

Reactions of acyl chlorides with LiAlHSeH. Preparation of diacyl selenides, diacyl diselenides, selenocarboxylates and cyclic selenoanhydrides

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Various diacyl selenides, diacyl diselenides and selenocarboxylates were synthesized by reaction of several acyl chlorides with LiAlHSeH. Reaction of diacyl chloride with LiAlHSeH afforded cyclic selenoanhydrides. In the ^{77}Se NMR spectra, we found that the chemical shifts of the diacyl selenides and the diacyl diselenides could facilitate their distinction.

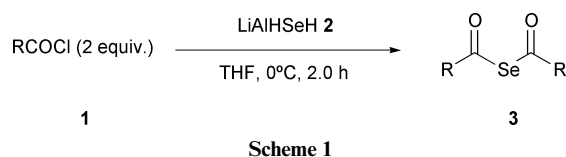
Introduction

Some methods for synthesizing diacyl selenides and diacyl diselenides have been reported.¹ These methods, however, include some disadvantages, such as the use of expensive reagents, the limited availability of the starting materials, the difficulty of purification and the tedious number of steps for preparation. A more convenient method is required to overcome these disadvantages.

Recently, we have reported that reaction of lithium aluminium hydride with elemental selenium in THF formed LiAlHSeH and also generated hydrogen gas quantitatively. We have reported that the use of the above-obtained LiAlHSeH can afford a wide range of selenium-containing compounds as a novel selenating reagent.² In this paper, we wish to describe the reaction of some kinds of acyl chloride with LiAlHSeH. We confirmed that ^{77}Se NMR spectroscopy is a useful method to distinguish between the diacyl selenides and the diacyl diselenides.

Results and discussion

Diacyl selenides **3** were prepared by a convenient method, as shown in Scheme 1. The reaction of 2 equiv. of acyl chloride **1**



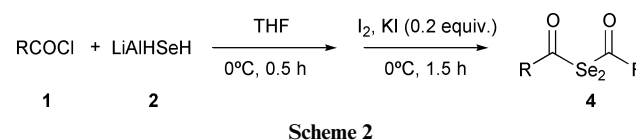
with LiAlHSeH **2** gave diacyl selenides in good yields (Table 1). While all the previous methods³ required many steps, the present method can easily isolate diacyl selenides **3** in a single step in very high yields. So far it has been relatively difficult to obtain aliphatic diacyl selenides **3** because of their instability.^{3e,4} The present reaction gave even lower aliphatic diacyl selenides, *i.e.* diacyl selenides bearing methyl, ethyl and propyl groups, in moderate to good yields. Both aromatic and aliphatic diacyl selenides **3** were obtained in excellent yields (Table 1).

A similar reaction of acyl chloride **1** with **2** is able to give diacyl diselenides. After reacting **1** with **2**, the oxidation of the mixture by iodine gave diacyl diselenides **4** in high yields (Scheme 2). Both aromatic and higher aliphatic diacyl diselenides **4** were obtained in excellent yields (Table 1). In the case of

Table 1 Synthesis of diacyl selenides **3** and diacyl diselenides **4**

R	Yield (%)	
	3	4
C ₆ H ₅	3a 86	4a 81
4-CH ₃ C ₆ H ₄	3b 91	4b 85
4-ClC ₆ H ₄	3c 96	4c 84
4-CH ₃ OC ₆ H ₄	3d 63	4d 82
C ₆ H ₅ CH ₂	3e 97	4e 86
C ₁₇ H ₃₅	3f 97	4f 75
C ₃ H ₇	3g 81	— ^a
C ₂ H ₅	3h 72	— ^a
CH ₃	3i 41	— ^a

^a Product was generated in a reaction mixture *in situ* quantitatively. However, it decomposed in the process of purification by silica gel column chromatography.



