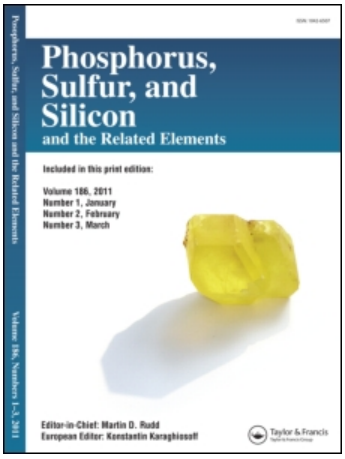


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS OF SELENOL ESTERS USING ACYL HALIDES AND A NOVEL SELENATING REAGENT, LiAlHSeH

Mamoru Koketsu[a]; Hiroshi Asada[a]; Hideharu Ishihara[a]
[a] Gifu University, Gifu, Japan

Online publication date: 12 August 2010

To cite this Article Koketsu, Mamoru , Asada, Hiroshi and Ishihara, Hideharu(2004) 'SYNTHESIS OF SELENOL ESTERS USING ACYL HALIDES AND A NOVEL SELENATING REAGENT, LiAlHSeH', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 3, 591 — 595
To link to this Article: DOI: 10.1080/10426500490422254
URL: http://dx.doi.org/10.1080/10426500490422254

Phosphorus, Sulfur, and Silicon, 179:591–595, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490422254

Taylor & Francis
Taylor & Francis Group

SYNTHESIS OF SELENOL ESTERS USING ACYL HALIDES AND A NOVEL SELENATING REAGENT, LiAlHSeH

Mamoru Koketsu, Hiroshi Asada, and Hideharu Ishihara
Gifu University, Gifu, Japan

(Received April 25, 2003; accepted September 25, 2003)

Several selenol esters were synthesized by the reaction of acyl chlorides with LiAlHSeH then with alkyl halides in moderate to good yields.

Keywords: Acyl chloride; lithium aluminium halide; selenium; selenol ester

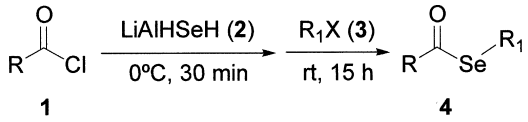
Selenol esters are important key intermediates in organic synthesis. They have been used as precursors of acyl radicals,[1] as acyl transfer reagents,[2] and for radical addition-cyclization reactions.[3] In spite of the growing interest in new organic transformations of these compounds, preparative methods available for their synthesis are still limited.[4] A facile method for the preparation of selenol esters would certainly be very useful. Recently, we developed a novel selenating reagent,[5] LiAlHSeH. This reagent is useful for preparing a variety of different selenium containing compounds.[6] Previously, we presented a possible method for the preparation of selenol esters.[6c] However, since the reaction conditions were not optimal, the yields were low and only two examples were presented. Herein, we report an optimal procedure for preparation of selenol esters using the novel reagent, LiAlHSeH.

RESULTS AND DISCUSSION

Optimal conditions for the preparation of *Se*-alkyl selenocarboxylates (**4**) from the corresponding acyl chlorides (**1**) were determined by trial

This work was supported by a Grant-in-Aid for Science Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan (No. 14540490) to which we are grateful.

Address correspondence to Mamoru Koketsu, Division of Instrumental Analysis, Life Science Research Center, Gifu University, Gifu 501-1193, Japan. E-mail: koketsu@cc.gifu-u.ac.jp



SCHEME 1

and error. When the reaction of acyl chlorides (**1**) with LiAlHSeH (**2**)[5] and then with alkyl halides (**3**) was carried out at 0°C for 2 h, the yields of (**4a**) and (**4c**) were 38% and 46% respectively. We found that the reaction at room temperature and a longer reaction time, 15 h, gave the highest yields of (**4**). The optimal reaction conditions leading to *Se*-alkyl selenocarboxylates (**4**) is shown in Scheme 1. 4-Methylbenzoyl chloride (**1a**) was added to an anhydrous THF solution of LiAlHSeH (**2**).[5] The reaction mixture was stirred at 0°C for 30 min under an argon atmosphere. A solution of methyl iodide (**3a**) in THF was added to the reaction mixture at room temperature. The reaction mixture was stirred for an additional 15 h. After work-up, *Se*-methyl 4-methylselenobenzoate (**4a**) was obtained in a 71% yield. Reactions of four different acyl chlorides (**1**) with four alkyl halides (**3**) also gave the corresponding *Se*-alkyl selenocarboxylates (**4**) in moderate to good yields (Table I). The reaction with aryl halides and secondary halides did not give desired products.

