Aliphatic Bis(acyl) Selenides – Synthesis and Characterization

Hideki Kageyama, Hideharu Tsutsumi, Toshiaki Murai, and Shinzi Kato*

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

Z. Naturforsch. **44b**, 1050–1052 (1989); received May 17, 1989

Bis(acyl) Selenide, Carboxylic Acid Selenoanhydride

A series of aliphatic bis(acyl) selenides **1** were isolated from the reaction of acyl chlorides with sodium selenide and characterized.

In general, the chalcogeno isologues of aliphatic carboxylic acid derivatives are less stable than the aromatic ones thermally and towards oxygen. In fact, though several aromatic bis(acyl) selenides have been isolated as crystals [1]. Only one aliphatic derivative has been described by Jensen and Hendriksen who isolated bis(ethanecarbonyl) selenide in low yield from the reaction of propanoyl chloride with hydrogen selenide [2]. In the course of our studies concerning selenocarboxylic acid derivatives, a series of aliphatic bis(acyl) selenides were required. Herein we wish to report the isolation and characterization of simple aliphatic bis(acyl) selenides **1.**

A series of aliphatic bis(acyl) selenides **1** were isolated in good yields from the reaction of sodium selenide with two equivalents of acyl chloride in ether (eq. (1)). For example, a solution of propanoyl chloride (22 mmol) in ether (10 ml) was added to sodium selenide (11 mmol) and the mixture was stirred at 15 °C for 10 h. The precipitates was removed by filtration and the solvent was evaporated under reduced pressure. Distillation of the residue *in vacuo* afforded 84% of bis(ethanecarbonyl) selenide **1b.** Similarly, the reaction with other acyl chlorides afforded the corresponding bis(acyl) selenides (**1a, c–g**) in 60–90% yields (Table 1). Their structures were established by mass, IR, and ^{13}C NMR spectra. For example, the IR spectrum of bis(acetyl) selenide **1a** shows a strong band which is splitted at 1740 and 1720 cm^{-1} due to carbonyl stretching frequencies. In the ^{13}C NMR spectrum, two characteristic peaks were observed at δ 36.6 and 194.9 due to the methyl and carbonyl carbons, respectively. In addition, the molecular ion peaks and fragments supported the structure of **1a.**

$$2\ \mathrm{RCCl} + \mathrm{Na_2Se} \xrightarrow[\text{Ether}]{10-20\ ^\circ\mathrm{C},\ 10\ \mathrm{h}} \underset{\mathbf{1}}{\mathrm{RC(=O)-Se-C(=O)R}} \quad (1)$$

No.	R	No.	R
1a	CH_3	**1e**	n-C_4H_9
1b	C_2H_5	**1f**	t-C_4H_9
1c	n-C_3H_7	**1g**	n-C_5H_{11}
1d	i-C_3H_7	**1h**	$cyclo$-C_6H_{11}

The obtained aliphatic bis(acyl) selenides **1** are nauseously smelling, colorless to pale yellow liquid. They are gradually decomposed in air at room temperature to give the corresponding acid anhydride and carboxylic acid with the precipitates of red selenium.

It is noted that the carbonyl carbon resonances of bisacyl selenides shows downfield shift in going from R = methyl, ethyl, *iso*-propyl, and to *tert*-butyl group.

Experimental

The IR spectra were measured on the JASCO grating IR spectrophotometer IR-G. The ^1H and ^{13}C NMR spectra were recorded on JEOL JNM-GX-270 (270 MHz) with tetramethylsilane as an internal standard. The high-resolution mass spectroscopy was taken from Shimazu GCMS-QP 1000 and GCMS-9020 DF high-resolution mass spectrometers.

Materials. Acyl chlorides were reagent grade and distilled before use. Sodium and potassium selenides were prepared according to the procedures in literature [3]. The solvent were dried by use of sodium metal or calcium chloride and degassed.

The preparation method of bis(acetyl) selenide **1a** as typical procedures was described in detail. All manipulations are carried out under argon atmosphere.

* Reprint requests to Dr. S. Kato.

Verlag der Zeitschrift für Naturforschung, D-7400 Tübingen
0932–0776/89/0900–1050/$ 01.00/0

Table I. Yields and physical properties of bis(acyl) selenides (**1**).