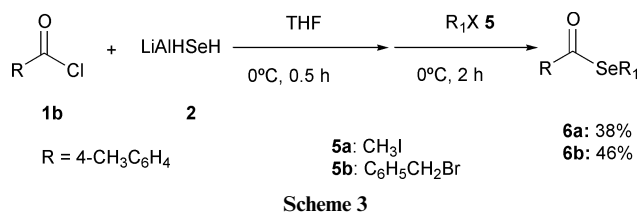
lower aliphatic diacyl selenides, *i.e.* methyl, ethyl and propyl, though the product **4** was apparently confirmed to be quantitatively formed in the reaction mixture from the result of TLC monitoring, **4** could not be isolated due to decomposition in the process of purification by silica gel column chromatography. Hence the present procedures give the selective preparation method of diacyl selenides **3** and diacyl diselenides **4**, individually, by the control of reaction conditions.

We were now interested in the reaction of the intermediate, which was obtained from treating acyl chloride **1** with **2**, with electrophile. After treating **1** with **2** in THF solution, the intermediate generated in the reaction mixture was reacted with alkyl halide **5** yielding *Se*-alkyl selenocarboxylates **6** in moderate yields (Scheme 3). Diacyl diselenides **4** were obtained *via* oxidation of the intermediate, while the intermediate was readily trapped with electrophile **5** to give **6** in this reaction.

^{77}Se NMR spectroscopy of diacyl selenides and diacyl diselenides is one of the useful methods for structure determination. However, reports including ^{77}Se NMR chemical shifts have scarcely appeared in any other paper. Typical spectroscopic properties of compounds **3** and **4** are summarized in Table 2.

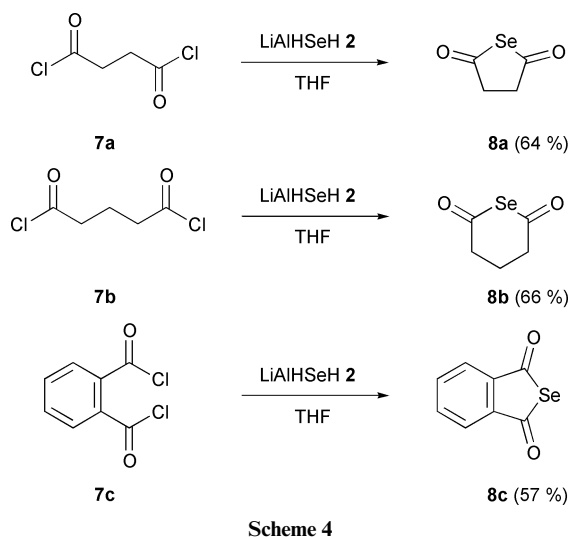
Table 2 Typical spectroscopic properties of compounds **3** and **4**

	^{77}Se NMR (δ)		^{13}C NMR (δ) ^a	
	3	4	3	4
C_6H_5 (a)	743.2	615.0	188.6	187.3
4- $\text{CH}_3\text{C}_6\text{H}_4$ (b)	740.5	608.2	188.1	186.8
4- ClC_6H_4 (c)	749.4	621.4	186.8	186.0
4- $\text{CH}_3\text{OC}_6\text{H}_4$ (d)	731.0	599.8	186.8	185.4
$\text{C}_6\text{H}_5\text{CH}_2$ (e)	818.8	644.2	195.3	193.0
$\text{C}_{17}\text{H}_{35}$ (f)	809.8	618.6	198.1	194.2
Mean	765.5 ± 38.4	617.9 ± 15.1	190.6 ± 4.8	188.8 ± 3.8

^a Chemical shifts of carbonyl carbon.

It was difficult to distinguish between diacyl selenides **3a–3f** (δ 190.6 \pm 4.8) and diacyl diselenides **4a–4f** (δ 188.8 \pm 3.8) from the differences of the chemical shifts of C=O in the ^{13}C NMR spectra. On the other hand, we found the significant differences in the chemical shifts of selenium between **3a–3f** (δ 765.5 \pm 38.4) and **4a–4f** (δ 617.9 \pm 15.1) were clear in the ^{77}Se NMR spectra (Table 2).

