Organotin Selenocarboxylates: Synthesis and Some Reactions

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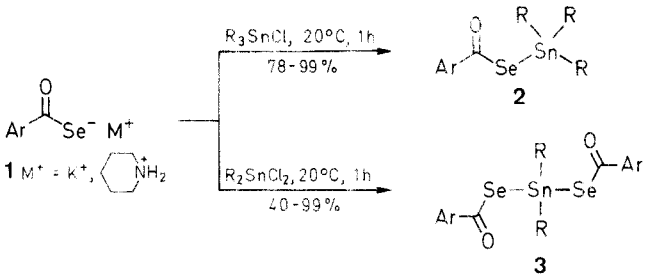
A series of di- **3** and triorganotin esters **2** of aromatic selenocarboxylic acid were synthesized and characterized. The organotin esters **2** and **3** are stable thermally, but labile towards moisture and oxygen. They readily reacted with benzyl bromide in the presence of aluminum chloride to afford benzyl selenocarboxylates **4** in moderate yields. The reaction of triphenyltin selenocarboxylates with phenylselenenyl bromide led to acyl phenyl diselenides **5** in good yields.

In an earlier study, we reported that potassium and piperidinium salts of thio- and dithiocarboxylic acids react with organotin chlorides to give the corresponding organotin thio- and dithiocarboxylates in good yields, and in addition some of their physical and chemical properties.[1-3] To our knowledge, however, no organotin selenocarboxylates $(R^1COSe)_xSn(R^2)_{4-x}$ ($x = 1-3$) except for trimethyltin benzenecarboselenoate[4] has been described in literature, though they are attractive compounds for spectroscopic studies.[5] In our previous studies, aromatic potassium and piperidinium selenocarboxylates were isolated from the reaction of bis(acyl) selenide with potassium hydroxide,[6,7] and from the reaction of bis(acyl) diselenide with piperidine,[8] respectively. These results stimulated us to synthesize organotin selenocarboxylates. We now wish to report the synthesis of a series of di- **3** and triorganotin selenocarboxylates **2** and some of their reactions.

Potassium selenocarboxylates **1** were found to readily react with triorganotin chlorides and diorganotin dichlorides at 0 °C to give the corresponding triorganotin selenocarboxylates **2** and diorganotin bis(selenocarboxylates) **3** in good yields (see experimental).

Similarly, the stoichiometric reaction of other selenocarboxylic acid potassium and piperidinium salts with trimethyltin and triphenyltin chlorides or dimethyltin and diphenyltin dichlorides afforded the corresponding tri- **2** and diorganotin selenocarboxylates **3** in 41–99% isolated yields. The structures of **2** and **3** were confirmed by IR, ^{1}H-, and ^{13}C-NMR, mass spectra and/or on the results of microanalyses (Table 1).



2	Ar	R	3	Ar	R
a	Ph	Me	**a**	Ph	Me
b	Ph	Bu	**b**	Ph	Ph
c	Ph	Ph	**c**	4-$CH_3C_6H_4$	Me
d	4-$CH_3C_6H_4$	Me	**d**	4-$CH_3C_6H_4$	Ph
e	4-$CH_3C_6H_4$	Bu	**e**	4-$MeOC_6H_4$	Me
f	4-$CH_3C_6H_4$	Ph	**f**	4-$MeOC_6H_4$	Ph
g	4-$MeOC_6H_4$	Me	**g**	4-ClC_6H_4	Me
h	4-$MeOC_6H_4$	Bu	**h**	4-ClC_6H_4	Ph
i	4-$MeOC_6H_4$	Ph			
j	4-ClC_6H_4	Me			
k	4-ClC_6H_4	Bu			
l	4-ClC_6H_4	Ph			

The organotin selenocarboxylates **2**, **3** obtained are thermally stable crystals or oils, but labile towards moisture and oxygen. For example, when trimethyltin 4-methylbenzenecarboselenoate **(2d)** was allowed to stand in air for 24 h, bis(4-methylbenzoyl) diselenide, trimethyltin hydroxide and red selenium were obtained as the decomposition products.