No.	RCOSeCOR R	Yield[a] [%]	b.p. [°C/Torr]	IR (Neat) νC=O [cm^{-1}]	^{13}C NMR[b] δ
1a	CH_3	58	38/1	1740, 1720	194.9
1b	C_2H_5	84	50/2	1730, 1710	198.7
1c	*n*-C_3H_7	90	72/0.5	1720, 1710	198.0
1d	*i*-C_3H_7	61[c]	56/3	1730, 1720	201.9
1e	*n*-C_4H_9	90	70/0.3	1730, 1720	198.2
1f	*t*-C_4H_9	89	76/0.6	1770, 1740, 1720, 1690	202.2
1g	*n*-C_5H_{11}	88	104/0.4	1720, 1710	197.9
1h	*cyclo*-C_6H_{11}	75	125/0.5	1730, 1710	200.8

[a] Isolated yield; [b] $CDCl_3$; [c] reddish pink crystals together **1e** were obtained.

Bis(acetyl) selenide (**1a**)

A solution of acetyl chloride (1.375 g, 17.5 mmol) in ether (40 ml) was added to sodium selenide (1.095 g, 8.8 mmol) in Schlenk tube and the mixture was stirred at 15 °C for 10 h. After the precipitates was filtered by Umkehrer glass filter (G4-grade) and the solvent was distilled under reduced pressure, vacuum distillation of the residue yielded 0.837 g (58%) of **1a** as a slightly yellow liquid; b.p. 38 °C/1 Torr; IR (Neat): 2950, 2850, 1740, 1720, 1420, 1360, 1090, 1000, 950, 570 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.60 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$): δ 36.0 (CH_3), 194.9 (C=O); Mass (CI): 166 $(M+1)^+$; Exact mass (70 eV) calcd for $C_4H_6O_2Se$; *m/z* 165.95328; found 165.95329.

Bis(ethanecarbonyl) selenide (**1b**)

The reaction of propanoyl chloride (2.025 g, 22 mmol) with sodium selenide (1.367 g, 11 mmol) yielded 1.774 g (84%) of **1b** as a slightly yellow liquid; b.p. 50 °C/2 Torr; IR (Neat): 2950, 2800, 1730, 1710, 1470, 1410, 1380, 1340, 1260, 1120, 1080, 1040, 1010, 900, 790, 690, 550 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.18 (t, 6H, CH_3), 2.87 (q, 6H, CH_2); ^{13}C NMR ($CDCl_3$): δ 8.73 (CH_3), 43.0 (CH_2), 198.4 (C=O); Mass (CI): 195 $(M+1)^+$; Exact mass (70 eV) calcd for $C_6H_{10}O_2Se$; *m/z* 193.98456; found 193.98453.

Bis(1-propanecarbonyl) selenide (**1c**)

The reaction of 1-butyryl chloride (2.230 g, 21 mmol) with sodium selenide (1.308 g, 10.5 mmol) yielded 1.985 g (90%) of **1c** as a slightly yellow liquid; b.p. 72 °C/0.5 Torr; IR (Neat): 2950, 2850, 1720, 1710, 1460, 1400, 1380, 1350, 1260, 1210, 1100, 1020, 970, 870, 800, 720, 670, 550 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.98 (t, 6H, CH_3), 1.70 (m, 4H, CH_2), 2.81 (t, 4H, CH_2CO); ^{13}C NMR ($CDCl_3$): δ 13.1 (CH_3), 18.4 (CH_2), 51.3 ($\underline{C}H_2CO$), 198.0 (C=O); Mass (CI): 223 $(M+1)^+$; Exact mass (70 eV) calcd for $C_8H_{14}O_2Se$; *m/z* 222.01584; found 222.01583.

Bis(1-methylethanecarbonyl) selenide (**1d**)

The reaction of isobutyryl chloride (2.621 g, 18 mmol) yielded 1.650 g (61%) of **1d** as pale yellow liquid; b.p. 56 °C/3 Torr; IR (Neat): 2950, 2900, 2850, 1730, 1720, 1470, 1390, 1370, 1270, 1170, 1090, 1020, 920, 840, 680, 560 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.21 (d, 6H, CH_3), 2.97 (sept, 2H, CH); ^{13}C NMR ($CDCl_3$): δ 18.3 (CH_3), 49.7 (CH), 201.9 (C=O); Mass (CI): 223 $(M+1)^+$; Exact mass (70 eV) calcd for $C_8H_{14}O_2Se$; *m/z* 222.01584; found 222.01586.

