A Convenient Synthesis of *S*-Acyl Phenylselenosulfides

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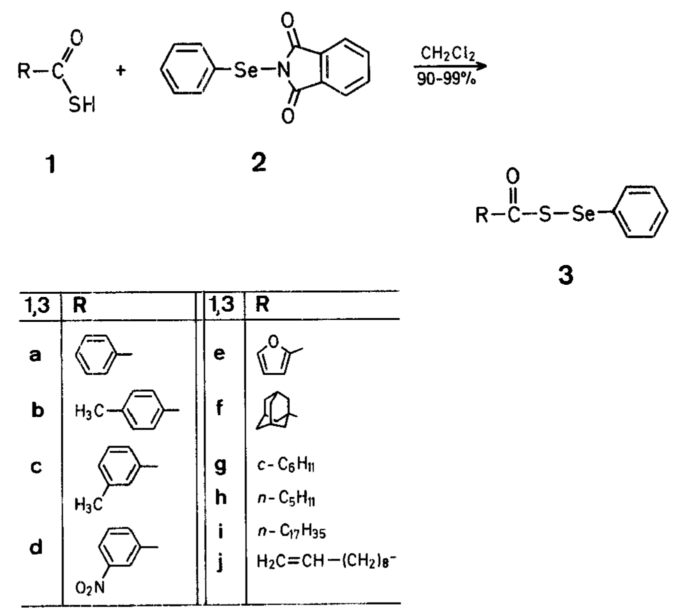
S-Acyl arylselenosulfides 3, sulfur-selenium analogs of peroxoic esters, are prepared from thiocarboxylic acids **1** and *N*-phenylselenophthalimide (**2**).

S-Acyl arylselenosulfides can be considered as sulfur-selenium substitutes of the peroxoic esters; their chemistry is of considerable synthetic as well as biological interest. Diacyl disulfides have been reported to have antifungal[1] and anti-irradiative activities[2]. It has been reported[3] that diaryl disulfides selectively inhibit 5-lipoxygenase, which is one of the important enzymes which convert arachidonic acid into leukotrienes in the arachidonate cascade[4]. Since the sulfur-sulfur bond in disulfides should play an important role in generation of these biological activities, *S*-acyl arylselenosulfides (**3**), hitherto little known[5,6], could be another compound type possessing biological and pharmacological properties.

Herein we describe a convenient synthesis of *S*-acyl phenylselenosulfides (**3**) by the reaction of thiocarboxylic acids (**1**) with *N*-phenylselenophthalimide[7,8] (**2**). Thus, a mixture of thiobenzoic acid (**1a**) and *N*-phenylselenophthalimide (**2**) in dichloromethane was stirred at −40 °C; immediate completion of the reaction was observed by T.L.C., giving *S*-benzoyl phenylselenosulfide (**3a**) in 95% yield after chromatographic purification.



The structure of the *S*-benzoyl phenylselenosulfide (**3a**) was confirmed as follows: In the I.R. spectra, the carbonyl absorption band appeared at $\nu = 1670\ cm^{-1}$ (KBr) and $1680\ cm^{-1}$ ($CHCl_3$), and the Field-Desorption mass spectrum showed only two fragmentation peaks at $m/e = 189$ (13%, ^{80}Se) due to C_6H_5—Se—$S^{\oplus}$ and 105 due to C_6H_5—$CO^{\oplus}$ (97%) as well as a molecular ion peak at $m/e = 294$ (^{80}Se) as base peak. The reactions of a variety of aromatic and aliphatic thiocarboxylic acids with *N*-phenylselenophthalimide were examined; they gave *S*-acyl phenylselenosulfides (**3a–j**) in high yield as illustrated in the