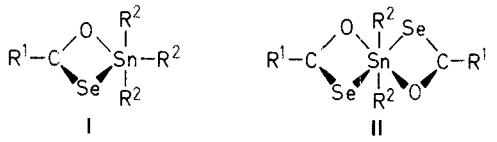
It is well known that triorganotin carboxylates are linear polymeric structures in solid state with bridging OCO group and planar R_3Sn moieties and their carbonyl stretching bands are observed in lower frequencies regions of 1550–1620 cm^{-1}.[9,10]

Table 1. Tri- and Diorganotin Selenocarboxylates **2**, **3** Prepared

Product	Yield[a] (%)	mp (°C) or bp (°C)/mbar	Molecular Formula[b]	IR (KBr) $\nu_{C=O}$ (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)	^{13}C-NMR ($CDCl_3$/TMS) δ	MS (70 eV) m/z (%)
2a	78	oil	$C_{10}H_{14}OSeSn$ (347.9)	1640	0.63 (s, 9H, CH_3, $J_{^{117}Sn,H}$ = 60, $J_{^{119}Sn,H}$ = 65); 7.7–8.0 (m, 5H_{arom})	−4.3 ($SnCH_3$); 128–140 (C_{arom}); 196.8 (C=O)	350 (M^+, < 1); 335 ($M^+ - 15$); 165 (Me_3Sn^+); 135 ($MeSn^+$); 105 ($PhCO^+$, 100); 77, 51
2b	98	166/0.8	$C_{19}H_{32}OSeSn$ (474.1)	1642	0.90 (t, 9H, J = 6.1); 1.3–1.8 (m, 18H); 7.3–8.1 (m, 5H)	13.8 ($SnCH_2$); 197.0 (C=O)	476 (M^+, < 1); 419, 371, 291, 235, 179, 105 (100)
2c	99	106–108	$C_{25}H_{20}OSeSn$ (534.1)	1640	7.3–8.0 (m)	195.5 (C=O)	539 (M^+, 1); 459, 431; 351; 197; 105 (100)
2d	94	oil	$C_{11}H_{16}OSeSn$ (361.9)	1640	0.62 (s, 9H, $^2J_{^{117}Sn,H}$ = 58, $^2J_{^{119}Sn,H}$ = 60); 2.36 (s, 3H); 7.2–7.9 (m, 4H)	−4.33 ($SnCH_2$); 21.7 ($ArCH_3$); 196.7 (C=O)	364 (M^+, < 1); 364, 349, 165, 139, 119 (100)
2e	97	167/0.7	$C_{20}H_{34}OSeSn$	1638	0.87 (t, 9H, J = 6.1); 1.3–1.8 (m, 18H, CH_2); 2.35 (s, 3H); 7.20 (d, 2H, J = 8.4); 7.90 (d, 2H, J = 8.4)	13.7 ($SnCH_2$); 21.8 ($ArCH_3$); 196.1 (C=O)	490 (M^+, < 1); 433; 371; 291; 235; 179; 119 (100)
2f	95	113–116	$C_{26}H_{22}OSeSn$ (548.1)	1635	2.34 (s, 3H, CH_3); 7.2–7.9 (m, 19H_{arom})	21.9 (CH_3); 128–138 (C_{arom}); 145.6 (C_{arom}); 194.9 (C=O)	705 ($Ph_3SnSeSnPh_2^+$); 550 (M^+, < 1); 459 ($M^+ - 77$); 431 (Ph_3SnSe^+); 351 (Ph_3Sn^+); 197 ($PhSn^+$); 119 ($CH_3C_6H_4CO^+$, 100); 91, 77
2g	80	oil	$C_{11}H_{16}O_2SeSn$ (377.9)	1640	0.62 (s, 9H, $^2J_{^{117}Sn,H}$ = 58, $^2J_{^{119}Sn,H}$ = 65); 3.86 (s, 3H), 6.9–8.0 (m, 4H)	−4.30 ($SnCH_3$); 55.8 (OCH_3); 194.6 (C=O)	380 (M^+, < 1); 365; 165; 135 (100)
2h	93	188/0.5	$C_{20}H_{34}O_2SeSn$ (504.1)	1640	0.96 (t, 9H, J = 6.2); 1.3–1.8 (m, 18H); 3.82 (s, 3H); 6.90 (d, 2H, J = 8.3); 8.00 (d, 2H, J = 8.3)	13.8 ($SnCH_2$); 55.8 (OCH_3); 194.7 (C=O)	506 (M^+, < 1); 449; 371; 291; 235; 179; 135 (100)