Bis(1-butanecarbonyl) selenide (**1e**)

The reaction of *n*-butanecarbonyl chloride (4.00 g, 33.2 mmol) with potassium selenide (2.69 g, 16.6 mmol) yielded 3.581 g (90%) of **1e** as a slightly yellow liquid; b.p. 70 °C/0.3 Torr; IR (Neat): 2950, 2900, 2850, 1730, 1720, 1470, 1410, 1380, 1340, 1280, 1250, 1110, 1030, 860, 760, 710, 670, 550 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.92 (t, 6H, CH_3), 1.39 (m, 2H, $CH_3C\underline{H}_2$), 1.65 (m, 2H, $CH_3CH_2C\underline{H}_2$), 2.93 (t, 2H, CH_2CO); ^{13}C NMR ($CDCl_3$): δ 13.7 (CH_3), 22.0 ($CH_3\underline{C}H_2$), 26.9 ($CH_3CH_2\underline{C}H_2$), 49.3 (CH_2CO), 198.2 (C=O); Mass (CI): 251 $(M+1)^+$; Exact mass (70 eV) calcd for $C_{10}H_{18}O_2Se$; *m/z* 250.04712; found 250.04710.

Bis(1,1-dimethylethanecarbonyl) selenide (**1f**)

The reaction of 1,1-dimethylethanecarbonyl chloride (2.943 g, 24 mmol) with potassium selenide (1.886 g, 12 mmol) yielded 2.658 g (89%) of **1f** as a pale yellow liquid; b.p. 76 °C/0.6 Torr; IR (Neat): 2950, 2900, 2850, 1770, 1740, 1720, 1690, 1470, 1400, 1390, 1360, 1215, 1025, 870, 770 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.2 (s, 9H, CH_3); ^{13}C NMR ($CDCl_3$): δ 27.2 (CH_3), 52.0 ($\underline{C}CH_3$), 202.2 (C=O); Mass (CI):

251 $(M+1)^+$; Exact mass (70 eV) calcd for $C_{10}H_{18}O_2Se$; *m/z* 250.04712; found 250.04712.

Bis(1-pentanecarbonyl) selenide (**1g**)

The reaction of 1-pentanecarbonyl chloride (2.825 g, 21 mmol) with sodium selenide (1.312 g, 10.5 mmol) yielded 2.800 g (89%) of **1g** as a slightly yellow liquid; b.p. 104 °C/0.4 Torr; IR (Neat): 2950, 2925, 2850, 1720, 1710, 1460, 1400, 1390, 1360, 1215, 1025, 870, 770, 580 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.90 (t, 6H, CH_3), 1.3–1.4 (m, 8H, $CH_3C\underline{H}_2C\underline{H}_2$), 1.67 (m, 4H, $C\underline{H}_2CH_2CO$), 2.82 (t, 4H, $\underline{CH}_2CO$); ^{13}C NMR ($CDCl_3$): δ 13.7 (CH_3), 22.2 ($CH_3\underline{C}H_2$), 24.3 ($CH_3CH_2\underline{C}H_2$), 30.8 ($\underline{C}H_2CH_2CO$), 44.3 ($\underline{C}H_2CO$), 197.9 (C=O); Mass (CI): 279 $(M+1)^+$; Exact mass (70 eV) calcd for $C_{12}H_{22}O_2Se$; *m/z* 278.07840; found 278.07843.

Bis(cyclohexanecarbonyl) selenide (**1h**)

The reaction of cyclohexanecarbonyl chloride (4.106 g, 28.1 mmol) with sodium selenide (1.762 g, 14.1 mmol) yielded 3.150 g (75%) of **1h** as a slightly yellow liquid; b.p. 122 °C/0.5 Torr; IR (Neat): 2925, 2850, 1730, 1710, 1450, 1360, 1300, 1280, 1230, 1175, 1130, 1070, 1040, 940, 910, 840, 830, 785, 730, 590, 510 cm^{-1}; ^{13}C NMR ($CDCl_3$): δ 25.2, 28.8 (CH_2), 57.2 (CH), 200.8 (C=O); Mass (CI): 303 $(M+1)^+$; Exact mass (70 eV) calcd for $C_{14}H_{22}O_2Se$; *m/z* 302.07840; found 302.07841.

[1] H. Ishihara, S. Sato, and Y. Hirabayashi, Bull. Chem. Soc. Jpn. **50,** 3007 (1977); S. Kato, T. Murai, and M. Ishida, Org. Prep. Proc. Int. **18,** 369 (1986).

[2] K. A. Jensen, L. Böje, and L. Henriksen, Acta Chem. Scand. **26,** 1465 (1972).

[3] W. Klemm, H. Hodomann, and P. Langmesser, Z. Anorg. Allg. Chem. **241,** 281 (1939); F. Fehér, „Handbook of Preparative Inorganic Chemistry", Vol. 1, p. 421, ed. by G. Bauer, Academic Press, New York (1963).