A Convenient Preparation of *Se*-Aryl Selenocarboxylates via *Se*-Aryl Acylmethanesulfenoselenoates

Shinzi Kato*, Hiroyuki Kabuto, Hideharu Ishihara, Toshiaki Murai

Department of Chemistry, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-11, Japan

Selenocarboxylates have attracted a great deal of recent attention as liquid crystals[1] and in the syntheses of steroids and sex hormones[2]. Several methods have become available for the preparation of selenocarboxylates (a) acylation of selenols[3] and their metal salts[4], (b) alkylation of selenocarboxylates[5], (c) reaction of carboxylic acids with diaryl diselenide[6] or aryl selenocyanates[7] in the presence of trialkylphosphines, and (d) reaction of aroylhydrazine with benzeneseleninic acid[8]. These preparations are accompanied by difficult removal of by-products such as diaryl diselenide, or by limitation to alkyl esters (**4**; R = alkyl), or in some cases, reagents that are not readily available. We now describe a method for the preparation of *Se*-aryl selenocarboxylates **4** via *Se*-aryl acylmethanesulfenoselenoates **3** (Scheme **B**) which, in turn, are conveniently prepared both from reactions of acylsulfenyl bromides **1** with diaryl diselenides (Path A) and from reactions of metal thiocarboxylates **2** with areneselenyl bromides (Path B, Scheme **A**).

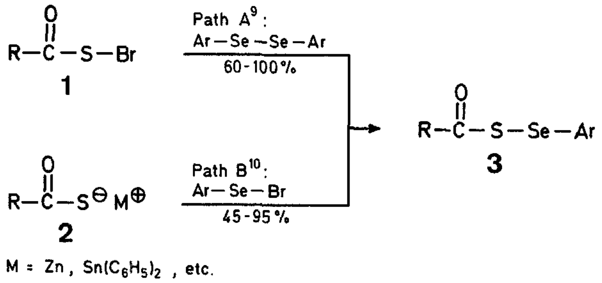
The yields and some physical properties are summarized in the Table. The desulfurization reactions are clean and completed at room temperature within 3 h. The procedures are simple and the yields isolated are better than 50 %, except for

Table. *Se*-Aryl Selenocarboxylates **4a**–**f** prepared

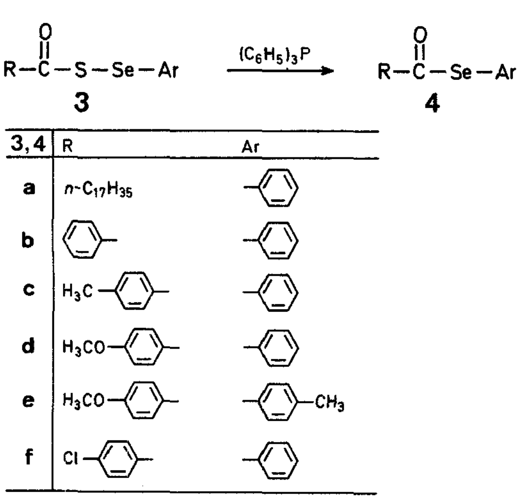
Product	Method	Yield[a] [%]	m.p. [°C]		I.R. (KBr) [cm^{-1}]		^{1}H-N.M.R. (CDCl$_3$) δ [ppm]
			found	reported	$\nu_{C=O}$	ν_{C-Se}	
4a	B	32	see experimental procedure				
4b	A	62	34–36°	35–37°[8]	1685	940	–
	B	61					
4c	A	57	93–94°	–[b]	1690	940	2.42 (s, 3H, CH$_3$); 7.1–8.2 (m, 9H$_{arom}$)
4d	A	60	61–62°	62–63°[7]	1680	940	3.89 (s, 3H, OCH$_3$); 6.8–8.1 (m, 9H$_{arom}$)
	B	56					
4e	A	64	58–59°	60°[1]	1680	940	2.44 (s, 3H, CH$_3$); 3.87 (s, 3H, OCH$_3$); 6.8–8.2 (m, 8H$_{arom}$)
	B	59					
4f	A	67	83–84°	83.5–84.5°[7]	1680	940	–
	B	63					

[a] Yield of isolated product; for Method B, based on diphenyltin bis[thiocarboxylates].

[b] $C_{14}H_{12}OSe$ (275.3) calc. C 61.10 H 4.40
found 61.01 4.22.



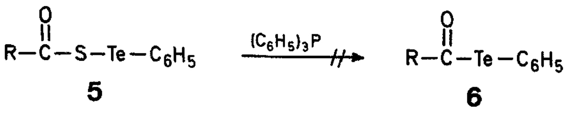
Scheme A



Scheme B

the aliphatic derivative **4a**. The structures of **4** were confirmed by comparison with authentic samples or by microanalysis.

A number of attempts to prepare *Te*-phenyl tellurocarboxylates **6** by similar desulfurization of *Te*-phenyl acylmethanesulfenotelluroates **5**[9,11] failed (Scheme C).



Scheme C

_Se_-Phenyl 4-Chlorobenzeneselenoate (4f); Typical Procedure for Path A:

Triphenylphosphine (105 mg, 0.40 mmol) is added to benzene (10 ml) containing *Se*-phenyl benzoylmethanesulfenoselenoate (**3f**; 131 mg, 0.40 mmol) according to Path A (yield of **3f**: 95%) and the mixture is stirred for 2.5 h at 10–13 °C. After evaporation of the solvent under reduced pressure, the residue is separated by preparative thin layer chromatography [silica gel (Fuji Devision BF-820 MH), carbon tetrachloride]. The second layer from the top is extracted with dichloromethane (30 ml), followed by evaporation of the solvent in a rotary evaporator, to give chemically pure **4f** as pale yellow crystals; yield: 79 mg (67%); m.p. 83–84 °C. The structure of **4f** was established by comparison of m.p., mass, and I.R. spectral data with those of an authentic sample[7].