2i	98	102–104	$C_{26}H_{22}O_2SeSn$ (564.1)	1638	3.77 (s, 3H); 6.8–8.0 (m, 19H)	55.6 (OCH_3), 193.3 (C=O)	566 (M^+, < 1); 459; 431, 351; 197; 135 (100)
2j	91	oil	$C_{10}H_{13}ClOSeSn$ (382.3)	1640	0.62 (s, 9H, $^2J_{^{117}Sn,H}$ = 58, $^2J_{^{119}Sn,H}$ = 65); 7.3–8.0 (m, 4H)	−4.22 ($SnCH_3$); 195.5 (C=O)	384 (M^+, < 1); 369; 165; 139 (100); 135
2k	99	143/0.4	$C_{19}H_{31}ClOSeSn$ (508.6)	1640	0.88 (t, 9H, J = 6.2); 1.3–1.8 (m, 18H); 7.50 (d, 2H, J = 8.3); 7.90 (d, 2H, J = 8.3)	13.8 ($SnCH_2$); 195.7 (C=O)	510 (M^+, < 1); 453; 371; 291; 235; 179; 139 (100)
2l	99	96–97	$C_{25}H_{19}ClOSeSn$ (568.5)	1648	7.3–8.1 (m)	194.9 (C=O)	571 (M^+, < 1); 459; 431; 351; 197; 139 (100)
3a	78		$C_{16}H_{16}O_2Se_2Sn$ (516.9)	1615	1.17 (s, 6H, $J_{^{117}Sn,H}$ = 63, $J_{^{119}Sn,H}$ = 72); 7.30–7.90 (m, 10H_{arom})	2.85 ($SnCH_3$); 128–140 (C_{arom}); 200.0 (C=O)	520 (M^+, < 1); 505 [$(PhCOSe)_2SnMe^+$]; 460 ($Me_2SnSe_2SnMe_2$); 445 ($Me_2SnSe_2SnMe^+$); 414 ($M^+ - 105$); 345 ($PhCOSeSnMe_2^+$); 105 ($PhCO^+$, 100); 77
3b	99	136–138	$C_{26}H_{20}O_2Se_2Sn$ (641.1)	1630	7.2–7.8 (m)	197.8 (C=O)	644 (M^+, < 1); 567; 459; 431; 351; 197; 105 (100)
3c	83	156–159	$C_{18}H_{20}O_2Se_2Sn$ (545.0)	1615	1.24 (s, 6H, $^2J_{^{117}Sn,H}$ = 63, $^2J_{^{119}Sn,H}$ = 72); 2.38 (s, 6H); 7.2–7.9 (m, 8H)	2.74 ($SnCH_3$); 21.6 ($ArCH_3$); 200.0 (C=O)	548 (M^+, < 1); 533; 429; 349; 119 (100)
3d	96	147–149	$C_{28}H_{24}O_2Se_2Sn$ (669.1)	1630	2.34 (s, 6H); 7.1–8.0 (m, 18H)	27.7 ($ArCH_3$); 197.2 (C=O)	672 (M^+, < 1); 595; 473; 431; 351; 197; 135 (100)
3e	41	159–162	$C_{18}H_{20}O_4Se_2Sn$ (577.0)	1600	1.22 (s, 6H, $^2J_{^{118}Sn,H}$ = 65, $^2J_{^{119}Sn,H}$ = 75); 3.38 (s, 6H); 6.9–7.9 (m, 8H)	2.93 ($SnCH_3$); 55.5 (OCH_3); 203.4 (C=O)	580 (M^+, < 1); 565; 445, 365, 135 (100)
3f	99	130–133	$C_{28}H_{24}O_4Se_2Sn$ (701.1)	1625	3.82 (s, 6H); 6.8–7.9 (m, 18H)	55.6 (OCH_3); 197.5 (C=O)	704 (M^+, < 1); 627; 489; 431; 351; 197; 135 (100)
3g	56	157–160	$C_{16}H_{14}Cl_2O_2Se_2Sn$ (585.8)	1626	1.24 (s, 6H, $^2J_{^{117}Sn,H}$ = 67, $^2J_{^{119}Sn,H}$ = 75); 7.3–8.0 (m, 8H)	2.90 ($SnCH_3$); 198.7 (C=O)	588 (M^+, < 1); 537; 449; 369; 139 (100)
3h	99	146–147	$C_{26}H_{18}Cl_2O_2Se_2Sn$ (709.9)	1642	7.2–7.9 (m)	196.7 (C=O)	712 (M^+, < 1); 635; 493; 431; 351; 197; 139 (100)

