Tetrahedron Letters 50 (2009) 438–441

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Nucleophilic cleavage of lactones and esters with zinc selenolates prepared from diselenides in the presence of Zn/$AlCl_3$

Mohammad Nazari, Barahman Movassagh *

Department of Chemistry, K.N. Toosi University of Technology, PO Box 16315-1618, Tehran, Iran

ARTICLE INFO

Article history:
Received 15 September 2008
Revised 3 November 2008
Accepted 11 November 2008
Available online 17 November 2008

Keywords:
Lactones
Esters
Ring opening
Diselenides
Zinc selenolate

ABSTRACT

The utility of zinc selenolates for effecting nucleophilic cleavage of simple lactones and esters has been investigated. When zinc selenolate generated via Zn/$AlCl_3$-promoted cleavage of diselenides was reacted with simple lactones and esters, efficient nucleophilic alkyl–oxygen bond cleavage proceeded generating the corresponding carboxylic acids in moderate to excellent yields.

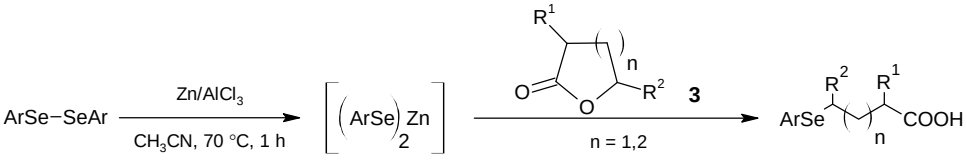
The impact of organoselenium chemistry on modern organic synthesis is undisputable.[1] Once selenium is incorporated into a substrate, it can be removed easily either via selenoxide *syn*-elimination or [2,3]-sigmatropic rearrangement. In addition, the carbon-selenium bond can be replaced by carbon–hydrogen, carbon–halogen, carbon–lithium, or carbon–carbon bonds. Thus, in general, organoselenium species can be introduced efficiently, manipulated, and removed in a variety of ways under mild reaction conditions. Also, the important roles of organoselenium in different biochemical processes as antioxidant, anticancer, and antiviral agents are well established.[2]

In spite of the fact that different methods and reagents for the introduction of organoselenium moieties have been developed, the reagent phenylselenolate ($PhSe^-$) is the most convenient organoselenium reagent and its role in effecting many synthetic transformations is known.[3–6]

Several procedures for generating selenolates have been reported,[3a,d,e,5] but most suffer from serious disadvantages such as odoriferous fumes and moisture sensitive selenium reagents, strong basic reaction conditions, and the use of hazardous organic solvents. Therefore, the development of a new synthetic procedure using stable selenium reagents under mild and neutral conditions would have significant synthetic value.

As far as we know, there are few reports using conventional methods for generating sodium phenylselenolate as a potent reagent for nucleophilic cleavage of esters and lactones.[5] However, these procedures have drawbacks such as the use of odoriferous, unstable compounds like benzeneselenol, the use of incompatible solvents such as HMPA or expensive crown ethers, and the necessity for an inert atmosphere.

In continuation of our previous work on the synthetic applications of zinc selenolates,[6] we now disclose that zinc selenolate,



Scheme 1.

* Corresponding author. Tel.: +98 21 2288 6575; fax: +98 21 2285 3650.
E-mail address: bmovass1178@yahoo.com (B. Movassagh).

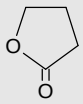
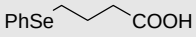
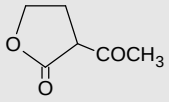
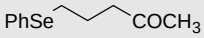
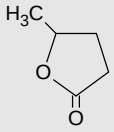
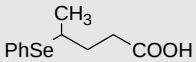
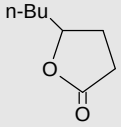
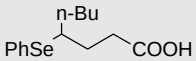
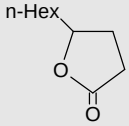
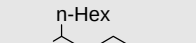
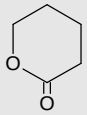
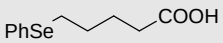
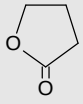
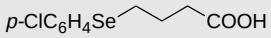
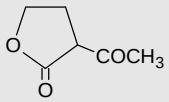
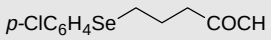
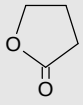
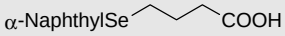
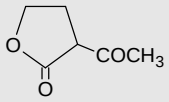
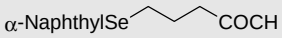
0040-4039/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2008.11.036

prepared in situ via reductive cleavage of diselenides in the presence of $Zn/AlCl_3$, is an especially effective reagent for the nucleophilic cleavage of both esters and lactones under relatively mild conditions (Scheme 1).