We also investigated the reaction of bis(acyl chlorides) **7** with LiAlHSeH **2** (Scheme 4). Previously, we reported the prepar-



ation of cyclic selenoanhydrides **8** by the reaction of primary selenoamides with bis(acyl chlorides) **7**.⁵ The reaction using LiAlHSeH **2**, which is prepared simply by stirring elementary selenium and lithium aluminium hydride in THF, gave cyclic selenoanhydrides **8** more easily than the reaction using primary selenoamide and gave **8** in higher yields.⁵

Experimental

General procedure

Melting points were determined by use of a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were measured on a Perkin–Elmer 1600 spectrometer. ^1H , ^{13}C and ^{77}Se NMR spectra were recorded on a JEOL-JNM- α 400 (400 MHz) spectrometer. Mass spectra were obtained on a Shimadzu 9020-DF mass spectrometer. Tetrahydrofuran was

distilled from sodium–benzophenone and used immediately. The ^{77}Se chemical shifts were expressed in ppm deshielded with respect to neat Me_2Se in CDCl_3 . LiAlHSeH **2** was prepared according to the previously reported method.² Briefly, the preparation of LiAlHSeH **2** is as follows: to a solution of selenium powder (0.80 g, 10.0 mmol) in dry THF (100 mL) was added lithium aluminium hydride (0.38 g, 10.0 mmol) at 0 °C under an argon atmosphere. The mixture was stirred for 30 min. The black selenium powder was consumed in less than 10 min. The reaction mixture became a heterogeneous grayish suspension. Compound **2** was formed *in situ* and was then ready for further reaction.

Dibenzoyl selenide **3a**

Benzoyl chloride (0.23 mL, 2.0 mmol) was added to the solution of LiAlHSeH **2** (1.0 mmol), prepared as described above. The reaction mixture was stirred at 0 °C for 2 h. The mixture was extracted with diethyl ether and washed with saturated NaCl solution. The organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by flash chromatography on silica gel with dichloromethane–*n*-hexane (1 : 1) to give **3a** 0.25 g (86%) as a white powder. Mp: 60.6–61.4 °C (lit.,⁴ 61.5–62.3 °C); ^1H NMR (CDCl_3) δ 7.49 (4H, t, J = 8.0 Hz, Ar), 7.63 (2H, t, J = 8.0 Hz, Ar), 7.95 (4H, d, J = 8.0 Hz, Ar); ^{13}C NMR (CDCl_3) δ 128.4, 128.9, 134.4, 138.5, 188.6; ^{77}Se NMR (CDCl_3) δ 746.2; IR (KBr) ν 1722, 1669 cm^{-1} ; MS (CI): m/z = 291 [M^+ + 1].

Bis(4-methylbenzoyl) selenide **3b**

Mp: 90.2–90.8 °C (lit.,⁴ 90–91 °C); ^1H NMR (CDCl_3) δ 2.40 (6H, s, CH_3), 7.26 (4H, d, J = 8.2 Hz, Ar), 7.83 (4H, d, J = 8.2 Hz, Ar); ^{13}C NMR (CDCl_3) δ 21.7, 128.5, 129.6, 136.0, 145.5, 188.1; ^{77}Se NMR (CDCl_3) δ 740.5; IR (KBr) ν 1738, 1690 cm^{-1} ; MS (CI): m/z = 319 [M^+ + 1].

Bis(4-chlorobenzoyl) selenide **3c**

Mp: 118.6–120.4 °C (lit.,⁴ 118.5–120.0 °C); ^1H NMR (CDCl_3) δ 7.45 (4H, d, J = 8.8 Hz, Ar), 7.87 (4H, d, J = 8.8 Hz, Ar); ^{13}C NMR (CDCl_3) δ 129.3, 129.7, 136.5, 141.1, 186.8; ^{77}Se NMR (CDCl_3) δ 749.4; IR (KBr) ν 1736, 1676 cm^{-1} ; MS (CI): m/z = 359 [M^+ + 1].

Bis(4-methoxybenzoyl) selenide **3d**

Mp: 77.8–79.8 °C (lit.,⁴ 77.8–80.2 °C); ^1H NMR (CDCl_3) δ 3.87 (6H, s, CH_3), 6.94 (4H, d, J = 9.2 Hz, Ar), 7.92 (4H, d, J = 9.2 Hz, Ar); ^{13}C NMR (CDCl_3) δ 55.6, 114.1, 131.0, 131.3, 164.6, 186.8; ^{77}Se NMR (CDCl_3) δ 731.0; IR (KBr) ν 1736, 1654 cm^{-1} ; MS (CI): m/z = 351 [M^+ + 1].

