**SHORT PAPER**

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# Zn/ZrCl$_4$ system induced reductive cleavage of the Se–Se bond in diaryl diselenides: a novel method for the synthesis of β-selenoesters and β-selenonitriles[†]

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The Se–Se bond in diselenides was reduced by Zn/ZrCl$_4$ to produce selenolate anions, which react with α,β-unsaturated esters or α,β-unsaturated nitriles to afford β-selenoesters and β-selenonitriles, respectively.

**Keywords:** β-selenoesters, β-selenonitriles

Recently, organoselenium compounds have received considerable attention as useful synthetic reagents and intermediates in organic synthesis.[1–3] β-Selenoesters are useful intermediates in the synthesis of natural compounds.[4] Some methods for the preparation of β-selenoesters and β-selenonitriles have been published, for example, selenols react with α,β-unsaturated esters or α,β-unsaturated nitriles to undergo Michad reaction respectively.[5] Diaryl diselenides react with α,β-unsaturated esters or α,β-unsaturated nitriles using NaBH$_4$[6] or SmI$_2$[7] as reductant, or with carbon monoxide and water using selenium under high pressure and high temperature.[8]

These methods have been applied to the synthesis of β-selenoesters. Unfortunately most of them suffer from significant drawbacks, which include strong base, high pressure and high temperature, and expensive starting materials. Therefore, we strive to look for other reagents to overcome these problems.

As an efficient, inexpensive high reactivity reagent, zinc has been employed in Barbier type reactions,[9] reductive coupling reactions[10] and Reformatsky reactions.[11] However to the best of our knowledge, there has been few reports on the application of zinc in the preparation of β-selenoesters. Herein we wish to report that reductive cleavage of Se–Se bond in diselenides by the Zn/ZrCl$_4$ system led to selenolate anions, which react with α,β-unsaturated esters or α,β-unsaturated nitriles to afford β-selenoesters in moderate yields in THF under mild and neutral conditions.

$$\mathrm{ArSeSeAr}\xrightarrow[40^\circ\mathrm{C}\ 5\mathrm{h}]{\mathrm{Zn/ZrCl_4}}[\mathrm{ArSe^-}]\xrightarrow{\mathrm{CH_2{=}C(R)X}}\mathrm{ArSeCH_2CH(R)X}$$

**Scheme 1**

**Table 1**

| Entry | Ar | R | X | Reaction times/t | Yield/%[a] |
|---|---|---|---|---|---|
| 1 | Ph | H | $CO_2Me$ | 3 | 62 |
| 2 | Ph | H | $CO_2Et$ | 3 | 67 |
| 3 | Ph | H | $CO_2$Bu-n | 3 | 62 |
| 4 | Ph | H | CN | 3 | 65 |
| 5 | Ph | $CH_3$ | $CO_2Me$ | 3 | 55 |
| 6 | *o*-$CH_3C_6H_4$ | H | $CO_2Me$ | 3 | 61 |
| 7 | *o*-$CH_3C_6H_4$ | H | $CO_2Et$ | 3 | 69 |
| 8 | *o*-$CH_3C_6H_4$ | H | $CO_2$Bu-n | 3 | 60 |
| 9 | *o*-$CH_3C_6H_4$ | H | CN | 3 | 63 |
| 10 | *o*-$CH_3C_6H_4$ | $CH_3$ | $CO_2Me$ | 3 | 52 |

[a]Isolated yields.

## Experimental

Melting points were uncorrected. IR spectra were obtained on a PE-683 infrared spectrophotometer. $^1$H NMR spectra were recorded on a PMX-60MHz instrument. All NMR samples were measured in CCl$_4$ using TMS as internal standard. Metallic zinc was activated before using. The solvent THF was freshly distilled from sodium/benzophenone ketyl prior to use. The reactions were performed in a Schlenk type glass apparatus under a dinitrogen atmosphere.

