A Convenient Synthesis of *Se*-Aryl Oxoarylmethanesulfenoselenoates and *Te*-Aryl Oxoarylmethanesulfenotelluroates: Electrophilic Thiocarboxylation of Diaryl Diselenides and Ditellurides

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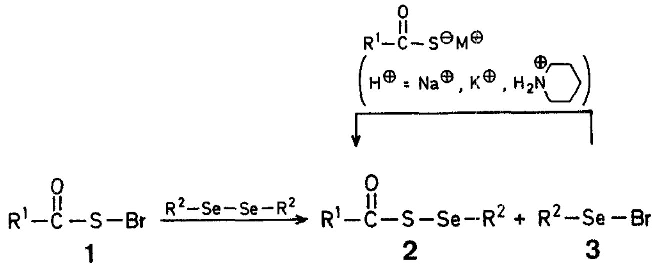
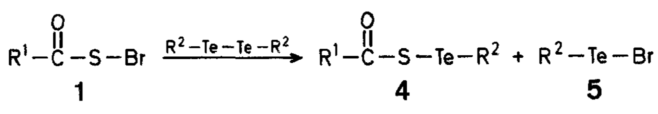
In previous papers[1], we have described the isolation of acyl- and thioacylsulfenyl halides. The electrophilic cleavage of organic diselenides by halogen is well known[2] and, thus, the electrophilic thiocarboxylation of organic diselenide seemed an interesting possibility. If successful, such reactions would provide a new route, based on readily available starting materials, to *Se*-aryl oxoarylmethanesulfenoselenoates **2**. We have found that the reaction using acylsulfenyl bromides **1** shown in Scheme **A** is easily effected (Table)[3]. The procedures are simple and the yields are high. If the piperidinium or alkali metal thiocarboxylates corresponding to the arenesulfenyl bromide simultaneously formed are available, the yield of the *Se*-aryl oxoarylmethanesulfenoselenoates **2** can be almost doubled.



Scheme **A**

In view of this facile electrophilic thiocarboxylation of organic diselenides, it was of interest to see if the thioacylation of organic ditellurides also could be effected (diaryl ditelluride is known to react with halogen to give arenetellurenyl bromide)[4]. Such a reaction does indeed occur (Scheme **B**). At present, the yields of **4** are relatively low (Table), because of the difficult purification.



Scheme **B**

The *Se*-aryl oxoarylmethanesulfenoselenoates **2** and *Te*-aryl oxoarylmethanesulfenotelluroates **4** are very stable at room temperature, both in the solid state and dissolved in dichloromethane. Further studies in progress are aimed at the *in situ* electrophilic thiocarboxylation of bis[acyl] disulfides, and diselenides to give the unsymmetrical bis[acyl] disulfides and sulfenoselenoates.

Se-Phenyl (4-Chlorophenyl)-oxomethanesulfenoselenoate (2 g); Typical Procedure for Method A:

A solution of diphenyl diselenide (156 mg, 0.50 mmol) in methanol (10 ml) is added to 4-chlorobenzoylsulfenyl bromide (**1d**; 246 mg, 1.0 mmol) at −70 °C under nitrogen. The mixture is warmed gradually to 0 °C (~ 10 min should be allowed for this rise in temperature) and then stirred for 10 min. The precipitate is filtered off and washed with *n*-hexane (3 x 10 ml) to give the product **2g** as pale yellow needles; yield: 107 mg (33 %); m.p. 90–91 °C (dec.).

$C_{13}H_9ClOSSe$	calc.	C 47.65	H 2.77
(327.7)	found	47.52	2.91

I.R. (KBr): ν = 1675 cm^{-1} (C=O).

Se-Phenyl (4-Methoxyphenyl)-oxomethanesulfenoselenoate (2e); Typical Procedure for Method B:

4-Methoxybenzoylsulfenyl bromide (**1c**; 61 mg, 0.25 mmol) is added to a solution of diphenyl diselenide (78 mg, 0.25 mmol) in methanol (10 ml) at room temperature (18 °C) and stirred for 10 min. The yellow solution turns to dark red within one minute. To the solution is added a solution of 4-methoxythiobenzoic acid (42 mg, 0.25 mmol) in methanol (5 ml) at room temperature. The dark red solution spontaneously turns to yellow. After evaporation of the solvent under reduced pressure, the residue is chromatographed on silica gel column (dichloromethane/*n*-hexane 1 : 5). Evaporation of the second yellow fraction under reduced pressure gives the product **2e**; yield: 130 mg (79 %); m.p. 60–61 °C (dec.).

$C_{14}H_{12}O_2SSe$	calc.	C 52.05	H 3.74
(323.3)	found	51.94	3.84

I.R. (KBr): ν = 1665, 1690 cm^{-1} (C=O).

