Synthesis of selenoesters

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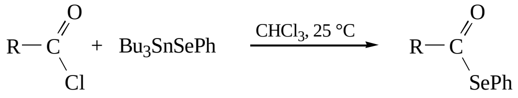
Tributyltin phenyl selenide, which was prepared from $Bu_3SnSnBu_3$ and PhSeSePh upon irradiation, easily reacts with acid halides to form selenoesters in very high yields.

Previously,[1] $Bu_3SnSePh$ was found to form upon irradiation of a mixture of the distannane $Bu_3SnSnBu_3$ and the diselenide PhSeSePh with daylight. This compound can be used as a source of the phenylseleno group, in particular, *in situ*, in cross-coupling reactions with aryl iodides or aryl triflates, catalysed by transition metal complexes, and with aryldiazonium salts.[2] Tributyltin phenyl selenide is more convenient in handling than commonly used selenols because of its stability to atmospheric oxygen and the absence of intense unpleasant odours.

We found that tributyltin phenyl selenide readily reacts with acid chlorides to form corresponding phenylselenoesters in almost quantitative yields. The rather general character of this reaction provides an opportunity to prepare selenoesters of aromatic, aliphatic and α,β-unsaturated acids (Table 1). The reaction was performed in chloroform at room temperature. The course of reaction was followed using ^{119}Sn and ^{77}Se NMR spectroscopy by monitoring the disappearance of signals due to the starting tributyltin phenyl selenide (^{119}Sn, δ 60 ppm; ^{77}Se, δ –489 ppm)[†] and the appearance of signals due to reaction products (Bu_3SnCl: ^{119}Sn, δ 145 ppm; ^{77}Se δ values for RCOSePh are given in Table 1).



1a–h **2** **3a–h**

a R = Ph
b R = 4-FC_6H_4
c R = 4-ClC_6H_4
d R = 4-BrC_6H_4
e R = 4-$(COCl)C_6H_4$
f R = (*E*)-PhCH=CH
g R = (*E*)-4-$NO_2C_6H_4$CH=CH
h R = Me

Scheme 1

In a typical procedure, a solution of 1 mmol of an acid chloride and 1 mmol of tributyltin phenyl selenide[‡] in 2 ml of dry chloroform was stirred at room temperature for 1 h. After completion of the reaction, the reaction mixture was treated with an aqueous KF solution to precipitate tin compounds, the solvent was evaporated, and the residue was recrystallised from hexane.[§]

The presence of electron-acceptor substituents in the acid chloride molecule accelerates the reaction. Thus, in the case of 4-nitrocinnamic acid chloride (Table 1, entry 8), the corresponding selenoester was formed almost immediately after mixing the reactants, whereas the reaction with cinnamic acid chloride (Table 1, entry 9) was completed in 1 h.

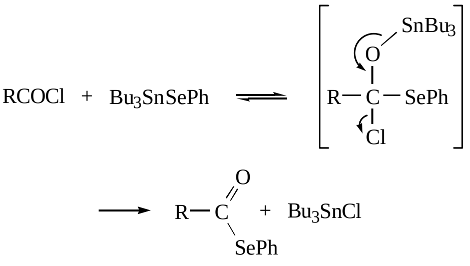
Terephthaloyl dichloride also readily reacts with two equivalents of $Bu_3SnSePh$ under the specified conditions (Table 1, entry 5) to give a double substitution product. The reaction can also be performed step-by-step to isolate a monosubstitution product in a high yield (Table 1, entries 6 and 7).

Table 1 Synthesis of selenoesters.

Entry	RCOCl	RCOSePh	^{77}Se, δ/ppm	Yield[a] (%)
1	PhCOCl	PhCOSePh[7]	168.6	99 (96)
2	4-FC_6H_4COCl	4-FC_6H_4COSePh	170.5	99 (97)
3	4-ClC_6H_4COCl	4-ClC_6H_4COSePh[5]	174.5	98 (96)
4	4-BrC_6H_4COCl	4-BrC_6H_4COSePh[7]	174.7	99 (97)
5	1,4-$C_6H_4(COCl)_2$[b]	1,4-$C_6H_4(COSePh)_2$	185.2	95 (93)
6	1,4-$C_6H_4(COCl)_2$[c]	4-$(ClOC)C_6H_4$COSePh	191.1	92 (89)
7	4-$PhSeOCC_6H_4$COCl	1,4-$C_6H_4(COSePh)_2$	185.2	99
8	PhCH=CHCOCl	PhCH=CHCOSePh[10]	154.3	97 (94)
9	4-$NO_2C_6H_4$CH=CH–COCl	4-$NO_2C_6H_4$CH=CH–COSePh	165.2	(96)
10	MeCOCl	MeCOSePh[9]	203.1	97 (90)

[a]According to ^{77}Se NMR data. The yields of isolated compounds are given in parentheses. [b]2 equiv. of $Bu_3SnSePh$. [c]1 equiv. of $Bu_3SnSePh$.

Although we did not examine the reaction mechanism in detail, the most probable mechanism is shown in Scheme 2.