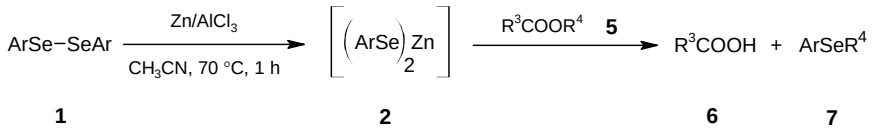
In order to optimize the reaction conditions with respect to temperature, time, and the molar ratio of the catalyst, we first studied the reaction of diphenyl diselenide with γ-butyrolactone as a model reaction in the presence of $Zn/AlCl_3$. We found that the reaction proceeded smoothly to give the corresponding γ-phenylselenylbutyric acid in a very good yield (Table 1, entry 1). With optimum conditions in hand, the reactions of various lactones were examined. Stirring a mixture of diaryl diselenide **1**, zinc dust, and anhydrous aluminum chloride in dry acetonitrile at 70 °C under aerial conditions generates zinc selenolate **2**; subsequent addition of lactone **3** gave the desired product in moderate to excellent yields.[7] The results are summarized in Table 1. Different zinc arylselenolates react with various five- and six-membered lactones very efficiently. As the size of the substituent at the carbinol carbon increases, the rate of the alkyl–oxygen cleavage process decreases (Table 1, entries 3–5) which is compatible with the S_N2 nature of the reaction.

We also examined that the viability of zinc selenolate induced nucleophilic lactone cleavage reactions with substrates containing acidic protons (Table 1, entries 2, 8, and 10). Due to the nonbasic nature of zinc selenolate,[8] no lowering of the rate of the cleavage process was observed, and the conversion of **3b** to **4b** proceeded

Table 1
Nucleophilic cleavage of lactones with zinc arylselenolates

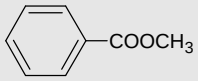
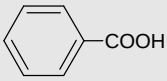
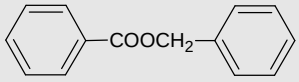
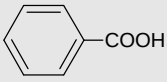
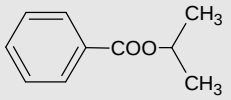
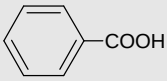
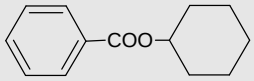
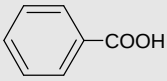
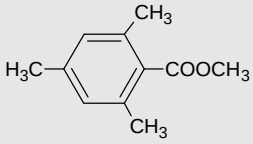
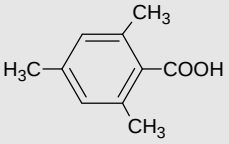
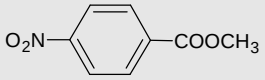
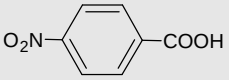
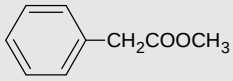
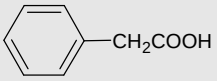
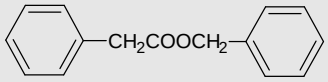
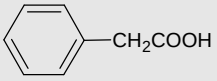
Entry	Ar	Lactone **3**	Product[a]		Time (h)	Yield[b] (%)
1	Ph			**4a**[5c]	5	87
2	Ph			**4b**[5a]	8	82
3	Ph			**4c**[5a]	24	70
4	Ph			**4d**[5c]	26	30[11a]
5	Ph			**4e**[5a]	24	29[11b]
6	Ph			**4f**[5c]	6	97
7	*p*-ClC_6H_4			**4g**	5	96
8	*p*-ClC_6H_4			**4h**	12	78
9	α-Naphthyl			**4i**	6	89
10	α-Naphthyl			**4j**	13	73

[a] References are provided for known compounds.
[b] Isolated yields.



Scheme 2.

Table 2
Nucleophilic reaction of zinc phenylselenolate with esters

Entry	Ester **5**	Product[a]		Yield (%)[b]	Time (h)
1			**6a**[12]	95	5
2			**6a**[12]	90	11
3			**6a**[12]	89	24
4			**6a**[12]	85	30
5			**6b**[12]	92	6
6			**6c**[12]	90	6
7			**6d**[12]	92	5.5
8			**6d**[12]	88	12

[a] References are provided for known compounds.
[b] Isolated yields.

with concurrent loss of carbon dioxide to yield the corresponding ketone, at a rate comparable to the conversion of **3a** to **4a**. The same activity is applicable for products **4h** and **4j**.

