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A Facile Preparation of Lithium Selenocarboxylates

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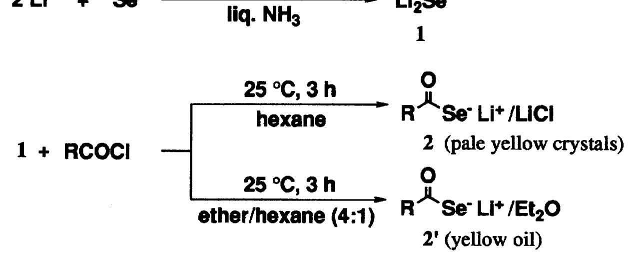
Synopsis. A series of lithium selenocarboxylates **2** were synthesized in good yields by the direct reaction of acyl chlorides with lithium selenide. The salts **2** were soluble in ether and tetrahydrofuran and readily reacted with alkyl iodides to give the corresponding *Se*-alkyl esters in quantitative yields.

Alkali metal selenocarboxylates are the most important class of compounds for the synthesis of selenocarboxylic acid derivatives. However, the preparation of lithium selenocarboxylates have been still remained unsuccessful due to the difficulty of synthesis. Previously, we have reported the preparation of lithium thio-[1] and dithiocarboxylates[2] by the reactions of the corresponding thio- and dithiocarboxylic acids with lithium hydride. This method, however, can not be applied to the selenium isologues because of the instability of common selenocarboxylic acids. As a part of our study concerning a new class of chalcogeno carboxylic acid derivatives, we now report a facile preparation of lithium selenocarboxylates (**2**) by the direct reaction of acyl chlorides with lithium selenide (Scheme 1).

The starting lithium selenide **1** was quantitatively obtained by the stoichiometric reaction of lithium metal with selenium in liquid ammonia. For the preparation of lithium selenocarboxylates (**2**), the following reaction conditions appear to be preferred. For example, 4-methylbenzoyl chloride was added to a suspension of excess of lithium selenide in pentane or hexane and the mixture was stirred at room temperature for 3 h. The filtration of the resulting precipitates afforded 96 % of lithium 4-methylbenzenecarboselenoate (**2g**) as pale yellow microcrystalline solids containing an equimolar amount of lithium chloride. Under similar conditions, other salts **2a**—**f**, **h**—**j** were obtained in good yields (Table 1). When a mixed solvent of ether and hexane (4 : 1) was employed, the salts **2′** were obtained without exception as a yellow oil containing an equimolar amount of ether,[3] being free from LiCl.[4]



Scheme 1.

The salts **2** obtained by using pentane or hexane as a solvent were colorless to slightly yellow microcrystalline solids, which were hygroscopic and sensitive towards oxygen. For example, exposing to air, the benzene derivative **2e** quickly decomposed with liberation of red selenium. Compound **2** was insoluble in pentane and hexane, but dissolved in ether, tetrahydrofuran, and protic solvents such as methanol and ethanol. The reaction of **2** with alkyl iodides readily proceeded at room temperature to give the corresponding selenocarboxylic acid *Se*-alkyl esters **3** in almost quantitative yields. For these esterification, the presence of lithium chloride in the salts **2** appeared to exhibit no influence.

Experimental

The IR spectra were measured on a JASCO grating IR spectrometer IR-G and a Perkin Elmer FT-IR 1640. The ^{1}H, ^{13}C, and ^{77}Se NMR spectra were recorded on a JEOL JNM-GX-270 at 270, 67.9, and 51.5 MHz, respectively. The mass spectra were taken from a Shimadzu high-resolution mass spectrometer (GCMS 9020-DF/PAC-1100).

Materials. Lithium, acyl chlorides, and methyl and propyl iodides were products of commercial grade. Pentane, hexane, and ether were refluxed with sodium metal by using benzophenone as indicator and distilled before use.

Lithium Selenide (1): Selenium powder (2.76 g, 35 mmol) and lithium metal (0.486 g, 70 mmol) were added in Shlenk tube under argon atmosphere. Ammonia (ca. 50 mL) was introduced at −70°C. *The mixture was allowed to stand at this temperature for 1 h* (this is important to regulate the reaction) and then stirred for 5 h (the solution changes from dark blue to colorless with the formation of white precipitate). The most of ammonia was evaporated by gradual warming to room temperature. The removal of traces of ammonia by heating at 70°C under reduced pressure for 5 min yielded 93 % of lithium selenide (**1**) as colorless microcrystalline solids.

