An Improved Procedure for the Formation of *Se*-Phenyl Selenoesters

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The reaction of carboxylic acids as their triethylammonium salts with benzeneselenenyl chloride in tetrahydrofuran at room temperature yields the corresponding *Se*-phenyl selenoesters in high yield.

The wide current interest[1] in the use of free radicals in organic synthesis has recently been extended to include both intra[2,3] and intermolecular[4] addition of acyl radicals to carbon–carbon multiple bonds. Amongst the various methods reported for generation of acyl radicals the azoisobutyronitrile initiated reaction of acyl selenides with tributylstannane is probably the one most suited to preparative work. Selenoesters have previously been prepared by the reaction of selenols, or better their sodium salts,[3] with carboxylic acids activated by the formation of acyl chlorides, imidazolides or mixed anhydrides.[5] Grieco has reported[6] on the formation of *Se*-phenyl selenoesters by reaction of carboxylic acids with tributylphosphine and phenylselenocyanate or *N*-phenylselenophthalimide. We report here that acyl phenylselenides are advantageously prepared by reaction of their triethylammonium salts with benzeneselenenyl chloride and tributylphosphine in tetrahydrofuran at room temperature.[7,8] The ready availability and crystallinity of benzeneselenenyl chloride render it the reagent of choice for this reaction when compared to the liquid malodorous phenylselenocyanate and the expensive difficult to purify *N*-phenylselenophthalimide.

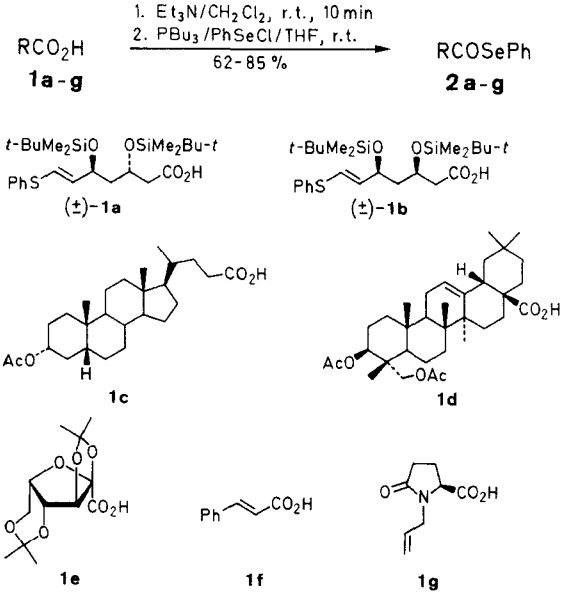

Table. *Se*-Phenyl Selenoesters **2a–g** Prepared

Substrate	Product	Yield (%)	mp (°C)	Molecular Formula[a]	IR ($CHCl_3$) ν (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS)[b] δ, J (Hz)
1a[9]	**2a**	72	–	$C_{31}H_{48}SSeSi_2$ (635.9)	1709	1.67–1.82 (m, 2H), 2.49 (m, 2H), 4.22–4.31 (m, 2H), 5.78 (m, 1H), 6.32 (d, 1H, J = 15), 7.25–7.40 (m, 10H)
1b[9]	**2b**	73	–	$C_{31}H_{48}O_3SSeSi_2$ (635.9)	1721	1.62–1.88 (m, 2H), 2.90 (d, 2H, J = 5.7), 4.28–4.36 (m, 2H), 5.78 (dd, 1H, J = 8.5, 7.5), 6.34 (d, 1H, J = 16), 7.24–7.52 (m, 10H)
1c[10]	**2c**	85	90–92	$C_{32}H_{46}O_3Se$ (557.7)	1716	0.84–1.96 (m, 35H), 2.03 (s, 3H), 2.68–2.76 (m, 2H), 4.62–4.78 (m, 1H), 7.36–7.53 (m, 5H)
1d[11]	**2d**	62	165–167	$C_{40}H_{56}O_5Se$ (695.8)	1723	0.82–1.98 (m, 41H), 2.03 (s, 3H), 2.07 (s, 3H), 3.71 (d, 1H, J = 6), 3.88 (d, 1H, J = 6), 4.72–4.86 (m, 1H), 5.28–5.38 (m, 1H), 7.33–7.44 (m, 5H)
1e[12]	**2e**	81	145	$C_{18}H_{22}O_6Se$ (413.3)	1713	1.45 (s, 3H), 1.46 (s, 3H), 1.54 (s, 3H), 4.18 (d, 2H, J = 2.3), 4.28 (d, 1H, J = 1.6), 4.35 (d, 1H, J = 2.2), 4.59 (s, 1H), 7.37–7.57 (m, 5H)
1f	**2f**	65	82	$C_{15}H_{12}OSe$ (287.2)	1677	6.76 (d, 1H, J = 15.7), 7.38–7.59 (m, 11H)
1g[3]	**2g**	65	–	$C_{14}H_{14}NO_2Se$ (307.2)	1704	3.38–3.76 (m, 1H), 4.24–4.56 (m, 2H), 5.00–5.58 (m, 3H), 7.34–7.44 (m, 5H)

