

Isolation of Crystalline Potassium Alkanecarboselenoates

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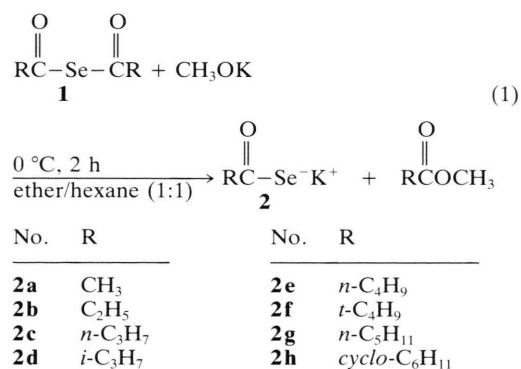
Potassium Alkanecarboselenoates, Potassium Selenocarboxylate,
Selenocarboxylic Acid Potassium Salts

A series of potassium alkanecarboselenoates (**2**) were isolated as crystals from the reaction of the corresponding bis(acyl) selenides with potassium methanolate. The salts **2** readily react with alkyl iodides at 0 °C to afford the corresponding alkyl alkanecarboselenoates (**3**) in quantitative yields.

Selenocarboxylic acid salts such as alkali metal and ammonium salts are the most important starting compounds for the synthesis of selenocarboxylic acid derivatives. However, their synthesis has been limited to aromatic potassium [1] and piperidinium selenocarboxylates [2, 3], because of the difficulties in the crystallization and purification of the aliphatic salts and of the limited availability of the starting bis(acyl) selenides. Recently we succeeded in the isolation of a series of aliphatic bis(acyl) selenides [4]. We now report the first isolation of simple potassium alkanecarboselenoates (**2**) and Se-alkyl alkanecarboselenoates (**3**), via the bis(acyl) selenides.

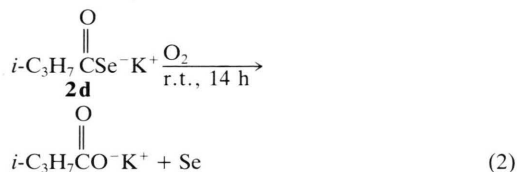
Results and Discussion

The expected aliphatic potassium selenocarboxylates (**2**) were isolated as crystals from the reaction of the corresponding aliphatic bis(acyl) selenides with potassium methanolate (eq. (1)).



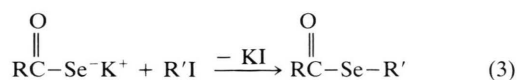
For example, potassium methanolate was added to a solution of an equivalent bis(1,1-dimethylethane-carbonyl) selenide in ether/hexane (1:1) at 0 °C, and the mixture was stirred for 2 h. Filtration of the resulting white precipitates, followed by washing with hexane afforded 98% of potassium 1,1-dimethylethanecarboselenoates (**2f**) as colorless microfine crystals. Similarly the reaction of other bis(acyl) selenides (**1a–e, g, h**) with potassium methanolate yielded the corresponding potassium selenocarboxylates (**2a–e, g, h**). The structures of **2** were established by IR and ¹³C NMR spectra and by conversion into the corresponding Se-alkyl alkanecarboselenoates (**3**).

The obtained potassium alkanecarboselenoates (**2**) are colorless microfine crystals. They are labile towards oxygen. For example, upon standing in air or oxygen at room temperature, potassium 1-methylethanecarboselenoate (**2d**) in ether was completely decomposed within 14 h to give potassium 1-methylpropanoate with liberation of reddish brown selenium metals (eq. (2)). To our knowledge, no Se-alkyl alkanecarboselenoate except for Se-*n*-butyl methanecarboselenoate [5] has been reported, probably because of the difficulties in the preparation of alkaneselenoates.



The salts (**2**) were found to readily react with alkyl iodides to afford the corresponding Se-alkyl alkanecarboselenoates (**3**) in almost quantitative yields (Table II) (eq. (3)).

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No.	R	R'	3
3a	CH ₃	<i>n</i> -C ₃ H ₇	
3b	C ₂ H ₅	<i>n</i> -C ₃ H ₇	
3c	<i>n</i> -C ₃ H ₇	CH ₃	
3d	<i>i</i> -C ₃ H ₇	CH ₃	
3e	<i>n</i> -C ₄ H ₉	CH ₂ COC ₆ H ₄ Br-4	
3f	<i>t</i> -C ₄ H ₉	CH ₃	
3g	<i>n</i> -C ₅ H ₁₁	CH ₂ COC ₆ H ₄ Br-4	
3h	<i>cyclo</i> -C ₆ H ₁₁	CH ₃	

Experimental

The melting points were obtained using a Yanagimoto micromelting apparatus and are uncorrected. The IR spectra were measured on a JASCO grating IR spectrometer. The ¹H and ¹³C NMR spectra were recorded on a JEOL JNM GX-270 (270 MHz) spectrometer with tetra-methylsilane as an internal standard. The high resolution mass spectra were taken from Shimadzu GCMS-QP1000 (A) (EI/CI, method) and GCMS-9020DF high resolution mass spectrometers.