Lithium Selenocarboxylates (2): The preparation of lithium ethaneselenoates (**2a**) and benzenecarboselenoate (**2′e**) as typical procedures are described in detail. The structures of **2** and **2′** were established by IR and ^{13}C NMR spectra and by conversion into *Se*-methyl or *Se*-propyl selenocarboxylates (**3**). The spectral data of **2** and **2′** are collected in Table 1. All manipulations were carried out under argon atmosphere.

Lithium Selenoacetate (2a): To a suspension of freshly prepared lithium selenide (0.65 g, 7 mmol) in hexane (10 mL), a solution of acetyl chloride (0.47 g, 6 mmol) in the same solvent (10 mL) was added dropwise at 0°C. The mixture was stirred at 25°C for 3 h. The filtration of the resulting precipitate by employing a glass filter (G-4) gave 0.90 g (88 %) of **2a** as colorless microcrystalline solids containing an equivalent of LiCl. The salt (**2a**, 1.00

Table 1. Yields and Spectral Data of Lithium Selenocarboxylates **2**

No.	RCOSe$^-$Li$^+$ R	Yield %	IR(cm^{-1})$^{a)}$ νC=O	NMR (CD$_3$OD), (δ) ^{1}H	^{13}C	^{77}Se$^{b)}$
2a	CH$_3$	88	1557	2.48 (s, 3H, CH$_3$)	44.9 (CH$_3$) 222.5 (CO)	409.0
2b	C$_2$H$_5$	61	1505	1.05 (t, 3H, J=7.5 Hz, CH$_3$) 2.72 (q, 2H, J=7.5 Hz, CH$_2$)	11.7 (CH$_3$), 50.6 (CH$_2$) 224.8 (CO)	
2c	i-C$_3$H$_7$	89	1574	1.05 (d, 6H, J=7.0 Hz, CH$_3$) 2.99 (sept., 1H, J=7.0 Hz, CH)	20.9 (CH$_3$), 54.4 (CH) 229.2 (CO)	357.6
2′c		54$^{c)}$		1.12 (d, 6H, J=7.0 Hz, CH$_3$)$^{d)}$ 1.21 (t, 6H, J=7.0 Hz, $\underline{\text{CH}_3}$CH$_2$)$^{d)}$ 2.87 (sept., 1H, J=7.0 Hz, CH)$^{d)}$ 3.52 (q, 4H, J=7.0 Hz, CH$_2$)$^{d)}$		
2d	t-C$_4$H$_9$	35	1569	1.16 (s, 9H, CH$_3$)	29.7 (CH$_3$), 52.6 ($\underline{\text{C}}$CO) 232.5 (CO)	296.9
2e	C$_6$H$_5$	98	1556	7.3—8.2 (m, 5H, Ar)	128.3, 129.2, 130.2, 147.4 (Ar) 217.5 (CO)	371.1
2′e		75$^{c)}$		1.16 (t, 6H, J=7.0 Hz, CH$_3$)$^{d)}$ 3.45 (q, 4H, J=7.0 Hz, CH$_2$)$^{d)}$ 7.1—8.0 (m, 5H, Ar)$^{d)}$		
2f	2-CH$_3$C$_6$H$_4$	93	1558	2.35 (s, 3H, CH$_3$) 7.1—7.6 (m, 4H, Ar)	19.9 (CH$_3$) 125.6, 127.9, 128.7, 131.0, 131.9, 152.4(Ar) 221.5 (CO)	
2g	4-CH$_3$C$_6$H$_4$	91 98$^{e)}$	1548	2.28 (s, 3H, CH$_3$) 7.1—8.1 (m, 4H, Ar)	21.6 (CH$_3$) 128.7, 129.5, 142.1, 144.9 (Ar) 216.5 (CO)	345.5
2h	2-CH$_3$OC$_6$H$_4$	78	1547	3.32 (s, 3H, CH$_3$) 6.8—7.7 (m, 4H, Ar)	56.3 (CH$_3$) 112.7, 120.5, 130.1, 130.6, 141.4, 154.2 (Ar) 218.0 (CO)	
2i	4-CH$_3$OC$_6$H$_4$	80	1538	3.81 (s, 3H, CH$_3$) 6.8—8.2 (m, 4H, Ar)	56.0 (CH$_3$) 113.2, 131.6, 140.6, 163.6 (Ar) 214.6 (CO)	
2j	1-Naph	82	1538	7.4—8.3 (m, 7H, Ar)	125.5, 125.6, 126.6, 126.7, 126.9, 127.1, 128.8, 129.2, 131.7, 135.0 (Ar) 220.9 (CO)	

