The First Synthesis of *Se*-Methyl Carboxylic Thionoselenolesters

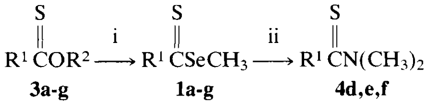
Mohamed Khalid, Jean-Louis Ripoll and Yannick Vallée*

Laboratoire de Chimie des Composés Thio-organiques, URA CNRS 480, ISMRA, 14050 Caen, France

Reaction of carboxylic thionoesters with dimethylaluminium methylselenolate in diethyl ether gave the corresponding *Se*-methyl thionoselenolesters in 87–98% yield.

Carboxylic thionoselenolesters have been the subject of limited investigation,[1] in contrast to the thiono- and dithioesters, which have received much attention.[2] Two methods have been reported for the synthesis of *Se*-aryl thionoselenolesters from bisthioacyl sulphide or thioacyl chloride,[3] but no general route to the corresponding *Se*-alkyl derivatives was available. In this communication, we report the first synthesis of *Se*-methyl thionoselenolesters **1**.

Dimethylaluminium methylselenolate **2** is known as an efficient reagent for the conversion of esters into selenolesters,[4,5] and we expected that it could also be used to transform the readily available and stable thionoesters **3**[6] into thionoselenolesters **1**. In fact, when a thionoester **3** was treated in diethyl ether with a slight excess of **2** at room temperature for ten hours, the desired seleno-compound **1** was isolated in high yield† (Scheme 1). Seven examples of the thionoselenolesters obtained are listed in Table 1 with some characteristic NMR data. Like their *Se*-aryl analogues,[3] they are orange or red compounds, are stable even in contact with air, and can be stored at room temperature for weeks without significant change.



$$\mathrm{R^1}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{OR^2} \xrightarrow{\text{i}} \mathrm{R^1}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{SeCH_3} \xrightarrow{\text{ii}} \mathrm{R^1}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{N(CH_3)_2}$$

3a-g **1a-g** **4d,e,f**

Scheme 1 *Reagents*: i, *ca.* 1.4 equiv. of $(CH_3)_2AlSeCH_3$ **2**, diethyl ether, room temp., 10 h; ii, $HN(CH_3)_2$, CH_2Cl_2

Kato *et al.* reported[3] that upon treatment with secondary amines, *Se*-phenyl thionoselenolesters surprisingly gave salts of dithioacids. On the other hand, when the corresponding

---

† Typical experimental procedure. Dimethylaluminium methylselenolate **2** (2 mol dm^{-3} solution in toluene,[4] 0.6 ml, 1.2 mmol) was added at room temperature under nitrogen to a solution of **3d** (156.8 mg, 0.87 mmol) in 5 ml of dry diethyl ether. The yellow mixture progressively turned orange and after ten hours was hydrolysed by wet magnesium sulphate. The diethyl ether was evaporated and the residue was chromatographed on a silica gel column using light petroleum as the eluant. The thionoselenolester **1d** (188 mg, 0.82 mmol, yield 94%) was isolated as an orange–red liquid. ^{1}H NMR (CCl_4): δ 2.48 (s, 3H), 4.32 (s, 2H), 7.32 (s, 5H). ^{13}C NMR ($CDCl_3$): 13.9, 60.9, 127.4, 128.6, 129.3, 136.8, 241.3. MS (*m*/*z*, %): 230 ($M^{+\cdot}$, 17), 135 ($PhCH_2CS^{+\cdot}$, 45), 91 (100), 65 (33).

Table 1

	R^1	R^2	Yield of **1**[a]	NMR ^{1}H SeMe[b]	 ^{13}C C=S
a	n-C_5H_{11}	C_2H_5	96%	2.56	245.1
b	n-C_7H_{15}	CH_3	98%	2.50	245.1
c	n-$C_{15}H_{31}$	CH_3	90%[c]	2.55	244.9
d	$C_6H_5CH_2$	C_2H_5	94%	2.48	241.3
e	C_6H_5	CH_3	91%	2.69	233.2
f	*p*-$CH_3OC_6H_4$	CH_3	87%	2.64	230.3
g	2-thienyl	CH_3	89%	2.67	216.1

[a] Yield of isolated product after liquid chromatography. [b] In every case a $^2J^{77}{}_{\text{SeH}}$ of *ca.* 12 Hz was observed. [c] Reaction time = 70 h.

Se-methyl compounds **1d,e,f** were treated with gaseous dimethylamine in dichloromethane, the corresponding thioamides **4d,e,f** and dimethyldiselenide were isolated in quantitative yields. Thus, in contrast with their *Se*-aryl analogues, *Se*-methyl thionoselenolesters appeared to be good thioacylating reagents.

We thank Professor André Thuillier for his fruitful comments about this work.

Received, 25th March 1991; Com. 1/01416A

References

1 Three previously known thionoselenolesters are cited in ref. 3; for other references see: S. Kato, T. Fukushima, H. Ishihara and T. Murai, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 638; S. Kato, H. Masumoto, S. Ikeda, M. Itoh, T. Murai and H. Ishihara, *Z. Chem.*, 1990, **30**, 67; S. Oae, K. Sakaki, M. Fukumura, S. Tamagaki, Y. Matsuura and M. Kakudo, *Heterocycles*, 1982, **19**, 657.

2 S. Scheithauer and R. Mayer, *Thio- and dithio-carboxylic acids and their derivatives.* ed. A. Senning, Georg Thieme, Stuttgart, 1979.

3 S. Kato, E. Yasui, K. Terashima, H. Ishihara and T. Murai, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 3931.

4 A. P. Kozikowski and A. Ames, *J. Org. Chem.*, 1978, **43**, 2735.

5 A. F. Sviridov, M. S. Ermolenko, D. V. Yashunsky and N. K. Kochetkov, *Tetrahedron Lett.*, 1983, **24**, 4355.

6 The thionoesters **3a–g** were obtained from the corresponding esters according to Lawesson's method: B. S. Pedersen, S. Scheibye, K. Clausen and S. O. Lawesson, *Bull. Soc. Chim. Belg.*, 1978, **87**, 293.