Materials: Aliphatic bis(acyl) selenides (**1**) were prepared according to the literature [4]. Alkyl iodides were commercial grade and used without further purification. Potassium methanolate were prepared from methanol with potassium metal. Solvents were dried with sodium metal and were distilled.

Typical procedures are described in detail for the synthesis of potassium alkanecarboseleenoates (**2**) and Se-alkyl alkanecarboseleenoates (**3**). The yields and spectral data are collected in Tables I and II. All

manipulations were carried out under an argon atmosphere.

Potassium methanecarboseleenoate (**2a**)

Potassium methanolate (500 mg, 7.1 mmol) was added to a solution of bis(acetyl) selenide (**1a**) (1.24 g, 7.5 mmol) in a mixed solvent (20 ml) of ether/hexane (1:1) at 0 °C, and the mixture was stirred for 3 h. Filtration of the resulting precipitates, followed by washing with hexane (2 × 3 ml), yielded 961 mg (84%) of potassium methanecarboseleenoate (**2a**) as colorless microfine crystals; m.p. 110–120 °C (dec.); IR (Nujol): 2900, 2850, 1575, 1450, 1400, 1370, 1340, 1115, 955, 605 cm⁻¹; ¹H NMR (CD₃OD): δ 2.52 (s, 3H, CH₃); ¹³C NMR (CD₃OD): δ 44.5 (CH₃), 219.6 (CO).

Potassium ethanecarboseleenoate (**2b**)

The reaction of bis(ethanecarbonyl) selenide (**1b**) (1.45 g, 7.5 mmol) with potassium methanolate (500 mg, 7.1 mmol) yielded 945 mg (76%) of potassium ethanecarboseleenoate (**2b**); m.p. 95–110 °C (dec.); IR (Nujol): 2950, 2975, 1610, 1460, 1410, 1360, 1290, 1065, 995, 920, 870, 805, 495 cm⁻¹; ¹H NMR (CD₃OD): δ 1.05 (t, 3H, CH₃), 2.72 (q, 2H, CH₂); ¹³C NMR (CD₃OD): δ 11.4 (CH₃), 50.7 (CH₂), 224.0 (CO).

Potassium 1-propanecarboseleenoate (**2c**)

The reaction of bis(1-propanecarbonyl) selenide (**1c**) (1.66 g, 7.5 mmol) with potassium methanolate (500 mg, 7.1 mmol) yielded 1.24 g (92%) of potassium 1-propanecarboseleenoate (**2c**); m.p. 95–115 °C (dec.); IR (Nujol): 2950, 2800, 1605, 1420, 1380,

Product No.	R	Yield ^a [%]	m.p. ^b [°C]	IR (Nujol) νC=O [cm ⁻¹]	¹³ C NMR (CD ₃ OD) δ
2a	CH ₃	84	110–120	1575	44.5 (CH ₃), 219.6 (CO)
2b	C ₂ H ₅	76	95–110	1610	50.7 (CH ₂ CO), 224.0 (CO)
2c	<i>n</i> -C ₃ H ₇	92	95–115	1605	59.4 (CH ₂ CO), 223.0 (CO)
2d	<i>i</i> -C ₃ H ₇	90	95–105	1580	53.8 (CHCO), 228.5 (CO)
2e	<i>n</i> -C ₄ H ₉	87	118–125	1610	57.3 (CH ₂ CO), 223.1 (CO)
2f	<i>t</i> -C ₄ H ₉	98	100–115	1560	52.4 (CCO), 230.7 (CO)
2g	<i>n</i> -C ₅ H ₁₁	85	125–136	1610, 1614	57.5 (CH ₂ CO), 223.1 (CO)
2h	<i>cyclo</i> -C ₆ H ₁₁	68	95–110	1580	57.0 (CHCO), 226.4 (CO)

Table I. Potassium alkanecarboseleenoates (**2**).

^a Yield of isolated product;
^b decomposition.

Table II. Se-Alkyl alkanecarboselenoates (**3**) prepared.