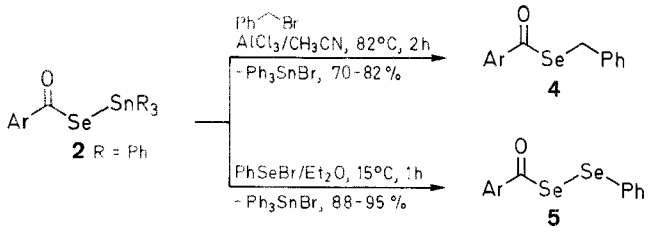
[a] Isolated yield.
[b] Satisfactory microanalyses obtained: C ±0.25, H ±0.18.

As shown in Table 1, the organotin selenocarboxylates **2**, **3** prepared, without exception, show a strong absorption band at 1600–1650 cm^{-1} due to carbonyl stretching frequencies, suggesting the monomeric structures **I** and **II**, where the carbonyl oxygen is coordinated to the tin atom rather than the linear polymeric structure, where the OCSe group is bridged between the tin atoms.



I **II**

In general, the reactions of the organotin selenocarboxylates **2**, **3** with alkyl halides do not occur below 100 °C. In the presence of a catalytic amount of aluminum chloride, however, triphenyltin selenocarboxylates **2c**, **2f**, **2i**, **2l** readily reacted with benzyl bromide at 82 °C to give the corresponding benzyl esters **4** in moderate yields.



2 R = Ph

4

5

4	Ar	5	Ar
a	Ph	**a**	Ph
b	4-$CH_3C_6H_4$	**b**	4-$CH_3C_6H_4$
		c	4-$MeOC_6H_4$
		d	4-ClC_6H_4

Previously, we reported the synthesis of acyl phenyl diselenide **5** from the reaction of potassium selenocarboxylates with benzeneselenenyl bromide.[11] However, their yields were below 60%, because of formation of byproducts such as bis(acyl) and diphenyl diselenides. Instead of the potassium salts **1**, the use of triorganotin selenocarboxylates was found to afford acyl phenyl diselenides **5** in quantitative yields (Table 2).

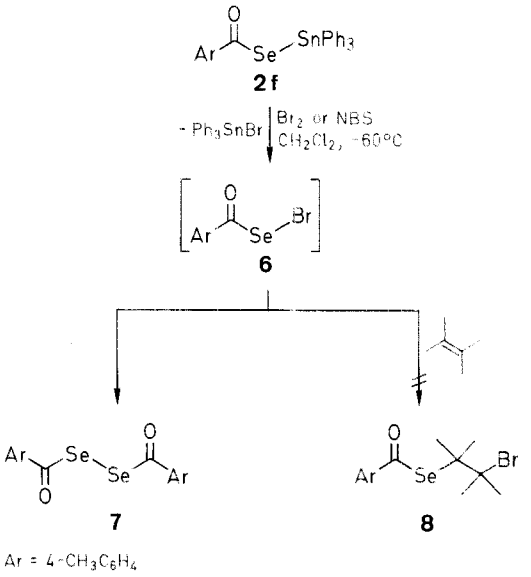
Table 2. Acyl Phenyl Diselenides **5** Prepared