a) KBr, broad. b) Relative to Me$_2$Se. c) Solvent: Ether/hexane (4 : 1). d) CDCl$_3$. e) Solvent: Pentane.

g, 5.9 mmol) was stirred in propyl iodide at 26°C for 3 h. Filtration of the precipitates and vacuum distillation of the filtrate yielded 0.87 g (91 %) of *Se*-propyl selenoacetate (**3a**): Bp 52—55°C/15 Torr (lit,[5] 54—56°C/15 Torr) (1 Torr= 133.322 Pa).

Lithium Selenopropanoate (2b): The reaction of propanoyl chloride (0.93 g, 10 mmol) with lithium selenide (1.03 g, 11.1 mmol) in hexane yielded 1.13 g (61 %) of **2b** as colorless microcrystalline solids.

Lithium 2-Methylselenopropanoate (2c): The reaction of 2-methylpropanoyl chloride (1.13 g, 10.6 mmol) with lithium selenide (0.99 g, 10.6 mmol) yielded 1.88 g (89 %) of **2c** as colorless microcrystalline solids.

Lithium 2,2-Dimethylselenopropanoate (2d): The reaction of 2,2-dimethylpropanoyl chloride (1.10 g, 9.2 mmol) with lithium selenide (0.85 g, 9.2 mmol) in pentane yielded 0.679 g (35 %) of **2d** as colorless microcrystalline solids.

Lithium Benzenecarboselenoate (2′e): A solution of benzoyl chloride (2.81 g, 20 mmol) in ether (16 mL) was added dropwise to a suspension of freshly prepared lithium selenide (1.86 g, 20 mmol) in hexane (4 mL) at 0°C. The mixture was stirred at 25°C for 3 h. Removal of the precipitate (LiCl) by filtration and evaporation of the solvent from the filtrate in vacuo (room temperature/0.5 Torr, 18 h) gave 3.95 g (75 %) of **2′e** as yellow oil containing an equivalent of ether.

Lithium 2-Methylbenzenecarboselenoate (2f): The reaction of 2-methylbenzoyl chloride (1.09 g, 7.1 mmol) with lithium selenide (0.66 g, 7.1 mmol) in hexane yielded 1.62 g (93 %) of **2f** as pale yellow microcrystalline solids.

Lithium 4-Methylbenzenecarboselenoate (2g): The reaction of 4-methylbenzoyl chloride (0.78 g, 5.0 mmol) with lithium selenide (0.46 g, 5.0 mmol) in hexane yielded

1.13 g (91 %) of **2g** as pale yellow microcrystalline solids.

Lithium 2-Methoxybenzenecarboselenoate (2h): The reaction of 2-methoxybenzoyl chloride (0.94 g, 5.5 mmol) with lithium selenide (0.51 g, 5.5 mmol) in hexane yielded 1.13 g (78 %) of **2h** as pale yellow microcrystalline solids.

Lithium 4-Methoxybenzenecarboselenoate (2i): The reaction of 4-methoxybenzoyl chloride (1.36 g, 8.0 mmol) with lithium selenide (0.74 g, 8.0 mmol) in hexane yielded 1.68 g (80 %) of **2i** as pale yellow microcrystalline solids.

Lithium 1-Naphthalenecarboselenoate (2j): The reaction of 1-naphthalenecarbonyl chloride (1.35 g, 7.1 mmol) with lithium selenide (0.66 g, 7.1 mmol) in hexane yielded 1.65 g (82. %) of **2j** as pale yellow microcrystalline solids.