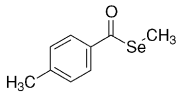
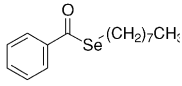
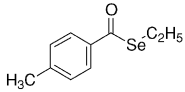
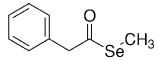
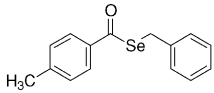
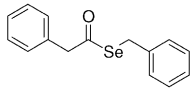
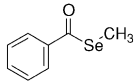
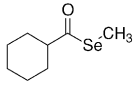
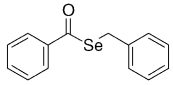
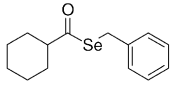
In conclusion, we report here a new synthesis procedure for preparation of various *Se*-alkyl selenocarboxylates by reaction of acyl halides (**1**) with LiAlHSeH (**2**) and then with alkyl halides (**3**).

Experimental

Melting points were determined by use of a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were measured on Perkin-Elmer 1600 spectrometer. ^{1}H, ^{13}C, and ^{77}Se spectra were recorded on a JEOL-JNM-α400 (400 MHz) spectrometer. Mass spectra were obtained on a Shimadzu 9020-DF mass spectrometer. Tetrahydrofuran was distilled from sodium-benzophenone immediately prior to use.

Se-Methyl 4-methylselenobenzoate (**4a**). *p*-Toluoyl chloride **1a** (0.13 mL, 1.0 mmol) was added to a THF solution (25 mL) of LiAlHSeH (**2**) (1.0 mmol). The reaction mixture was stirred at 0°C for 0.5 h. Methyl iodide **3a** (0.076 mL, 1.2 mmol) was added to the reaction mixture. The resulting reaction mixture was stirred at room temperature for 15 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

TABLE I Synthesis of *Se*-Alkyl Selenocarboxylates (**4**)

Products (**4**)		Yield (%)[a]	Products (**4**)		Yield (%)[a]
	**4a**[b]	71		**4f**[e]	46
	**4b**[c]	68		**4g**[b]	64
	**4c**[d]	77		**4h**[d]	78
	**4d**[b]	67		**4i**[b]	46
	**4e**[d]	75		**4j**[d]	65

[a]Isolated yield.
[b]Methyl iodide (**3a**) was used.
[c]Ethyl iodide (**3b**) was used.
[d]Benzyl bromide (**3c**) was used.
[e]Octyl bromide (**3d**) was used.

chromatography on silica gel with dichloromethane:*n*-hexane (1:2) to give **4a** 0.15g (71%) as pale yellow liquid; IR (neat): 1681, 1662 cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$): δ 2.37 (3H, s, CH_3, $^2J(^{77}Se\text{-}^1H) = 10.7$ Hz), 2.39 (3H, s, CH_3), 7.24 (2H, d, $J = 7.6$ Hz, Ar), 7.81 (2H, d, $J = 8.0$ Hz, Ar),^{13}C NMR (100 MHz, $CDCl_3$): δ 4.9, 21.7, 127.1, 129.4, 136.5, 144.4 (Ar), 194.3 (C=O), ^{77}Se NMR (76 MHz, $CDCl_3$): δ 438.0, MS (CI): m/z = 215 (M^++1), lit.[6c]

Se-Ethyl 4-methylselenobenzoate (**4b**). Yellow liquid, IR (neat): 1683, 1662 $cm^{-1,}$ ^1H NMR (400 MHz, $CDCl_3$): δ 1.49 (3H, t, $J = 7.4$ Hz, CH_3), 2.39 (3H, s, CH_3), 3.07 (2H, q, $J = 7.6$ Hz, CH_2), 7.23 (2H, d, $J = 8.4$ Hz, Ar), 7.79 (2H, d, $J = 8.0$ Hz, Ar), ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.9, 19.3, 21.7, 127.2, 129.4, 136.7, 144.4 (Ar), 194.4 (C=O), ^{77}Se NMR (76 MHz, $CDCl_3$): δ 550.7, MS (CI): m/z = 229 ($M^+ + 1$), lit.[7]

Se-Benzyl 4-methylselenobenzoate (**4c**). White crystals, m.p.: 55.2–56.0°C, IR (KBr): 1681, 1661 cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$): δ 2.38 (3H, s, CH_3), 4.33 (2H, s, CH_2), 7.20–7.30 (5H, m, Ar), 7.35–7.37 (2H, m, Ar), 7.79 (2H, d, $J = 8.4$ Hz, Ar), ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 28.9, 126.9, 127.3, 128.6, 129.0, 129.4, 136.3, 144.7 (Ar), 193.9 (C=O), ^{77}Se NMR (76 MHz, $CDCl_3$): δ 595.5, MS (CI): m/z = 291 ($M^+ + 1$), lit.[6c]

