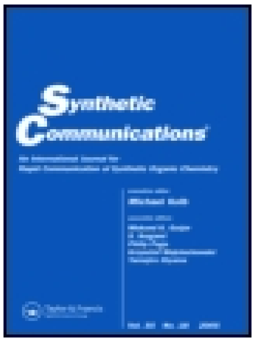

Synthetic Communications

ISSN: 0039-7911 (Print) 1532-2432 (Online) Journal homepage: http://www.tandfonline.com/loi/lsyc20

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To cite this article: Ping Zhong , Zhi-Xing Xiong & Xian Huang (2000) A Stereoselective Synthetic Route to (E)-α,β-Unsaturated Selenoesters, Synthetic Communications, 30:5, 887-893, DOI: 10.1080/00397910008087101

To link to this article: http://dx.doi.org/10.1080/00397910008087101

SYNTHETIC COMMUNICATIONS, 30(5), 887–893 (2000)

A STEREOSELECTIVE SYNTHETIC ROUTE TO (*E*)-α,β-UNSATURATED SELENOESTERS

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ABSTRACT: Terminal alkynes **1** react with $Cp_2Zr(H)Cl$ ($Cp = \eta^5$-C_5H_5) and CO to give acylzirconocene chloride derivatives **2**, which are trapped with diaryldiselenides to afford (*E*)-α,β-unsaturated selenoesters.

Selenoesters have attracted much attention as effective precursors of acyl radicals for use in both intra[1] and intermolecular[2] addition of acyl radicals to carbon-carbon multiple bonds. However, there are only a few reports on the preparation of α,β-unsaturated selenoesters[3-6].

Recently, it has become popular to transform acylzirconocene chlorides to other functional groups. It was reported that Lewis acid-mediated reaction of acylzirconocene chlorides with aldehydes afforded α-ketol derivatives.[7] Coupling reactions of acylzirconocene chlorides with organic halides afforded

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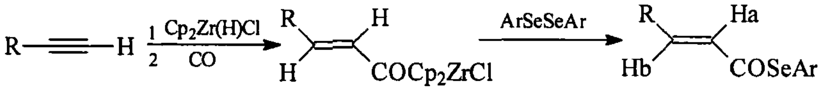
corresponding ketones.[8] Considering the high electrophility of diaryldiselenide, we attempted to react them with the α,β-unsaturated acylzirconocene chlorides **2**. Experimental results show that, $Cp_2Zr(H)Cl$[9] adds to terminal alkynes **1** in CH_2Cl_2 at room temperature stereospecifically with high regioselectivity to yield vinylic Zr^{IV} complex which was stirred under CO atmosphere to give the α,β-unsaturated acylzirconocene chlorides **2**. **2** reacts with diaryldiselenide[10] at room temperature to afford α,β-unsaturated selenoesters **3**. Yields are moderate to good (Scheme 1 and Table 1).



1 **2** **3**

R = Ph, $4\text{-}ClC_6H_4$, $4\text{-}BrC_6H_4$, $n\text{-}C_4H_9$, $n\text{-}C_5H_{11}$;
Ar = Ph, $4\text{-}MeC_6H_4$, $4\text{-}ClC_6H_4$, $4\text{-}Br\ C_6H_4$

Scheme 1

The compounds **3a**,[4] **3b**,[11] **3c**,[11] **3d**, **3e**, **3f**,[11] **3g**, **3h**, **3i**, **3j**, **3k** and **3l** were purified by preparative TLC on silica gel and fully characterized by MS, ^1H NMR and IR spectroscopy. The stereochemistry of the α,β-unsaturated selenoesters was easily established. The ^1H NMR spectroscopy of products **3a-l** gave rise to a doublet (or dt) at 6.80-7.70 (H_b) with a coupling constant ca. 16 Hz typical of *trans* positioned protons.[4]

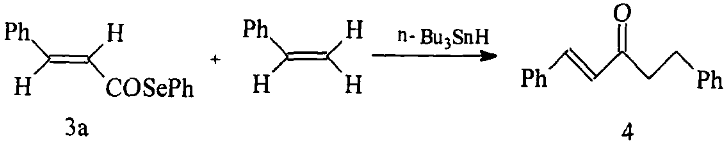
α,β-Unsaturated selenoesters **3** have recently emerged as valuable reagents for organic synthesis.[1,2] For example, selenoesters **3a** was transformed into (*E*)-1,5-