Product	Yield[a] (%)	mp (°C)	Molecular Formula[b]	IR (KBr/film) $\nu_{C=O}$ (cm^{-1})
5a	99 (96)	oil	$C_{13}H_{10}OSe_2$ (340.1)	1684
5b	82 (88)	85–86	$C_{14}H_{12}OSe_2$ (354.2)	1698
5c	78 (81)	43–44	$C_{14}H_{12}O_2Se_2$ (370.2)	1681
5d	91 (85)	76–78	$C_{13}H_9ClOSe_2$ (374.6)	1690, 1730

[a] Yield of **5** using triphenyl selenocarboxylates **2**. The yields given in the parenthesis refers to product **5** obtained using diphenyltin bis(selenocarboxylates) **3**.

[b] Satisfactory microanalyses obtained: C ±0.18, H ±0.09.

Acylselenenyl halogenides (RCOSeX, X = halogen) are interesting compounds synthetically and spectroscopically. To our knowledge, however, their synthesis has not been described in the literature. In our earlier studies, organotin thio- and dithiocarboxylates react with halogen or *N*-halosuccinimide to afford acyl- (RCOSX),[12–14] and thioacylsulfenyl halogenides (RCSSX)[15] in good yields. Therefore, the reactions of triphenyltin selenocarboxylates with bromine or *N*-bromosuccinimide (NBS) were carried out under various conditions, expecting the isolation of acylselenenyl halogenide **6**. In fact, when a chloroform solution containing bromine was added dropwise to triphenyltin 4-methylbenzenecarboselenoate (**2f**) in dichloromethane at −60 °C, the reddish brown color of bromine immediately disappeared. After adding an equivalent of bromine, the color of the reaction mixture remained yellow.[16] However, when the temperature of the reaction mixture was raised to 0 °C, or the solvent was removed below −15 °C, bis(4-methylbenzoyl) diselenide (**7**) was obtained quantitatively with liberation of bromine. Similarly, treatment of **2f** with NBS at −10 °C led to the formation of the yellow compound,[17] which was quickly decomposed near 0 °C to give bis(4-methylbenzoyl) diselenide (**7**) with liberation of bromine. Presumably the diselenide **7** would be formed via the expected 4-methylbenzoylselenenyl bromide (**6**), although specific spectral evidence is not on hand and no addition product **8** to olefin has been obtained.



Melting points were determined using a Yanagimoto micromelting apparatus and are uncorrected. The IR spectra were measured on JASCO IR spectrometers IR-G and IRA-3. The ^1H- and ^{13}C-NMR spectra were recorded on a JEOL-JMN-GX270 (270 MHz) with TMS as internal standard. High resolution mass spectra were taken by a Shimazu 9020-DF mass spectrometer at an ionizing voltage of 70 eV. Elemental analyses were carried out by Analytical Center of Kyoto University and Analytische Laboratorien, Engelskirchen, Germany.

Potassium arencarboselenoates **1** were made according to literature and were green crystals containing a selenium atom. Trimethyltin chloride and dimethyltin dichloride were prepared according to literature.[17] Diphenyltin dichloride, triphenyltin chloride, benzyl bromide, 4-methylbenzoyl chloride were commercial grade and were recrystallized or distilled before use. Phenylselenenyl bromide was prepared from the reaction of diphenyl diselenide with bromine.[18] Solvents were dried with sodium metal or $CaCl_2$. All manipulations were carried out under Ar atmosphere.

Trimethyltin Benzenecarboselenoate (2a); Typical Procedure:
Trimethyltin chloride (199 mg, 1.0 mmol) is added to a suspension of potassium benzenecarboselenoate (**1a**; 302 mg, 1.0 mmol) in Et_2O

(20 mL) at 20 °C and the mixture is stirred for 1 h. The dark green color of the mixture quickly changes to light yellow and grey precipitates (KCl and Se) are formed. The mixture is filtered, the solvent evaporated and the residue is washed with petroleum ether (bp < 40 °C, 3 × 5 mL) to give chemically pure trimethyltin benzenecarboselenoate (**2a**) as a slight yellow oil; yield: 271 mg (78%).