RCOSeR'	Molecular Formula	IR (Neat) [cm ⁻¹]		¹ H NMR (CDCl ₃)		¹³ C NMR (CDCl ₃)	Mass (CI) ^a
		νC=O	νC-Se	δ		δ	m/z
CH ₃ COSeC ₃ H _{7-n}	C ₅ H ₁₀ OSe 165.1	1705	940	0.95 (t, 3H, CH ₃) 1.71 (m, 2H, CH ₂) 2.40 (s, 3H, CH ₃) 2.89 (t, 2H, CH ₂ Se)		9.4 (CH ₃) 14.3 (CH ₂) 23.7 (CH ₂ Se) 27.9 (CH ₃ CO) 197.7 (C=O)	167 [M + 1] ⁺
C ₂ H ₅ COSeC ₃ H _{7-n}	C ₆ H ₁₂ OSe 179.1	1705	940	0.97 (t, 3H, CH ₃ CH ₂ CO) 1.17 (t, 3H, CH ₃) 1.69 (m, 2H, CH ₂) 2.69 (q, 2H, CH ₂ CO) 2.89 (t, 2H, CH ₂ Se)		9.4 (CH ₃) 14.3 (CH ₂) 23.7 (CH ₂ Se) 27.3 (CH ₃) 41.5 (CH ₂ CO) 202.5 (C=O)	181 [M + 1] ⁺
<i>n</i> -C ₃ H ₇ COSeCH ₃	C ₅ H ₁₀ OSe 165.1	1700	965	0.97 (t, 3H, CH ₃) 1.70 (m, 2H, CH ₂) 2.21 (s, 3H, CH ₃ Se) 2.61 (t, 2H, CH ₂ CO)		4.6 (CH ₃ Se) 13.3 (CH ₃) 18.9 (CH ₂) 49.6 (CH ₂ CO)	167 [M + 1] ⁺
<i>i</i> -C ₃ H ₇ COSeCH ₃	C ₅ H ₁₀ OSe 165.1	1705	965	1.21 (d, 6H, CH ₃) 2.19 (s, 3H, CH ₃ Se) 2.79 (sept, 1H, CH)		4.4 (CH ₃ Se) 19.1 (CH ₃) 65.1 (CH) 207.0 (C=O)	167 [M + 1] ⁺
<i>n</i> -C ₄ H ₉ COSeCH ₂ COC ₆ H ₄ Br-4	C ₁₃ H ₁₅ O ₂ SeBr 362.1	1700 1740	980	0.97 (t, 3H, CH ₃) 1.36 (m, 2H, CH ₃ CH ₂) 1.67 (m, 2H, CH ₂ CH ₂ CO) 2.66 (t, 2H, CH ₂ COSe) 4.27 (s, 2H, SeCH ₂ CO) 7.6–7.9 (Ar)		13.7 (CH ₃) 22.2 (CH ₂) 27.0 (CH ₂) 30.2 (SeCH ₂ CO) 65.7 (CH ₂ COSe) 128–134 (Ar) 173.2 (CO) 191.5 (COSe)	365 [M + 1] ⁺
<i>i</i> -C ₄ H ₉ COSeCH ₃	C ₆ H ₁₂ OSe 179.1	1700	925	1.20 (s, 9H, CH ₃) 2.15 (s, 3H, CH ₃ Se)		4.3 (CH ₃ Se) 27.0 (CH ₃) 49.1 [C(CH ₃) ₃] 209.8 (C=O)	181 [M + 1] ⁺
<i>n</i> -C ₃ H ₁₁ COSeCH ₂ COC ₆ H ₄ Br-4	C ₁₄ H ₁₇ O ₂ SeBr 376.2	1700 1740	975	0.91 (t, 3H, CH ₃) 1.3–1.4 (m, 4H, CH ₃ CH ₂ CH ₂) 1.70 (m, 2H, CH ₂ CH ₂ CO) 2.66 (t, 2H, CH ₂ COSe) 4.27 (s, 2H, SeCH ₂ CO) 7.6–7.9 (Ar)		13.9 (CH ₃) 22.3 (CH ₃ CH ₂) 24.6 (CH ₃ CH ₂ CH ₂) 31.3 (SeCH ₂ CO) 33.9 (CH ₂ CH ₂ CO) 65.7 (CH ₂ COSe) 129–133 (Ar) 173.2 (CO) 191.5 (COSe)	379 [M + 1] ⁺
<i>cyclo</i> -C ₆ H ₁₁ COSeCH ₃	C ₈ H ₁₄ OSe 205.2	1700	960	1.2–2.6 (m, 11H, CH, CH ₂) 2.18 (s, 3H, CH ₃ Se)		4.4 (CH ₃) 25.4, 25.6, 29.3 (CH ₂) 56.1 (CH) 205.9 (C=O)	207 [M + 1] ⁺

^a Gas: isobutane.