M.S. (70 eV): *m/e* = 296 (M$^+$).

I.R. (KBr): ν = 1680 cm^{-1} (C=O).

_Se_-Phenyl Octadecaneselenoate (4a); Typical Procedure for Path B: A tetrahydrofuran solution (0.5 ml) containing benzeneselenyl bromide (118 mg, 0.5 mmol) is added to a suspension of potassium octadecanethioate (**2a**; 193 mg, 0.5 mmol) in dichloromethane (10 ml). After being stirred at ~25 °C for 1 h, the mixture is washed with water (3 × 3 ml) and dried with anhydrous sodium sulfate. The solvent is evaporated in a rotary evaporator and the residue is chromatographed on silica gel (*n*-hexane/dichlormethane, 5:1) to give *Se*-phenyl octadecaneselenoate (**3a**) as colorless plates; yield: 98 mg (43%); m.p. 50–53 °C.

$C_{24}H_{40}OSSe$ (455.6) calc. C 63.27 H 8.85
found 63.01 8.99

I.R. (KBr): ν = 1727 cm^{-1} (C=O).

^{1}H-N.M.R. (CDCl$_3$): δ = 0.8–1.7 (m, 33H); 2.79 (t, 2H); 7.5–7.8 ppm (m, 5H).

Triphenylphosphine (105 mg, 0.40 mmol) is added to benzene (10 ml) containing freshly prepared **3a**, (182 mg, 0.4 mmol) and the mixture is stirred for 2.5 h at 10–13 °C. After evaporation of the solvent under reduced pressure, the residue is separated by preparative thin layer chromatography [silica gel (Fuji Devison BF-820 MH), carbon tetrachloride]. The second layer from the top is extracted with dichloromethane (30 ml), followed by evaporation of the solvent in a rotary evaporator, to give chemically pure **4a** as colorless crystals; yield: 53 mg (32%); m.p. 31.5–32.5 °C.

$C_{24}H_{40}OSe$ (423.5) calc. C 68.06 H 9.52
found 68.01 9.58

M.S. (20 eV): *m/e* = 422 (M$^+$).

I.R. (KBr): ν = 1711 cm^{-1} (C=O)

^{1}H-N.M.R. (CDCl$_3$): δ = 0.9–1.8 (m, 33H); 2.7 (t, 2H); 7.4–7.6 ppm (m, 5H).

Received: October 24, 1984
(Revised form: January 2, 1985)

---

* Address for correspondence.

[1] Heppke, G., K. Martence, J., Fraefcke, K., Simon, H. *Angew. Chem.* **1977**, *89*, 328; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 318.

[2] Pheninger, J., Heuberger, C., Graf, W. *Helv. Chim. Acta* **1980**, *63*, 2308.

[3] (a) Loevenich, J., Fremdling, H., Föhr, M. *Ber. Dtsch. Chem. Ges.* **1929**, *62*, 2859.
(b) Günther, W.H.H., Mautner, H.G. *J. Med. Chem.* **1964**, *2*, 229.
(c) Scheithauer, S., Mayer, R., *Z. Chem.* **1966**, *6*, 375.
(d) Gais, D. *Angew. Chem.* **1977**, *89*, 251; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 244.

[4] (a) Taboury, F. *Bull. Soc. Chim. Fr.* **1908**, *35*, 672.
(b) Keimatsu, S., Yokota, K. *J. Pharm. Soc. Jpn.* **1931**, *51*, 89.
(c) Reinboldt, H., Giesbrecht, D. *Chem. Ber.* **1955**, *88*, 674.
(d) Günther, W.H.H. *J. Org. Chem.* **1967**, *32*, 3931.

[5] (a) Ishihara, H., Hirabayashi, Y. *Chem. Lett.* **1976**, 203.
(b) Ishihara, H., Sato, S., Hirabayashi, Y. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3007.
(c) Ishihara, H., Hirabayashi, Y., *Chem. Lett.* **1978**, 1007.

[6] See Ref. 17 in Masamune, S., Hayase, H., Schilling, W., Chan, W.K., Bates, G.S. *J. Am. Chem. Soc.* **1977**, *99*, 6756.

[7] Grieco, P.A., Yokoyama, Y., Williams, E. *J. Org. Chem.* **1978**, *43*, 1238.

[8] Back, T.G., Collins, S., Kerr, R.G. *J. Org. Chem.* **1981**, *46*, 1564.

[9] Kato, S., Kabuto, H., Kimura, M., Ishihara, H., Murai, T. *Synthesis* **1985**, 519.

[10] A number of the starting thioates such as potassium, silver, piperidium, and phenylmercury thioates, and diphenylgermanium, diphenyltin, diphenyllead, cupric, and cadmium bis [thioates] have been examined. Though the reactions of zinc, diphenyltin, and diphenyllead bis[thioates] with benzeneselenyl bromide give *Se*-phenyl acylmethanesulfenoselenoates (**3**) in more than 80 % yields, the other salts lead to low yields.

[11] The reactions of piperidinium and potassium thiocarboxylates with benzenetelluryl bromide have been found to give *Te*-phenyl acylmethanesulfenotelluroates (**5**) in more than 60 % yields.