In another study, we investigated the utility of zinc selenolates for nucleophilic cleavage of esters (Scheme 2). Upon exposure to phenylselenolate anions, methyl esters (Table 2, entries 1 and 5–7) underwent facile alkyl–oxygen cleavage reactions, irrespective of how hindered the ester is. Excellent yields of cleavage products, carboxylic acids, were obtained, despite a large increase in the relative degree of steric hindrance around the ester. No evidence of acyl–oxygen cleavage leading to the corresponding selenol ester was observed. According to the literature, S_N2-type cleavage reactions which employ nucleophiles such as halides, amines, *tert*-butoxide, or thiocyanates usually work well only with methyl esters.[9] In contrast, selenolate anions react cleanly and in high yields with a variety of more heavily substituted esters. Thus, benzyl, cyclohexyl, and isopropyl esters (Table 2, entries 2, 8, 4, and 3, respectively) react with selenolate anions to give the corresponding acids in high yields. In addition, in all the conversions listed in Table 2 (except entries 3 and 4), the related alkyl phenyl selenide **7** was isolated in quantitative yield as a byproduct (Scheme 2).

In conclusion, we have reported a new, selective, simple, and efficient one-pot procedure for S_N2-type cleavage of lactones and esters with zinc selenolates in the presence of $Zn/AlCl_3$,[10] under atmospheric, neutral, and relatively mild reaction conditions in moderate to excellent yields. Regarding operational simplicity and cost, this method offers significant advantages over previously reported methods.[5a–c]

Acknowledgments

We thank the K. N. Toosi University of Technology Research Council and Iranian National Science Foundation (INSF, Grant No. 86063/21) for financial support of this study.