Bis(phenylacetyl) selenide **3e**

Mp: 53.0–53.4 °C; ^1H NMR (CDCl_3) δ 3.95 (4H, s, CH_2), 7.11–7.15 (4H, m, Ar), 7.21–7.26 (6H, m, Ar); ^{13}C NMR (CDCl_3) δ 55.2, 127.8, 128.8, 129.8, 131.8, 195.3; ^{77}Se NMR (CDCl_3)

δ 818.8; IR (KBr) ν 1760, 1699 cm^{-1} ; MS (CI): $m/z = 319$ [$M^+ + 1$]; Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{Se}$: C, 60.58; H, 4.45. Found: C, 60.27; H, 4.58%.

Distearoyl selenide 3f

Mp: 75.0–75.6 °C (lit.,⁴ 75.3–75.8 °C); ^1H NMR (CDCl_3) δ 0.88 (6H, t, $J = 6.4$ Hz, CH_3), 1.26 (56H, s, CH_2), 1.56–1.70 (4H, m, CH_2), 2.81 (4H, t, $J = 7.2$ Hz, CH_2); ^{13}C NMR (CDCl_3) δ 14.1, 22.7, 24.8, 28.7, 29.2, 29.3, 29.5, 29.7, 31.9, 49.5, 198.1; ^{77}Se NMR (CDCl_3) δ 809.8; IR (neat) ν 1774, 1718 cm^{-1} ; MS (CI): $m/z = 615$ [$M^+ + 1$].

Dibutylryl selenide 3g

^1H NMR (CDCl_3) δ 0.91 (6H, t, $J = 7.4$ Hz, CH_3), 1.57–1.68 (4H, m, CH_2), 2.74 (4H, t, $J = 7.4$ Hz, CH_2); ^{13}C NMR (CDCl_3) δ 13.2, 18.3, 51.2, 197.9; ^{77}Se NMR (CDCl_3) δ 811.6; IR (neat) ν 1771, 1719 cm^{-1} ; MS (CI): $m/z = 223$ [$M^+ + 1$]; Anal. Calcd for $\text{C}_8\text{H}_{14}\text{O}_2\text{Se}$: C, 43.45; H, 6.38. Found: C, 43.55; H, 6.42%.

Dipropionyl selenide 3h

^1H NMR (CDCl_3) δ 1.18 (6H, t, $J = 7.6$ Hz, CH_3), 2.86 (4H, q, $J = 7.6$ Hz, CH_2); ^{13}C NMR (CDCl_3) δ 8.8, 43.1, 198.5; ^{77}Se NMR (CDCl_3) δ 801.6; IR (neat) ν 1783, 1717 cm^{-1} ; MS (CI): $m/z = 195$ [$M^+ + 1$]; Anal. Calcd for $\text{C}_6\text{H}_{10}\text{O}_2\text{Se}$: C, 37.32; H, 5.22. Found: C, 37.44; H, 5.22%.

Diacetyl selenide 3i

^1H NMR (CDCl_3) δ 2.53 (6H, s, CH_3); ^{13}C NMR (CDCl_3) δ 35.9, 194.7; ^{77}Se NMR (CDCl_3) δ 836.1; IR (neat) ν 1773, 1723 cm^{-1} ; MS (CI): $m/z = 167$ [$M^+ + 1$]; Anal. Calcd for $\text{C}_4\text{H}_6\text{O}_2\text{Se}$: C, 29.11; H, 3.66. Found: C, 29.12; H, 3.78%.