### General procedure

Under an inert atmosphere of dinitrogen, zinc powder (1.5 mmol, 0.1 g), zirconium(IV) chloride (0.2 mmol, 0.05 g) and diaryl diselenides (0.5 mmol) was placed in a well-dried, two neck, round bottom flask containing a magnetic stirrer bar. Freshly distilled, dry THF (10 ml) was added through a rubber septum by a syringe. The resulting mixture was stirred at 40°C for about 5h, the green solution became grey-white, which indicates the cleavage of the Se–Se bond and the generation of selenoate anions. Then α,β-unsaturated esters (1.5mmol) or α,β-unsaturated nitriles (1.5 mmol) in THF (1 ml) and *n*-BuOH (1 mmol) were added by a syringe to the mixture and stirred for given times (see Table 1, TLC as monitored). Then the whole solution was poured into dilute HCl (1.2 mol/l, 20 ml) and the mixture was extracted with ether (15 ml × 3). The organic layer was washed with saturated NaCl and dried over anhydrous Na$_2$SO$_4$. The solvent was removed under reduced pressure, the residue was then purified by preparative TLC on silica gel (light petroleum: ether = 5:1 as eluent). Some results were summarised in Table 1.

In summary, a novel method for the preparation of β-selenoesters has been provided, the advantages of which are easily available and cheap materials, single product, simple manipulation, and mild and neutral conditions.

### Data of products

**1**:[8] Oil, PhSeCH$_2$CH$_2$CO$_2$Me, $^1$H NMR 7.10–7.60 (5H, m), 3.53 (3H, s), 2.90 (2H, t), 2.66 (2H, t); $\upsilon_{max}$(cm$^{-1}$), 3060, 2926, 2855, 1741, 1576, 1469, 1335, 1283, 1230, 1172, 1134, 1032, 748, 692.

**2**:[8] Oil, PhSeCH$_2$CH$_2$CO$_2$Et, $^1$H NMR 7.07–7.70 (5H, m), 4.00 (2H, q), 2.97 (2H, t), 2.63 (2H, t), 1.67 (3H, t); $\upsilon_{max}$(cm$^{-1}$). 3058, 2926, 2854, 1738, 1579, 1478,1438, 1371, 1339, 1283, 1220, 1164, 1130, 1022, 918, 737, 692.

**3**:[8] Oil, PhSeCH$_2$CH$_2$CO$_2$Bu-n, $^1$H NMR 7.03–7.60 (5H, m) 3.97 (2H, t), 2.97 (2H, t), 2.60 (2H, t), 1.20–1.60 (6H, m), 0.90 (3H, t); $\upsilon_{max}$(cm$^{-1}$), 3060, 2926, 2854, 1742, 1464, 1378, 1285, 1176, 1100, 1032, 754, 694.

**4**:[8] Oil, PhSeCH$_2$CH$_2$CN, $^1$H NMR 7.06–7.60 (5H, m), 2.93 (2H, t), 2.53 (2H, t); $\upsilon_{max}$(cm$^{-1}$), 3045, 2925, 2854, 2249,

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

1577, 1476, 1438, 1303, 1266, 1203, 1071, 1022, 1000, 935, 891, 739, 691.

**5**:[8] Oil, $PhSeCH_2CH(CH_3)CO_2Me$, $^1H$ NMR 7.03–7.60 (5H, m), 3.50 (3H, s), 3.00 (2H, d), 2.50–2.80 (1H, m), 1.15 (3H, d); $\upsilon_{max}(cm^{-1})$, 3058, 2954, 2927, 2855, 1744, 1579, 1458, 1377, 1272, 1202, 1087, 1022, 979, 953, 761, 692.

**6**:[12] Oil, $o$-$CH_3C_6H_4SeCH_2CH_2CO_2Me$, $^1H$ NMR 7.10–7.60 (4H, m), 3.53 (3H, s), 2.93 (2H, t), 2.57 (2H, t), 2.33 (3H, s); $\upsilon_{max}(cm^{-1})$, 3060, 2985, 2925, 2854, 1741, 1523, 1437, 1348, 1224, 1165, 1037, 980, 810, 746, 658.

**7**:[12] Oil, $o$-$CH_3C_6H_4SeCH_2CH_2CO_2Et$, $^1H$ NMR 6.93–7.43 (4H, m), 4.00 (2H, q), 2.93 (2H, t), 2.56 (2H, t), 2.33 (3H, s), 1.16 (3H, t); $\upsilon_{max}(cm^{-1})$, 3061, 2985, 2925, 2854, 1739, 1592, 1466, 1371, 1339, 1283, 1221, 1161, 1132, 1097, 1037, 862, 745, 658.