Triphenyltin 4-methylbenzenecarboselenoate (2f):
Triphenyltin chloride (772 mg, 2.0 mmol) is added to a suspension of potassium 4-methylbenzenecarboselenoate (**1b**; 632 mg, 2.0 mmol) in dry Et_2O (40 mL) and the mixture is stirred at 20 °C for 1 h. The precipitates (KCl and Se) are filtrated and the solvent is evaporated *in vacuo*. Recrystallization of the resulting residue from a mixed solvent of hexane/Et_2O (5:1) affords **2f** as colorless plates; yield: 1.04 g (95%); mp: 113–116 °C.

Dimethyltin bis(benzenecarboselenoate) (3a):
Dimethyltin dichloride (220 mg, 1.0 mmol) is added to a suspension of potassium benzenecarboselenoate (**1a**; 604 mg, 2.0 mmol) in Et_2O (30 mL) at 20 °C and the mixture is stirred for 1 h. The dark green color of the mixture quickly changes to light yellow and gray precipitates (KCl and Se) are formed. The mixture is filtered, the filtrate evaporated and the residue is recrystallized from CH_2Cl_2/hexane to afford chemically pure dimethyltin bis(benzenecarboselenoate) (**3a**) as colorless crystals; yield: 403 mg (78%); mp: 127–130 °C.

Typical Procedure for the Reaction of Triphenyltin Benzenecarboselenoate (2c) with Benzyl Bromide; Benzyl Benzenecarboselenoate (4a):
Triphenyltin benzenecarboselenoate (**2c**; 267 mg, 0.5 mmol) is added to a solution of CH_3CN (4 mL) containing benzyl bromide(86 mg, 0.5 mmol) and $AlCl_3$ (14 mg, 0.1 mmol) and the mixture is refluxed for 2 h. The mixture is washed with 2% HCl (10 mL), 5% aq. Na_2Co_3 (20 mL), and water (3 × 10 mL). After drying (Na_2SO_4), the solvent is removed *in vacuo*. Separation of the residue by TLC (hexane/benzene, 5:1; R_f = 0.22) affords benzyl benzenecarboselenoate (**4a**) as a slightly yellow liquid; yield: 112 mg (82%).

HRMS; *m/z*: $C_{14}H_{12}OSe$ calc.: 276.0053; found: 276.0037 (M^+).

IR (neat): ν = 3050, 3020, 2950, 1678 (C=O), 1602, 1575, 1490, 1456, 1437, 1205, 1174, 1080, 1030, 1000, 890 [C(O)–Se], 790, 768, 738, 698, 690, 677, 625, 610, 555 cm^{-1}.

^{1}H-MNR ($CDCl_3$): δ = 4.34 (s, 2H, CH_2); 7.20–7.90 (m, 10H, H_{arom}).

^{13}C-NMR ($CDCl_3$): δ = 29.1 (CH_2), 127–139 (C_{arom}), 194.5 (C=O).

MS: *m/z* = 77, 91, 105, 171 ($PhCH_2Se^+$), 276 (M^+).

Typical Procedure for the Reaction of Triphenyltin 4-Methylbenzenecarboselenoate (2f) with Phenylselenenyl Bromide; 4-Methylbenzoyl Phenyl Diselenide (5b):
To a solution of triphenyltin 4-methylbenzenecarboselenoate (**2f**; 274 mg, 0.5 mmol) in Et_2O (20 mL), phenylselenenyl bromide (118 mg, 0.5 mmol) is added and the mixture is stirred at 15 °C for 1 h. The mixture is concentrated to ca 5 mL and hexane (10 mL) added and allowed to stand at −20 °C for 5 h. Filtration of the resulting yellow crystals affords 4-methylbenzoyl phenyl diselenide (**5b**); yield: 145 mg (82%); mp 85–86 °C (Table 2).

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