Reaction of the Lithium Salts (2) with Alkyl Iodides. The general procedures are described. The salts **2** except for **2a** and **2b** which were converted into *Se*-propyl esters (**3a** and **3b**) were alkylated by methyl iodide. The IR, and ^{1}H and ^{13}C NMR spectra of the products **3** were exactly consistent with those of the authentic samples which were prepared by esterification of the corresponding sodium[6] or potassium selenocarboxylates.[5] The spectral data of the new compounds (**3f**—**j**) are shown below.

General Procedures: To the freshly prepared lithium selenocarboxylates **2** (5 mmol) is added methyl or propyl iodide (5 mL) and the mixture is stirred at 20°C for 2 h. Filtration of the precipitates and removal of the solvent or vacuum distillation affords *Se*-methyl or *Se*-propyl selenocarboxylates (**3**) of pale yellow liquid in quantitative yields.

***Se*-Methyl 2-Methylbenzenecarboselenoate (3f):** Yield 71 %; IR (Neat) 1688 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.33 (s, 3H, C$\underline{H}_3$Ar), 2.46 (s, 3H, CH$_3$Se), 7.3—7.9 (m, 4H, Ar); ^{13}C NMR (CDCl$_3$) δ=5.8 (CH$_3$Se), 20.6 ($\underline{C}$H$_3$Ar), 125.8, 128.6, 131.6, 131.8, 135.7, 139.1 (Ar), 196.6 (CO). Found: *m/z* 213.9928. Calcd for $C_9H_{10}OSe$: M, 213.9896.

***Se*-Methyl 4-Methylbenzenecarboselenoate (3g):** Yield 91%; IR (Neat) 1681 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.31 (s, 3H, CH$_3$), 2.32 (s, 3H, CH$_3$Se), 7.1—7.8 (m, 4H, Ar), ^{13}C NMR (CDCl$_3$) δ=4.6 (CH$_3$Se), 21.3 ($\underline{C}$H$_3$Ar), 126.8, 129.1, 136.2, 144.0 (Ar), 193.6 (CO). Found: *m/z* 213.9878. Calcd for $C_9H_{10}OSe$: M, 213.9896.

***Se*-Methyl 2-Methoxybenzenecarboselenoate (3h):** Yield 95 %; IR (Neat) 1692 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.27 (s, 3H, SeCH$_3$), 3.91 (s, 3H, CH$_3$O), 6.8—7.9 (m, 4H, Ar); ^{13}C NMR (CDCl$_3$) δ=5.2 (CH$_3$Se), 55.4 (CH$_3$O), 112.0, 120.4, 127.4, 128.8, 133.8, 150.2 (Ar), 191.8 (CO). Found: *m/z* 229.9843. Calcd for $C_9H_{10}O_2Se$: M, 229.9846.

***Se*-Methyl 4-Methoxybenzenecarboselenoate (3i):** Yield 97 %; IR (Neat) 1645 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.34 (s, 3H, CH$_3$Se), 3.82 (s, 3H, CH$_3$O), 6.7—8.0 (m, 4H, Ar), ^{13}C NMR (CDCl$_3$) δ=4.7 (CH$_3$Se), 55.4 (CH$_3$O), 113.9, 129.2, 132.0, 163.9 (Ar), 192.5 (CO). Found: *m/z* 229.9839. Calcd for $C_9H_{10}O_2Se$: M, 229.9846.

***Se*-Methyl 1-Naphthalenecarboselenoate (3j):** Yield 90 %; IR (Neat) 1682 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.43 (s, 3H, CH$_3$Se), 7.1—8.6 (m, 4H, Ar), ^{13}C NMR (CDCl$_3$) δ=6.4 (CH$_3$Se), 124.4, 124.5, 125.1, 125.2, 126.7, 127.9, 128.1, 128.2, 131.8, 133.0 (Ar), 197.0 (CO). Found: *m/z* 250.9882. Calcd for $C_{12}H_{10}OSe$: M, 250.9897.

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3) Diethyl ether contained in the salts **2′** was determined by ^{1}H NMR spectra, showing proton ratios (4:1) of the CH$_2$/CH groups for **2′c** and (6:5) of the CH$_3$/phenyl groups for **2′e**, respectively. The ether molecules appear to be tightly coordinated to RCOSeLi, because the presence of an equimolar amount of ether was observed even after evacuation (0.5 Torr) at room temperature over 18 h.

4) The solubility of lithium chloride to a mixed solvent of ether and hexane (4:1) appears to be very low.

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