**8**:[12] Oil, $o$-$CH_3C_6H_4SeCH_2CH_2CO_2Bu$-n, $^1H$ NMR 6.96–7.50 (4H, m), 3.93 (2H, t), 2.56 (2H, t), 2.33 (2H, s), 1.30–1.60 (4H, m), 1.00 (3H, t); $\upsilon_{max}(cm^{-1})$, 3050, 2960, 2936, 2874, 1736, 1637, 1476, 1408, 1380, 1342, 1296, 1193, 1065, 1037, 810, 746.

**9**:[12] Oil, $o$-$CH_3C_6H_4SeCH_2CH_2CN$, $^1H$ NMR 6.93–7.40 (4H, m), 2.87 (2H, t ), 2.47 (2H, t), 2.33 (3H, s); $\upsilon_{max}(cm^{-1})$, 3050, 2957, 2924, 2954, 2240, 1464, 1378, 1310, 1285, 1150, 1070, 980, 942, 810, 775.

**10**:[12] Oil, $o$-$CH_3C_6H_4SeCH_2CH(CH_3)CO_2Me$, $^1H$ NMR 6.93–7.40 (4H, m), 3.50 (3H, s), 2.97 (2H, d), 2.50–2.80 (1H, m), 2.33 (3H, s), 1.15 (3H, d); $\upsilon_{max}(cm^{-1})$, 3059, 2985, 2926, 2854, 1747, 1591, 1422, 1378, 1273, 1203, 1088, 1036, 980, 953, 833, 747, 658.

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## References

1 H.T. Peich, *Acc. Chem. Res.*, 1979, **12**, 22.
2 S. Kato, T. Murai and M. Masura, *Org. Prep. Proced. Int.*, 1986, **18**, 369.
3 L.T. Perrick, *Tetrahedron*, 1978, **34(8)**, 1049.
4 P.A. Griceo, Y. Yokoyama and E. Williams, *J. Org. Chem.*, 1978, **43**, 1283.
5 E.G. Kataev and F.G. Gabdrakhmanav, *Zh. Obshch. Khim.*, 1967, **37**, 772.
6 M. Miyashita and A.Yoshikashi, *Synthesis*, 1980, **8**, 664.
7 H. Jiang and Y. Zhang, *Hecheng Huaxue*, 1993, **3**, 248.
8 A. Ogawa, Y. Nishiyama, N. Kambe, S. Murai and N. Sonoda, *Tetrahedron Lett.*, 1987, **28**, 3271.
9 (a) Y.S. Cho, J.E. Lee, A.N. Pae, K.I. Choi and H.Y. Koh, *Tetrahedron Lett*., 1999, **40**, 1725; (b) J.L. Renaud, C. Aubert and M. Malacria, *Tetrahedron Lett.*, 1999, **40**, 5015; (c) L.W. Bieber, M.F. Silva, R.C. Costa and L.O.S. Silva, *Tetrahedron Lett*., 1998, **39**, 3655; (d) F. Rubasam, S. Seek and A. Giannis, *Tetrahedron*, 1997, **52**, 2823. (e) D. Wang, L. Dai, X. Hou, and Y. Zhang, *Tetrahedron Lett*., 1996, **37**, 4187; (f) Z. Wang, and G.B. Hammond, *Tetrahedron Lett*., 2000, **41**, 2339; (g) S.H. Kim and E. H. Ham, *Tetrahedron Lett.*, 2000, **41**, 6479.
10 (a) T.C. Handa and J.J. Inanaga, *Tetrahedron Lett*., 1987, **28**, 5717; (b) J.E. McMurry, Chem. Rev., 1989, **89**, 1513; (c) D.K. Dutta and D. Konwar, *Tetrahedron Lett.*, 2000, **41**, 6227; (d) J. Chen, J. Li, M. Yu and W. Chen, Org. *Prep. Proced. Int.*, 1997, **29**, 569; (e) J.H. So, M.K. Park and P. Boudjouk, *J. Org. Chem.*, 1988, **53**, 5871; (f) T.A. Lioaki, M.A. Hilfiker and S. Nelson, *J. Org. Chem.*, 1997, **62**, 4566.
11 (a) O. Kitagawa, T. Takeo and Y. Kobayashi, *Tetrahedron Lett.*, 1988, **29**, 1803; (b) Kyoung Soon Kim Ligang Qian, *Tetrahedron Lett*., 1993, **34**, 7195; (c) Jose M Andres, Refael Pedrosa and Alfonso Perez-Encabo, *Tetrahedron*, 2000, **56**, 1217.
12 S. Zhang and Y. Zhang, *Chinese Chem. Lett.*, 1998, **9**, 885.