1340, 1310, 1260, 1130, 1105, 1035, 995, 965, 870, 760, 700, 580, 485 cm^{-1} ; ^1H NMR (CD_3OD): δ 0.91 (t, 3H, CH_3), 1.61 (m, 2H, CH_2), 2.69 (t, 2H, CH_2CO); ^{13}C NMR (CD_3OD): δ 13.9 (CH_3), 20.8 (CH_2), 59.4 (CH_2CO), 223.0 (CO).

Potassium 1-methylethanecarboselenoate (**2d**)

The reaction of bis(1-methylethanecarbonyl) selenide (**1d**) (1.66 g, 7.5 mmol) with potassium methanolate (500 mg, 7.1 mmol) yielded 1.21 g (90%) of potassium 1-methylethanecarboselenoate (**2d**); m.p. 95–105 °C (dec.); IR (Nujol): 2975, 2950, 1580, 1410, 1390, 1360, 1280, 1090, 965, 950, 845, 830, 760, 680, 570, 510 cm^{-1} ; ^1H NMR (CD_3OD): δ 1.11 (s, 6H, CH_3), 3.01 (sept, 1H, CH); ^{13}C NMR (CD_3OD): δ 21.0 (CH_3), 53.8 (CH), 228.5 (CO).

Potassium 1-butanecarboselenoate (**2e**)

The reaction of bis(1-butanecarbonyl) selenide (**1e**) (2.50 g, 8.0 mmol) with potassium methanolate (528 mg, 7.5 mmol) yielded 1.32 g (87%) of potassium 1-butanecarboselenoate (**2e**); m.p. 118–125 °C (dec.); IR (Nujol): 2900, 2850, 1610, 1420, 1360, 1320, 1240, 1120, 1020, 950, 740, 700, 585, 485 cm^{-1} ; ^1H NMR (CD_3OD): δ 0.92 (t, 3H, CH_3), 1.33 (m, 2H, CH_2CH_2), 1.60 (m, 2H, $\text{CH}_2\text{CH}_2\text{CO}$), 2.71 (t, 2H, CH_2CO); ^{13}C NMR (CD_3OD): δ 14.3 (CH_3), 23.8, 30.3 (CH_2), 57.3 (CH_2CO), 223.1 (CO).

Potassium 1,1-dimethylethanecarboselenoate (**2f**)

The reaction of bis(1,1-dimethylethanecarbonyl) selenide (**1f**) (1.87 g, 7.5 mmol) with potassium methanolate (500 mg, 7.1 mmol) yielded 1.41 g (98%) of potassium 1,1-dimethylethanecarboselenoate (**2f**); m.p. 100–115 °C (dec.); IR (Nujol): 2950, 2800, 1560, 1450, 1415, 1370, 1360, 1220, 1020, 930, 885, 795, 775, 580, 430 cm^{-1} ; ^1H NMR (CD_3OD): δ 1.18 (s, 9H, CH_3); ^{13}C NMR (CD_3OD): δ 29.6 (CH_3), 52.4 ($\text{C}(\text{CH}_3)_2$), 230.7 (CO).

Potassium 1-pentanecarboselenoate (**2g**)

The reaction of bis(1-pentanecarbonyl) selenide (**1g**) (2.07 g, 7.5 mmol) with potassium methanolate (500 mg, 7.1 mmol) yielded 1.31 g (85%) of potassium 1-pentanecarboselenoate (**2g**); m.p. 125–136 °C (dec.); IR (Nujol): 2900, 2800, 1614, 1610, 1450, 1410, 1380, 1220, 1170, 1000, 950, 850, 730, 580, 485 cm^{-1} ; ^1H NMR (CD_3OD): δ 0.89 (t, 3H, CH_3), 1.30–1.32 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.15 (m, 2H, CH_2), 2.70 (t, 2H, CH_2CO); ^{13}C NMR (CD_3OD): δ 14.3 (CH_3), 23.5, 27.8, 33.0 (CH_2), 57.5 (CH_2CO), 223.1 (CO).