Scheme 2

Commonly used methods for the synthesis of selenoesters are based on the reactions of acid chlorides with selenols in the presence of bases.[3] Recently,[4] it was proposed to use $Hg(SePh)_2$ in this reaction in the presence of Bu_4NX; however, only one of the two phenylseleno groups was involved in this reaction. Carboxylic acids can also be converted into corresponding selenoesters by the treatment with arylselenocyanates in the presence of equivalent amounts of tributylphosphine.[5]

[†] The ^{77}Se and ^{119}Sn NMR spectra were measured on a Bruker WP-200 SY spectrometer at 38.19 and 74.6 MHz, respectively, in chloroform; Me_4Sn and PhSeSePh were used as external standards.

[‡] Tributyltin phenyl selenide can be prepared *in situ* by irradiation of a mixture of 0.5 mmol of diphenyl diselenide and 0.5 mmol of hexabutyldistannane with daylight for 1 h. An acid chloride was added to the resulting solution. In this case, the selenoester yield remained unchanged.

[§] **3b**: ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.17 (t, 2H, *o*-H in 4-FC_6H_4), 7.45 (m, 3H, Ph), 7.60 (m, 2H, Ph), 7.97 (dd, 2H, *m*-H in 4-FC_6H_4, $^3J_{H-F}$ 3.66 Hz, $^3J_{H-H}$ 8.66 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 116.11 (*m*-CH in 4-FC_6H_4, $^2J_{C-F}$ 22 Hz), 125.52 (Ph), 129.17 (*p*-CH in Ph), 129.41 (Ph), 129.89 (*o*-CH in 4-FC_6H_4, $^3J_{C-F}$ 9.5 Hz), 134.85 (1-C in 4-FC_6H_4, $^4J_{C-F}$ 2.9 Hz), 136.31 (Ph), 166.12 (*p*-C in 4-FC_6H_4, $^1J_{C-F}$ 255 Hz), 191.79 (C=O). MS, *m/z*: 280 [M$^+$].

3e: ^{1}H NMR (CDCl$_3$) δ: 7.45 (m, 6H, Ph), 7.61 (m, 4H, Ph), 8.02 (s, 4H, C_6H_4). ^{13}C NMR (CDCl$_3$) δ: 125.43 (C), 127.71 (CH), 129.29 (CH), 129.47 (CH), 136.12 (CH), 142.32 (C), 189.11 (CO). Found (%): Se, 36.21. Calc. for $C_{20}H_{14}O_2Se_2$ (%): Se, 35.55. MS, *m/z*: 446 [M$^+$].

3g: ^{1}H NMR (CDCl$_3$) δ: 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-$O_2NC_6H_4$, *J* 8.4 Hz), 8.25 (d, 2H, 4-$NO_2C_6H_4$, *J* 8.4 Hz). ^{13}C NMR (CDCl$_3$) δ: 124.01, 125.47, 128.86, 129.06, 129.29, 129.54, 135.48, 137.18, 139.80, 148.38, 190.43. Found (%): Se, 22.94. Calc. for $C_{15}H_{11}NO_3Se$ (%): Se, 23.77. MS, *m/z*: 333 [M$^+$].

The procedure proposed for the synthesis of selenoesters has a number of advantages over previous methods due to the more convenient reagent $Bu_3SnSePh$.

In contrast to tributyltin phenyl selenide, silicon organoselenides do not directly react with acid chlorides. Thus, the reaction of tris(trimethylsilyl)silicon phenyl selenide with chlorocarbonic acid esters is catalysed by palladium complexes,[6] and the reaction of trimethylsilyl phenyl selenide with RCOCl was performed in the presence of equimolar amounts of SmI_2.[7] However, trimethylsilyl phenyl telluride can directly react with ArCOCl to form corresponding telluroesters in good yields. Analogous tellurium derivatives directly react with acid chlorides.[8]

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References

1 I. P. Beletskaya, A. S. Sigeev, A. S. Peregudov, P. V. Petrovskii, S. V. Amosova, V. A. Potapov and L. Hevesi, *Sulf. Lett.*, 2000, **23**, 145.

2 I. P. Beletskaya, A. S. Sigeev, A. S. Peregudov and P. V. Petrovskii, *J. Organomet. Chem*., 2000, **605**, 96.

3 (*a*) M. Renson and C. Draguet, *Bull. Soc. Chim. Belg*., 1962, **71**, 260; (*b*) H. Rheinboldt, in *Houben-Weyl. Methoden der organischen Chemie*, ed. E. Muller, Georg Thieme Verlag, Stuttgart, 1955, vol. IX, p. 1205.

4 C. C. Silveira, A. L. Braga and E. L. Larghi, *Organometallics*, 1999, **18**, 5183.

5 P. A. Grieco, Y. Yokoyama and E. Williams, *J. Org. Chem*., 1978, **43**, 1283.

6 C. H. Schiesser and M. A. Skidmore, *J. Chem. Soc., Perkin Trans. 1*, 1997, 2689.

7 S. Zhang and Y. Zhang, *Synth. Commun*., 1998, **28**, 3999.

8 K. Sasaki, Y. Aso, T. Otsubo and F. Ogura, *Chem. Lett.*, 1986, 977.

9 M. Baiwir and G. Llabres, *Spectrochim. Acta, Part A*, 1982, **38A**, 575.

10 T. Jayachandran, T. Manimaran and V. T. Ramakrishnan, *Indian J. Chem., Ser. B*, 1984, **23B**, 328.

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