Dibenzoyl diselenide 4a

Benzoyl chloride (0.23 mL, 2 mmol) was added to the solution of **2** (2.0 mmol). The reaction mixture was stirred at 0 °C for 30 min. Iodine (0.25 g, 2.0 mmol) and potassium iodide (0.07 g, 0.40 mmol) in THF (10 mL) were added to the reaction mixture. The reaction mixture was stirred at 0 °C for 1.5 h. The mixture was extracted with dichloromethane and washed with 1% sodium hydrogen sulfite and water. The organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by chromatography on silica gel with dichloromethane–*n*-hexane (1 : 1) to give **4a** 0.30 g (81%) as a yellow powder. Mp: 131.0–133.6 °C (lit.,^{1a} 129–130 °C; lit.,^{1b} 130–131 °C; lit.,⁴ 131–132 °C); ^1H NMR (CDCl_3) δ 7.50 (4H, t, $J = 7.6$ Hz, Ar), 7.65 (2H, t, $J = 7.6$ Hz, Ar), 8.01 (4H, d, $J = 7.6$ Hz, Ar); ^{13}C NMR (CDCl_3) δ 128.1, 129.1, 134.3, 136.7, 187.3; ^{77}Se NMR (CDCl_3) δ 615.0; IR (KBr) ν 1740, 1686 cm^{-1} ; MS (CI): $m/z = 371$ [$M^+ + 1$].

Bis(4-methylbenzoyl) diselenide 4b

Mp: 109.6–111.2 °C (lit.,^{1a} 110–111 °C; lit.,^{1b,4} 111.0–111.5 °C); ^1H NMR (CDCl_3) δ 2.42 (6H, s, CH_3), 7.29 (4H, d, $J = 8.0$ Hz, Ar), 7.90 (4H, d, $J = 8.0$ Hz, Ar); ^{13}C NMR (CDCl_3) δ 21.8, 128.2, 129.7, 134.1, 145.5, 186.8; ^{77}Se NMR (CDCl_3) δ 608.2; IR (KBr) ν 1743, 1702 cm^{-1} ; MS (CI): $m/z = 399$ [$M^+ + 1$].

Bis(4-chlorobenzoyl) diselenide 4c

Mp: 122.4–123.8 °C (lit.,^{1a,1b,4} 122–124 °C); ^1H NMR (CDCl_3) δ 7.49 (4H, d, $J = 8.8$ Hz, Ar), 7.94 (4H, d, $J = 8.8$ Hz, Ar); ^{13}C NMR (CDCl_3) δ 129.4, 129.5, 134.9, 141.0, 186.0; ^{77}Se NMR (CDCl_3) δ 621.4; IR (KBr) ν 1735, 1699 cm^{-1} ; MS (CI): $m/z = 439$ [$M^+ + 1$].

Bis(4-methoxybenzoyl) diselenide 4d

Mp: 106.0–107.2 °C (lit.,^{1a} 105.5–107 °C; lit.,^{1b,4} 106–107 °C); ^1H

NMR (CDCl_3) δ 3.88 (6H, s, CH_3), 6.96 (4H, d, $J = 8.8$ Hz, Ar), 7.99 (4H, d, $J = 8.8$ Hz, Ar); ^{13}C NMR (CDCl_3) δ 55.6, 114.2, 129.4, 130.5, 164.4, 185.4; ^{77}Se NMR (CDCl_3) δ 599.8; IR (KBr) ν 1746, 1703 cm^{-1} ; MS (CI): $m/z = 431$ [$M^+ + 1$].

Bis(phenylacetyl) diselenide 4e

Mp: 85.6–87.2 °C; ^1H NMR (CDCl_3): δ 4.00 (4H, s, CH_2), 7.25–7.36 (10H, m, Ar); ^{13}C NMR (CDCl_3): δ 52.0, 128.3, 128.9, 130.2, 132.0, 193.0; ^{77}Se NMR (CDCl_3): δ 644.2; IR (KBr) ν 1736, 1724 cm^{-1} ; MS (CI): $m/z = 399$ [$M^+ + 1$]; Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{Se}_2$: C, 48.50; H, 3.56. Found: C, 48.55; H, 3.66%.

Distearoyl diselenide 4f

Mp: 79.8–80.3 °C (lit.,⁴ 79.8–80.3 °C); ^1H NMR (CDCl_3): δ 0.88 (6H, t, $J = 6.8$ Hz, CH_3), 1.26 (56H, s, CH_2), 1.61–1.75 (4H, m, CH_2), 2.79–2.86 (4H, m, CH_2); ^{13}C NMR (CDCl_3): δ 14.1, 22.7, 25.5, 28.8, 29.2, 29.3, 29.5, 29.6, 31.9, 46.1, 194.2; ^{77}Se NMR (CDCl_3): δ 618.6; IR (KBr) ν 1732 cm^{-1} ; MS (CI): $m/z = 695$ [$M^+ + 1$].

