magnetic stirrer was added in an argon flow 1 mmol (0.464 g) of $4\text{-}FC_6H_4SeSnBu_3$ in 1 ml of anhydrous DMF. The reaction conditions are indicated in Table 3. Further workup was performed as in the previous method.

Reaction of acetic anhydride with $Bu_3SnSeAr$ in the presence of boron trifluoride etherate. To a solution of 1 mmol (0.102 g) of acetic anhydride in 1 ml of anhydrous solvent and 10 mol% of $BF_3{\cdot}Et_2O$ in a Schlenk vessel equipped with a magnetic stirrer was added in an argon flow 1 mmol (0.464 g) of $4\text{-}FC_6H_4SeSnBu_3$ in 1 ml of anhydrous DMF. The mixture was kept for 7 h at room temperature. Further workup was performed as in the previous method. Yield of selenoester **IIIu** 0,192 g (88%).

Reaction of acetic anhydride with $(4\text{-}FC_6H_4Se)_2$ and $NaBH_4$. To a solution of 1 mmol (0.348 g) of $(4\text{-}FC_6H_4Se)_2$ in 4 ml of anhydrous THF containing 15% of ethanol in a two-neck flask equipped with a condenser was added at stirring under argon atmosphere finely ground $NaBH_4$ till the solution get colorless (about 0.1 g). Then to the solution was added 2 mmol (0.204 g) of acetic anhydride, and the mixture was boiled for 4 h. On completion of the reaction the reaction mixture was poured into water and extracted with benzene. The extract was dried

with Na_2SO_4, the solvent was removed in a vacuum. The selenoester was purified by column chromatography on SiO_2, eluent hexane + 5% of $CHCl_3$. Yield of selenoester **IIIu** 0.307 g (70%, according to ^{19}F NMR data 77%).

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