Table. Compounds **2a–h** and **4a–c** prepared

Product	R^1	R^2	Yield [%][a] (Method)	m.p.[b] [°C]	Molecular[c] Formula	I.R. (KBr) $\nu_{C=O}$ [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]
2a	C_6H_5	C_6H_5	98 (A)	62–63°	$C_{13}H_{10}OSSe$ (293.2)	1665	
2b	C_6H_5	4-$H_3C-C_6H_4$	94 (A)	46–48°	$C_{14}H_{12}OSSe$ (307.4)	1680	2.23 (s, 3H, CH_3); 6.7–8.0 (m, 9H_{arom})
2c	4-$H_3C-C_6H_4$	C_6H_5	85 (A) 166 (B)	86–88°	$C_{14}H_{12}OSSe$ (307.4)	1660	2.38 (s, 3H, CH_3); 6.9–8.1 (m, 9H_{arom})
2d	4-$H_3C-C_6H_4$	4-$H_3C-C_6H_4$	60 (A)	68–70°	$C_{15}H_{14}OSSe$ (321.3)	1665 1685	2.23 (s, 3H, CH_3); 2.26 (s, 3H, CH_3); 6.7–8.0 (m, 8H_{arom})
2e	4-$H_3CO-C_6H_4$	C_6H_5	85 (A) 158 (B)	60–61°	$C_{14}H_{12}O_2SSe$ (323.3)	1665 1690	3.78 (s, 3H, CH_3O); 6.5–8.0 (m, 9H_{arom})
2f	4-$H_3CO-C_6H_4$	4-$H_3C-C_6H_4$	53 (A)	65–67°	$C_{15}H_{14}O_2SSe$ (337.3)	1665 1690	2.26 (s, 3H, CH_3); 3.80 (s, 3H, CH_3O); 6.1–8.1 (m, 8H_{arom})
2q	4-$Cl-C_6H_4$	C_6H_5	95 (A) 186 (B)	84–86°	$C_{13}H_9ClOSSe$ (327.7)	1675	
2h	4-$Cl-C_6H_4$	4-$H_3C-C_6H_4$	85 (A)	84–86°	$C_{14}H_{11}ClOSSe$ (341.7)	1675	2.25 (s, 3H, CH_3); 6.7–8.0 (m, 9H_{arom})
4a	C_6H_5	C_6H_5	20	66°	$C_{13}H_{10}OSTe$ (342.0)	1675	
4b	4-$H_3C-C_6H_4$	C_6H_5	44	109–111°	$C_{14}H_{12}OSTe$ (355.9)	1658 1675	2.38 (s, 3H, CH_3); 7.0–8.1 (m, 9H_{arom})
4c	4-$Cl-C_6H_4$	C_6H_5	69	113–115°	$C_{13}H_9ClOSSe$ (376.4)	1665	

[a] Yield of isolated product.

[b] Decomposition.

[c] Satisfactory microanalyses obtained: C ±0.37, H ±0.24; exceptions: **2b** C +0.65; **2h** C +0.54; H +0.37.

***Te*-Phenyl (4-Methylphenyl)-oxomethanesulfenotelluroate (4b); Typical Procedure:**

4-Methylbenzoylsulfenyl bromide (**1b**; 164 mg, 0.40 mmol) is added to a solution of diphenyl ditelluride (90 mg, 0.40 mmol) in methanol (5 ml) at 0 °C under nitrogen and stirred for 1 h. The resulting precipitate is filtered and redissolved in *n*-hexane (100 ml). The solution is then allowed to stand in a refrigerator (−25 °C) for three days. Filtration of the resulting precipitates give the product **4b**; yield: 62 mg (44%); m.p. 113–115 °C (dec.).

$C_{14}H_{12}OSTe$	calc.	C 47.25	H 3.63
(355.9)	found	47.46	3.81

I.R. (KBr): ν = 1660, 1695 cm^{-1} (C=O).

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[1] (a) Kato, S., Hattori, E., Mizuta, M., Ishida, M. *Angew. Chem.* **1982**, *94*, 148; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 150.
(b) Kato, S., Miyagawa, K., Ishida, M. *Synthesis* **1982**, 1013.
(c) Kato, S., Komatsu, Y., Miyagawa, K., Ishida, M. *Synthesis* **1983**, 552.
(d) Kato, S., Itoh, K., Miyagawa, K., Ishida, M. *Synthesis* **1983**, 814.

[2] Klayman, D. L., in *Organic Selenium Compounds: Their Chemistry and Biology*, Klayman, D. L., Günther, W. H. H., Eds., Wiley-Interscience, New York, 1973, p. 139.

[3] We reported these results at *14th Congress of Central Regional Joint Meeting of Japan Chemical Society* **1983**, Abstract Paper, p. 234 (1E–21).
Very recently, an alternative preparation of **2** using thiocarboxylic acid and *N*-phenylselenophthalimide was reported: Tohru, T., et al. *15th Congress of Central Regional Joint Meeting of Japan Chemical Society* **1984**, Abstract Paper p. 501 (3K–09).

[4] Vicentini, G., Giesbrecht, E., Pitombo, L. R. *Chem. Ber.* **1959**, *92*, 40.