Se-Methyl 4-methylbenzeneselenocarboxylate 6a

p-Toluoyl chloride **1b** (0.15 g, 1.0 mmol) was added to a solution of **2** (1.0 mmol). The reaction mixture was stirred at 0 °C for 0.5 h. Methyl iodide **5a** (0.14 mL, 1.0 mmol) was added to the reaction mixture. The reaction mixture was stirred at 0 °C for 2 h. The mixture was extracted with dichloromethane and washed with saturated sodium carbonate solution. The organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by chromatography on silica gel to give **6a** 0.08 g (38%). Mp: 55.2–56.0 °C; ^1H NMR (CDCl_3): δ 2.37 (3H, s, CH_3), 2.39 (3H, s, CH_3), 7.23 (2H, d, $J = 7.6$ Hz, Ar), 7.80 (2H, d, $J = 7.6$ Hz, Ar); ^{13}C NMR (CDCl_3): δ 4.9, 21.6, 127.1, 129.3, 136.4, 144.4, 194.2; ^{77}Se NMR (CDCl_3): δ 438.0; IR (KBr) ν 1661, 1681 cm^{-1} ; MS (CI): $m/z = 215$ [$M^+ + 1$].

Se-Benzyl 4-methylbenzeneselenocarboxylate 6b

^1H NMR (CDCl_3): δ 2.36 (3H, s, CH_3), 4.32 (2H, s, CH_2), 7.18–7.22 (3H, m, Ar), 7.25–7.29 (2H, m, Ar), 7.35 (2H, d, $J = 7.3$ Hz, Ar), 7.78 (2H, d, $J = 8.3$ Hz, Ar); ^{13}C NMR (CDCl_3): δ 21.6, 28.8, 126.9, 127.3, 128.5, 129.0, 129.4, 136.2, 139.1, 144.6, 193.8; ^{77}Se NMR (CDCl_3): δ 595.7; IR (KBr) ν 1661, 1681 cm^{-1} ; MS (CI): $m/z = 291$ [$M^+ + 1$], lit.⁶

Cyclic succinic selenoanhydride 8a

Glutaryl chloride **7a** (0.20 g, 1.0 mmol) was added to the solution of **2** (1.0 mmol). The reaction mixture was stirred at room temperature for 2 h. The mixture was extracted with dichloromethane and washed with saturated sodium carbonate solution. The organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by chromatography on silica gel with dichloromethane–*n*-hexane (1 : 1) to give **8a** 0.12 g (66%) as an orange oil. ^1H NMR (CDCl_3): δ 2.91 (4H, s, CH_2); ^{13}C NMR (CDCl_3): δ 45.0, 204.6; ^{77}Se NMR (CDCl_3): δ 700.2; IR (KBr) ν 1709 cm^{-1} ; MS (CI): $m/z = 165$ [$M^+ + 1$], lit.⁵

Cyclic glutaric selenoanhydride 8b

^1H NMR (CDCl_3): δ 2.16 (2H, m, CH_2), 2.77 (4H, t, $J = 6.0$ Hz, CH_2); ^{13}C NMR (CDCl_3): δ 19.2, 43.6, 200.7; ^{77}Se NMR (CDCl_3): δ 827.4; IR (KBr) ν 1698 cm^{-1} ; MS (CI): $m/z = 179$ [$M^+ + 1$], lit.⁵

Cyclic phthalic selenoanhydride 8c

Mp: 60.1–61.2 °C; 7.74–7.79 (2H, m, Ph), 7.93–7.99 (2H, m, Ph); ^{13}C NMR (CDCl_3): δ 123.5, 134.9, 141.6, 193.9; ^{77}Se NMR (CDCl_3): δ 611.6; IR (KBr) ν 1690 cm^{-1} ; MS (CI): $m/z = 213$ [$M^+ + 1$], lit.⁵

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