Potassium cyclohexanecarboselenoate (**2h**)

The reaction of bis(cyclohexanecarbonyl) selenide (**1h**) (2.26 g, 7.5 mmol) with potassium methanolate (500 mg, 7.1 mmol) yielded 1.11 g (68%) of potassium cyclohexanecarboselenoate (**2h**); m.p. 95–110 °C (dec.); IR (Nujol): 2950, 2850, 2825, 1580, 1445, 1410, 1275, 1220, 1145, 1100, 955, 885, 760, 745, 630, 500 cm^{-1} ; ^1H NMR (CD_3OD): δ 1.3–2.7 (m, 11H, CH, CH_2); ^{13}C NMR (CD_3OD): δ 27.2, 31.6, 44.1 (CH_2), 57.0 (CH), 226.4 (CO).

Se-1-Propyl methanecarboselenoate (**3a**)

Potassium methanecarboselenoate (**2b**) (677 mg, 4.20 mmol) was stirred in 1-iodopropane (5 ml, 50 mmol) at 0 °C for 2 h. After filtration of the precipitates (KI), the excess 1-iodopropane was removed in reduced pressure. Distillation of the residue yielded 541 mg (78%) of Se-*n*-propyl methanecarboselenoate (**3a**) as a slightly yellow liquid; b.p. 54–56 °C/15 Torr.

Se-1-Propyl ethanecarboselenoate (**3b**)

Similarly to **3a**, the reaction of potassium ethanecarboselenoate (**2b**) (704 mg, 4.02 mmol) with 1-iodopropane (5 ml, 50 mmol) yielded 648 mg (90%) of Se-1-propyl ethanecarboselenoate (**3b**) as a slightly yellow liquid; b.p. 84 °C/45 Torr.

Se-Methyl 1-propanecarboselenoate (**3c**)

The reaction of potassium 1-propanecarboselenoate (**2c**) (805 mg, 4.26 mmol) with iodomethane (5 ml, 50 mmol) yielded 610 mg (88%) of Se-methyl 1-propanecarboselenoate (**3c**) as a slightly yellow liquid; b.p. 110 °C/760 Torr.

Se-Methyl 1-methylethanecarboselenoate (**3d**)

The reaction of potassium 1-methylethanecarboselenoate (**2d**) (642 mg, 3.34 mmol) with iodomethane (5 ml, 50 mmol) yielded 498 mg (89%) of Se-methyl 1-methylethanecarboselenoate (**3d**) as a slightly yellow liquid; b.p. 65 °C/760 Torr.

Se-4-Bromophenacyl 1-butanecarboselenoate (**3e**)

The reaction of potassium 1-butanecarboselenoate (**2e**) (1.06 g, 5.20 mmol) with 4-bromophenacyl bromide (1.45 g, 5.20 mmol) yielded 1.69 g (90%) of Se-4-bromophenacyl 1-butanecarboselenoate (**3e**) as slightly yellow crystals; m.p. 54–56 °C.

Se-Methyl 1,1-dimethylethanecarboselenoate (**3f**)

The reaction of potassium 1,1-dimethylcarboselenoate (**2f**) (1.07 g, 5.30 mmol) with

iodomethane (5 ml, 50 mmol) yielded 703 mg (74%) of Se-methyl 1,1-dimethylethanecarboselenoate (**3f**) as a slightly yellow liquid; b.p. 70 °C/760 Torr.

Se-4-Bromophenacyl 1-pentanecarboselenoate (3g)

The reaction of potassium 1-pentanecarbosele-noate (**2g**) (1.04 g, 4.80 mmol) with 4-bromo-phenacyl bromide (1.33 g, 4.80 mmol) yielded 1.66 g (92%) of Se-4-bromophenacyl 1-pentanecarbosele-noate (**3g**) as slightly yellow crystals; m.p. 52–54 °C.

Se-Methyl cyclohexanecarboselenoate (3h)

The reaction of potassium cyclohexanecarbo-selenoate (**2h**) (500 mg, 2.18 mmol) with

iodomethane (5 ml, 50 mmol) yielded 416 mg (93%) of Se-methyl cyclohexanecarboselenoate (**3h**) as a slightly yellow liquid; b.p. 110 °C/760 Torr.

Reaction of potassium 1-methylethanecarboselenoate with oxygen

Potassium 1-methylethanecarboselenoate (**2d**) (346 mg, 2 mmol) was stirred in ether (5 ml) at 20 °C for 14 h under an oxygen atmosphere. The ether was evaporated under reduced pressure. To the residue was added methanol (1 ml). Filtration of the precipi-tates (black selenium) and evaporation of the filtrate *in vacuo* gave 198 mg (90%) of potassium 1-methyl-propanoate as confirmed by comparison of the ¹H NMR spectrum with that of authentic sample.

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