References and notes

1. (a) Back, T. G. *Organoselenium Chemistry: A Practical Approach*; Oxford University Press: Oxford, UK, 1999; (b) Liotta, D. *Organoselenium Chemistry*; Wiley: New York, 1987.
2. (a) Mugesh, G.; du Mont, W. W.; Sies, H. *Chem. Rev.* **2001**, *101*, 2125; (b) Malmstrom, J.; Jonsson, M.; Cotgreave, I. A.; Hammarstrom, L.; Sjodin, M.; Engman, L. *J. Am. Chem. Soc.* **2001**, *123*, 3434; (c) Back, T. G.; Moussa, Z. *J. Am. Chem. Soc.* **2003**, *125*, 13455; (d) Lucas, M. A.; Nagugen, O. T. K.; Schiesser, C. H.; Zheng, S. L. *Tetrahedron* **2000**, *56*, 3995.
3. (a) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 2697; (b) Sharpless, K. B.; Lauer, R. F.; Teranishi, A. Y. *J. Am. Chem. Soc.* **1973**, *95*, 6137; (c) Grieco, P. A.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1976**, *41*, 1485; (d) Zhang, Y.; Yu, Y.; Lin, R. *Synth. Commun.* **1993**, *23*, 189; (e) Suzuki, H.; Yoshinaga, M.; Takaoka, K.; Hiroi, Y. *Synthesis* **1985**, 497.
4. (a) Scarborough, R. M., Jr.; Toder, B. H.; Smith, A. B., III. *J. Am. Chem. Soc.* **1980**, *102*, 3904; (b) Smith, A. B.; Scarborough, R. M., Jr. *Tetrahedron Lett.* **1978**, 1649; (c) Meinwald, J.; Crandall, K. *J. Am. Chem. Soc.* **1966**, *88*, 1292.
5. (a) Liotta, D.; Sunay, U.; Santiesteban, H.; Markiewicz, W. *J. Org. Chem.* **1981**, *46*, 2605; (b) Liotta, D.; Markiewicz, W.; Santiesteban, H. *Tetrahedron Lett.* **1977**, 4365; (c) Liotta, D.; Santiesteban, H. *Tetrahedron Lett.* **1977**, 4369; (d) Scarborough, R. M., Jr.; Smith, A. B. *Tetrahedron Lett.* **1977**, 4361.
6. (a) Movassagh, B.; Tatar, A. *Synlett* **2007**, 1954; (b) Movassagh, B.; Mirshojaei, F. *Monatsh. Chem.* **2003**, *134*, 831; (c) Movassagh, B.; Shamsipoor, M. *Synlett* **2005**, 1316; (d) Movassagh, B.; Fazeli, A. *Z. Naturforsch.* **2006**, *61B*, 194; (e) Movassagh, B.; Shamsipoor, M.; Joshaghani, M. *J. Chem. Res. (S)* **2004**, 148; (f) Movassagh, B.; Shamsipoor, M. *Synlett* **2005**, 127; (g) Movassagh, B.; Fazeli, A. *Monatsh. Chem.* **2007**, *138*, 863.
7. *General procedure*: A mixture of diaryl diselenide (0.5 mmol), zinc dust (3.0 mmol), and dry MeCN (15 mL) was stirred at 70 °C. After 15 min, anhydrous $AlCl_3$ (2.5 mmol) in dry MeCN (2 mL) was added to the reaction mixture cautiously. The mixture was stirred for about 1 h at 70 °C until the yellow solution became colorless. Then, lactone or ester (1.05 mmol) was added to the solution, and the mixture was stirred at 70 °C for the time specified in Tables 1 and 2. The progress of the reaction was monitored by TLC. After the reaction was complete, the solution was filtered and the solvent was evaporated. Aqueous 10% HCl (30 mL) was added to the crude product which was extracted with EtOAc (3 × 30 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. Purification by preparative TLC (silica gel, eluent, *n*-hexane–EtOAc = 2:1) gave the corresponding arylselenenyl-functionalized carboxylic acid. All new compounds have been characterized by ^1H and ^{13}C NMR, IR, mass spectroscopy, and elemental analysis. Compound **4g**: mp 100–101 °C. IR (KBr) ν 1709, 2450–3500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.99 (quin, J = 7.2 Hz, 2H), 2.51 (t, J = 7.2 Hz, 2H), 2.94 (t, J = 7.3 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 11.50 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.8, 27.1, 33.5, 127.7, 129.3, 133.3, 134.2, 179.3; MS (EI): *m/z* (%) = 280 (10) $[M+4]^+$, 278 (24) $[M+2]^+$, 276 (11) $[M]^+$, 192 (21), 156 (16), 112 (24), 87 (100), 43 (44). Anal. Calcd for $C_{10}H_{11}ClO_2Se$: C, 43.27; H, 3.99. Found: C, 43.16; H, 3.83.
   Compound **4h**: IR (neat) ν 1714 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.96 (quin, J = 7.1 Hz, 2H), 2.13 (s, 3H), 2.59 (t, J = 7.0 Hz, 2H), 2.91 (t, J = 7.2 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.9, 27.5, 30.0, 42.9, 128.2, 129.2, 133.1, 134.0, 207.7; MS (EI): *m/z* (%) 278 (7) $[M+4]^+$, 276 (15) $[M+2]^+$, 274 (7) $[M]^+$, 191 (4), 156 (3), 125 (3), 85 (100), 43 (86). Anal. Calcd for $C_{11}H_{13}ClOSe$: C, 47.93; H, 4.75. Found: C, 47.83; H, 4.39.
   Compound **4i**: IR (neat) ν 1708, 2400–3500 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.01 (quin, J = 7.2 Hz, 2H), 2.53 (t, J = 7.3 Hz, 2H), 3.02 (t, J = 7.2 Hz, 2H), 7.41 (t, J = 7.7 Hz, 1H), 7.51–7.63 (m, 2H), 7.80–7.90 (m, 3H), 8.45 (d, J = 8.4 Hz, 1H), 11.41 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.0, 27.1, 33.8, 125.8, 126.3, 126.7, 127.6, 128.5, 128.7, 129.1, 132.5, 134.1, 134.4, 179.3; MS (EI): *m/z* (%) 294 (87) $[M + 2]^+$, 292 (47) $[M]^+$, 208 (38), 141 (14), 128 (100), 115 (65), 87 (67), 43 (24). Anal. Calcd for $C_{14}H_{14}O_2Se$: C, 57.35; H, 4.81. Found: C, 56.99; H, 5.03.
   Compound **4j**: IR (neat) ν 1714 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.96 (quin, J = 7.1 Hz, 2H), 2.13 (s, 3H), 2.59 (t, J = 7.1 Hz, 2H), 2.99 (t, J = 7.1 Hz, 2H), 7.40 (t, J = 7.7 Hz, 1H), 7.50–7.62 (m, 2H), 7.78–7.89 (m, 3H), 8.40 (d, J = 8.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.0, 27.5, 29.7, 43.1, 125.8, 126.2, 126.6, 127.5, 128.3, 128.7, 129.2, 132.3, 134.1, 134.3, 207.9; MS (EI): *m/z* (%) 292 (17) $[M+2]^+$, 290 (10) $[M]^+$, 207 (6), 165 (6), 141 (6), 128 (15), 115 (17), 85 (100), 43 (99). Anal. Calcd for $C_{15}H_{16}OSe$: C, 61.86; H, 5.54. Found: C, 62.17; H, 5.76.
8. Monahan, R.; Brown, D.; Waykole, L.; Liotta, D. In *Organoselenium Chemistry*; Liotta, D., Ed.; Wiley: New York, 1987.
9. (a) McMurry, J. *Org. React.* **1977**, *24*, 187; (b) Bartlett, P. A.; Johnson, W. S. *Tetrahedron Lett.* **1970**, 4459; (c) Müller, P.; Siegfried, B. *Helv. Chim. Acta* **1974**, *57*, 987.
10. In the absence of $AlCl_3$ no nucleophilic cleavage of lactones or esters was observed.
11. (a) The isolated yield was 32% after 50 h; (b) The isolated yield was 30% after 52 h.
12. Merck Catalogue, 2005–2007.