[a] Satisfactory microanalysis obtained: C ±0.28, H ±0.18.
[b] Varian XL 200.

The reaction is applicable to both aliphatic and α,β-unsaturated carboxylic acids. The examples in the Table are chosen so as to illustrate the compatibility of the method with diverse functional groups and steric environments.

***Se*-Phenyl 3α-Acetoxy-5β*H*-selenocholanate (2c); Typical Procedure:**

To a stirred solution of 3α-acetoxy-5βH-cholanic acid (**1c**, 250 mg, 0.6 mmol) in dry CH_2Cl_2 (3 mL) under a nitrogen atmosphere at r.t. is added a solution of triethylamine (60 mg; 0.6 mmol) in CH_2Cl_2 (1 mL). The mixture is stirred for 10 min then evaporated under reduced pressure to give the crude triethylammonium salt as a colourless oil. Tributylphosphine (181 mg; 0.9 mmol) is added with stirring at r.t. to a solution of PhSeCl (172 mg; 0.9 mmol) in THF (5 mL) under a nitrogen atmosphere followed after 10 min by the triethylammonium salt in THF (4 mL). After complete consumption of the acid (20 min; TLC control) the reaction mixture is poured onto Et_2O (50 mL) and 2 M NaOH solution (50 mL). The aqueous layer is further extracted with Et_2O (3 × 25 mL) and the combined organic phases washed with water (50 mL), and sat. aq NaCl (50 mL). The ethereal solution is dried ($MgSO_4$), filtered and evaporated to give a yellow oil which after chromatography on silica gel (petroleum ether (bp 40–60°C)/Et_2O 2:1) provides a colourless crystalline solid, yield: 282 mg (85%) (Table).

***Se*-Phenyl Selenocinnamate (2f); Typical Procedure:**

To a stirred solution of cinnamic acid (1 f; 1.48 g; 10 mmol) in dry CH_2Cl_2 (20 mL) under a nitrogen atmosphere at r.t. is added a solution of triethylamine (1.01 g; 10 mmol) in CH_2Cl_2 (10 mL). The mixture is stirred for 10 min and then evaporated under reduced pressure to give the crude triethylammonium salt as a colourless oil. Tributylphosphine (4.05 g; 20 mmol) is added with stirring at r.t. to a solution of PhSeCl (3.83 g, 20 mmol) in dry THF (30 mL) under a nitrogen atmosphere followed after 10 min by the triethylammonium salt in THF (25 mL). After complete consumption of the acid (120 min; TLC control) the reaction mixture is poured onto Et_2O (300 mL and water (300 mL). The aqueous layer is further extracted with Et_2O (3 × 100 mL) and the combined organic phases washed with water (300 mL), and sat. aq NaCl (300 mL). The ethereal solution is dried ($MgSO_4$); filtered and evaporated to give a yellow oil which after chromatography on silica gel (petroleum ether (bp 40–60°C)/Et_2O, 8:1) provides a yellow crystalline solid; yield: 2.10 g (73%) (Table).

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