Table. *S*-Acyl Phenylselenosulfides (**3**) prepared

3	Yield[a] [%]	m.p.[b] [°C] (solvent)	Molecular Formula[c]	M.S.[d] m/e (M^+)	I.R.[e] $\nu_{C=O}$ [cm^{-1}]	U.V.[f] (C_2H_5OH) λ_{max} [nm] (ε)	^{1}H-N.M.R.[g] (CCl_4/TMS_{int}) δ [ppm]
a	95	57° (hexane)	$C_{13}H_{10}OSSe$ (293.2)	294	1670	240 (2.38×10^4)	7.0–8.1 (m, 10H)
b	93	93° (hexane)	$C_{14}H_{12}OSSe$ (307.2)	308	1678	253 (2.13×10^4)	2.39 (s, 3H); 7.05–7.38 (m, 5H); 7.52–7.97 (m, 4H)
c	98	oil	$C_{14}H_{12}OSSe$ (307.2)	308	1680	245 (1.85×10^4)	2.38 (s, 3H); 7.09–7.55 (m, 5H); 7.55–8.05 (m, 4H)
d	91	oil	$C_{13}H_9NO_3SSe$ (338.2)	339	1680	223 (3.90×10^4)	7.10–7.45 (m, 3H); 7.45–8.01 (m, 3H); 8.12–8.50 (m, 2H); 8.74 (t, 1H, J = 8 Hz)
e	90	56–57° (hexane)	$C_{11}H_8O_2SSe$ (283.15)	284	1673	276 (2.17×10^4) 222 (2.05×10^4)	6.40–6.51 (m, 1H); 7.10–7.41 (m, 5H); 7.45–7.82 (m, 2H)
f	98	oil	$C_{17}H_{20}OSSe$ (351.3)	352	1710	227 (1.59×10^4)	1.49–2.51 (m, 15H); 7.05–7.64 (m, 5H)
g	93	oil	$C_{13}H_{16}OSSe$ (299.2)	300	1715	228 (2.10×10^4)	1.0–2.28 (m, 10H); 2.30–2.92 (m, 1H); 6.98–7.26 (m, 3H); 7.26–7.67 (m, 2H)
h	90	oil	$C_{12}H_{16}OSSe$ (287.2)	288	1720	232 (2.97×10^4)	0.7–1.0 (m, 3H); 1.2–1.9 (m, 6H); 2.67 (t, 2H, J = 8 Hz); 6.8–7.5 (m, 3H); 7.6–7.8 (m, 2H)
i	99	43–44° (hexane)	$C_{24}H_{40}OSSe$ (455.5)	456	1720	226 (1.5×10^4)	0.65–1.00 (m, 3H); 1.00–2.00 (m, 30H); 2.70 (t, 2H, J = 8 Hz); 7.04–7.38 (m, 3H); 7.38–7.75 (m, 2H)
j	93	oil	$C_{17}H_{24}OSSe$ (355.3)	356	1718	225 (1.44×10^4)	1.20–2.00 (m, 14H); 2.69 (t, 2H, J = 8 Hz); 4.70–5.10 (m, 2H); 5.40–5.90 (m, 1H); 7.10–7.40 (m, 3H); 7.40–7.80 (m, 2H)

[a] Products isolated via flash chromatography.
[b] Not corrected.
[c] Satisfactory microanalyses obtained: C ± 0.29, H ± 0.23.
[d] Recorded on a ESCO EMD-053 instrument. Molecular ions of ^{80}Se isotope are given. All compounds show a peak at m/e = 314 due to $(C_6H_5Se)_2^+$ possibly derived from thermal decomposition during mass measurement.
[e] Measured in KBr for solids and in liquid film for oils on a JASCO A-102 spectrometer.
[f] Recorded on a JASCO UVIDEC-505 spectrometer.
[g] Measured on a Hitachi R-24A spectrometer (60 MHz).

Table. The experimental procedure is easy to carry out; it involves simple mixing of substrate **1** and *N*-phenylselenophthalimide (**2**) in dichloromethane and evaporation of the solvent followed by chromatographic separation of the product. We have found that the reaction can be carried out at room temperature or at −78 °C without any substantial differences in result.

The synthetic utility of the *S*-acyl selenosulfides **3**, in particular, *S*-benzoyl phenylselenosulfide, has been demonstrated by the reaction with unsaturated substrates. This reaction provides a new synthetic method for introducing an organoseleno group as well as a thiocarboxy group into a substrate by a one-pot procedure. Details of this work will be published elsewhere.

_S_-Acyl Phenylselenosulfides 1; Typical Procedure:

To a −40 °C solution of *N*-phenylselenophthalimide (**2**; 971 mg, 3.22 mmol) in dichloromethane (4 ml) is added dropwise, over a 5-min period, a solution of thiobenzoic acid[9] (**1a**; 403 mg, 2.92 mmol) in dichloromethane (1 ml, and 2 portions of 0.3 ml for rinse); a white precipitate appears. Immediately after the addition, T.L.C. analysis (silica gel, Merck 0.25 mm thick plates; hexane/benzene 6/4) indicates complete absence of thiobenzoic acid (R_f: 0.17) and the presence of a new product (R_f: 0.45). The solvent is evaporated in vacuo and the residue is chromatographed on silica gel (40 g, hexane/benzene 9/1 and then 8/2); yield of **3a**: 817 mg (95 %); m.p. 57 °C.

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