Se-Methyl selenobenzoate (**4d**). Yellow liquid, IR (neat): 1673 cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$): δ 2.39 (3H, s, CH_3, $^2J(^{77}Se\text{-}^1H) = 10.7$ Hz), 7.43–7.47 (2H, m, Ar), 7.57–7.60 (1H, m, Ar), 7.9 (2H, dd, $J = 1.6$, 8.4 Hz, Ar), ^{13}C NMR (100 MHz, $CDCl_3$): δ 5.1, 127.0, 128.7, 133.5, 139.0 (Ar), 194.9 (C=O), ^{77}Se NMR (76 MHz, $CDCl_3$): δ 444.2, MS (CI): m/z = 201 ($M^+ + 1$), lit.[8]

Se-Benzyl selenobenzoate (**4e**). Yellow liquid, IR (neat): 1671 cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$): δ 4.34 (2H, s, CH_2, $^2J(^{77}Se\text{-}^1H) = 11.2$ Hz), 7.19–7.23 (1H, m, Ar), 7.27–7.30 (2H, m, Ar), 7.35–7.37 (2H, m, Ar), 7.41–7.45 (2H, m, Ar), 7.54–7.59 (1H, m, Ar), 7.89 (2H, dd, $J = 1.6$, 8.4 Hz, Ar), ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.0, 127.0, 127.2, 128.8, 133.7, 138.8, 139.0 (Ar), 194.5 (C=O), ^{77}Se NMR (76 MHz, $CDCl_3$): δ 600.8, MS (CI): m/z = 277 ($M^+ + 1$), lit.[8,9]

Se-Octyl selenobenzoate (**4f**). Yellow liquid, IR (neat): 1674 cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (3H, t, $J = 6.8$ Hz, CH_3), 1.25–1.45 (10H, m, CH_2), 1.71–1.79 (2H, m, CH_2), 3.09 (2H, t, $J = 7.6$ Hz, CH_2), 7.42–7.47 (2H, m, Ar), 7.55–7.59 (1H, m, Ar), 7.91 (2H, dd, $J = 1.6$, 8.4 Hz, Ar), ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.6, 25.8, 29.1, 29.2, 30.0, 30.5, 31.8, 127.1, 128.7, 133.4, 139.2 (Ar), 195.0 (C=O), ^{77}Se NMR (76 MHz, $CDCl_3$): δ 524.7, MS (CI): m/z = 299 ($M^+ + 1$); Anal. Calcd for $C_{15}H_{22}OSe$: C, 60.60; H, 7.46. found: C, 60.48; H, 7.24%.

Se-Methyl phenylselenoacetate (**4g**). Yellow liquid, IR (neat): 1697 cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$): δ 2.17 (3H, s, CH_3), 3.84 (2H, s, CH_2), 7.27–7.35 (5H, m, Ar), ^{13}C NMR (100 MHz, $CDCl_3$): δ 5.34, 53.9, 127.6, 128.7, 129.9, 133.0 (Ar), 200.4 (C=O), ^{77}Se NMR (76 MHz, $CDCl_3$): δ 474.6, MS (CI): m/z = 215 ($M^+ + 1$), lit.[4b]

Se-Benzyl phenylselenoacetate (**4h**). White crystals, m.p.: 44.0–45.0°C, IR (KBr): 1686 cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$): δ 3.85 (2H, s, CH_2), 4.10 (2H, s, CH_2), 7.15–7.34 (10H, m, Ar), ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.4, 53.8, 126.9, 127.7, 128.6, 128.9, 130.0, 132.8, 138.8 (Ar), 200.2 (C=O), ^{77}Se NMR (76 MHz, $CDCl_3$): δ 632.8, MS (CI): m/z = 291 ($M^+ + 1$), lit.[10]

Se-Methyl cyclohexanecarboselenoate (**4i**).Yellow liquid, IR (neat): 1700 cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$): δ 1.22–1.31 (3H, m), 1.44–1.48 (2H, m), 1.63–1.66 (1H, m), 1.77–1.79 (2H, m), 1.93–1.97 (2H, m), 2.18 (3H, s, CH_3, $^2J_{(^{77}Se-^1H)} = 10.7$ Hz), 2.53 (1H, tt, $J = 3.6$, 11.6 Hz, CH), ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.34, 25.4, 25.6, 29.3, 56.1, 206.0 (C=O), ^{77}Se NMR (76 MHz, $CDCl_3$): δ 440.8, MS (CI): m/z = 207 ($M^+ + 1$), lit.[7]

Se-Benzyl cyclohexanecarboselenoate (**4j**). Yellow liquid, IR (neat): 1695 cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$): δ 1.18–1.32 (3H, m), 1.41–1.51 (2H, m), 1.64–1.69 (1H, m), 1.76–1.80 (2H, m), 1.93–1.97 (2H, m), 2.53 (1H, tt, $J = 3.6$, 11.6 Hz, CH), 4.11 (2H, s, CH_2), 7.16–7.27 (5H, m, Ar),

^{13}C NMR (100 MHz, $CDCl_3$): δ 25.3, 25.6, 28.3, 29.3, 56.0, 126.8, 128.5, 128.8, 139.4 (Ar), 205.5 (C=O), ^{77}Se NMR (76 MHz, $CDCl_3$): δ 601.8, (CI): m/z = 283 ($M^+ + 1$); Anal. Calcd for $C_{14}H_{18}OSe$: C, 59.79; H, 6.45. found: C, 60.01; H, 6.29%.

REFERENCES

[1] a) G. E. Keck and M. C. Grier, *Synlett*, 1657 (1999); b) D. L. Boger and R. J. Mathvink, *J. Org. Chem.*, **57,** 1429 (1992); c) C. Chen, D. Crich, and A. Papadatos, *J. Am. Chem. Soc.*, **114,** 8313 (1992).

[2] a) A. F. Sviridov, M. S. Ermolenko, D. V. Yashunsky, and N. K. Kochetkov, *Tetrahedron Lett.*, **24,** 4355 (1983); b) R. J. Anderson, C. A. Henrick, and L. D. Rosenblum, *J. Am. Chem. Soc.*, **96,** 3654 (1974); c) T. Mukaiyama, M. Araki, and H. Takei, *J. Am. Chem. Soc.*, **95,** 4763 (1973).

[3] a) J. Quirante, X. Vila, C. Escolano, and J. Bonjoch, *J. Org. Chem.*, **67,** 2323 (2002); b) S. M. Allin, W. R. S. Barton, W. R. Bowman, and T. McInally, *Tetrahedron Lett.*, **42,** 7887 (2001); c) M.-L. Bennasar, T. Roca, R. Griera, and J. Bosch, *J. Org. Chem.*, **66,** 7547 (2001); d) M.-L. Bennasar, T. Roca, R. Griera, and J. Bosch, *Org. Lett.*, **3,** 1697 (2001); e) P. A. Evans, T. Manangan, and A. L. Rheingold, *J. Am. Chem. Soc.*, **122,** 11009 (2000).

[4] a) Y. Nishiyama, K. Tokunaga, H. Kawamatsu, and N. Sonoda, *Tetrahedron Lett.*, **43,** 1507 (2002); b) A. L. Braga, T. L. C. Martins, C. C. Silveira, and O. E. D. Rodrigues, *Tetrahedron*, **57,** 3297 (2001); c) A. G. M. Barrett, G. G. Graboski, and M. A. Russell, *J. Org. Chem.*, **51,** 1012 (1986); d) T. Inoue, T. Takanobu, N. Kambe, A. Ogawa, I. Ryu, and N. Sonoda, *J. Org. Chem.*, **59,** 5824 (1994).

[5] H. Ishihara, M. Koketsu, Y. Fukuta, and F. Nada, *J. Am. Chem. Soc.*, **123,** 8408 (2001).

[6] a) M. Koketsu, Y. Fukuta, and H. Ishihara, *J. Org. Chem.*, **67,** 1008 (2002); b) M. Koketsu, M. Ishida, N. Takakura, and H. Ishihara, *J. Org. Chem.*, **67,** 486 (2002); c) M. Koketsu, F. Nada, S. Hiramatsu, and H. Ishihara, *J. Chem. Soc., Perkin Trans. 1*, 737 (2002); d) M. Koketsu, N. Takakura, and H. Ishihara, *Synthetic. Commun.*, **32,** 3075 (2002); e) M. Koketsu, Y. Okayama, H. Aoki, and H. Ishihara, *Heteroatom Chem.*, **13,** 195 (2002); f) M. Koketsu, Y. Fukuta, and H. Ishihara, *Tetrahedron Lett.*, **42,** 6333 (2001).

[7] S. Kato, H. Kageyama, K. Takagi, K. Mizoguchi, and T. Murai, *J. Prakt. Chem. (Leipzig)*, **332,** 898 (1990).

[8] Y. Nishiyama, A. Katsuura, A. Negoro, S. Hamanaka, N. Miyoshi, Y. Yamana, A. Ogawa, and N. Snoda, *J. Org. Chem.*, **56,** 3776 (1991)

[9] H. Ishihara, S. Muto, T. Endo, M. Komada, and S. Kato, *Synthesis*, 929 (1989).

[10] M. Tingoli, A. Temperini, L. Testaferri, and M. Tiecco, *Synlett*, 1129 (1995).