Table 1 Synthesis of Compounds **3a-l**

Compound	R	Ar	Mp/°C	Yield(%)[a]
3a	Ph	Ph	80-81	76
3b	4-ClC_6H_4	Ph	99-100	74
3c	4-BrC_6H_4	Ph	111-112	71
3d	n-C_4H_9	Ph	oil	58
3e	n-C_5H_{11}	Ph	oil	51
3f	Ph	4-MeC_6H_4	84-85	63
3g	n-C_4H_9	4-MeC_6H_4	oil	53
3h	n-C_5H_{11}	4-MeC_6H_4	oil	57
3i	Ph	4-ClC_6H_4	93-94	65
3j	n-C_4H_9	4-ClC_6H_4	oil	54
3k	n-C_5H_{11}	4-ClC_6H_4	oil	61
3l	Ph	4-BrC_6H_4	119-120	74

[a] Isolated yield.

dipheneyl-1-penten-3-one **4**[12] in 70 % yield by treatment with styrene in the presence of n-Bu_3SnH. (Scheme 2)



Scheme 2

In conclusion, the acylation reaction of diaryldiselenide with α,β-unsaturated acylzirconocene chlorides provides a direct route to (*E*)-α,β-unsaturated selenoesters from terminal alkynes. The method has some attractive advantages such as ready availability of starting materials, high yields, mild reaction conditions, simple procedure, shorter reaction time and high regio- and stereoselectivity.

EXPERIMENTAL

^1H NMR spectra were recorded on AZ-300 spectrometer with TMS as internal standard. Mass spectra were obtained on Finigan 8230 mass spectrometer. IR spectra were determined on PE-683 instrument as neat films. All reactions were carried out in pre-dried glassware (140 °C, 4 h) and cooled under a stream of dry nitrogen. All solvents were dried, deoxygenated and redistilled before use.

General procedure for the synthesis of 3a-l: Under nitrogen atmosphere, to a suspension of $Cp_2Zr(H)Cl$ (1.5 mmol) in CH_2Cl_2 (10 ml) was added terminal alkynes **1** (3 mmol) and the mixture was stirred at room temperature for 30 min to yield a clear solution. After the mixture was stirred under CO atmosphere for 2 h, into the resulting solution was added diaryldiselenide (1 mmol) at room temperature and the mixture was stirred for 1 h. The solvent was removed by rotary evaporator under reduced pressure. The residue was extracted with low boiling petroleum ether (3 × 6 ml) and filtered through a short plug of silica gel. After evaporation of the filtrate, the residue was purified by preparative TLC on silica gel eluting with CCl_4.

3a: a pale yellow solid, Mp 80-81 °C (lit.[4] 81 °C). IR (KBr): ν/cm^{-1} 1700, 1620; $\delta_H(CDCl_3)$: 7.50 (d, J=15.7Hz, 1H, *H*C=), 7.25-7.55 (m, 10H, Ph), 6.60 (d, J=15.7Hz, 1H, *H*C=); MS: *m/z* 288 (M^+, 0.5), 131 (M - SePh, 100), 103 (41), 77 (28), 57 (68 %).

3b: a pale yellow solid, Mp 99-100 °C (lit.[11] 98-100 °C). IR (KBr): ν/cm^{-1} 1685, 1615; δ_H $(CDCl_3)$: 7.55 (d, J=16Hz, 1H, *H*C=), 7.20-7.60 (m, 9H, Ph), 6.70 (d, J=16Hz, 1H, *H*C=); MS: *m/z* 324 (M + 2, 1.2), 322 (M^+, 2), 165 (M - SePh, 100), 103 (30), 77 (23 %).

3c: a pale yellow solid, Mp 111-112 °C (lit.[11] 110-112 °C). IR (KBr): ν/cm^{-1} 1685, 1614; δ_H ($CDCl_3$): 7.55 (d, J=16Hz, 1H, *H*C=), 7.20-7.60 (m, 9H, Ph), 6.70 (d, J=16Hz, 1H, *H*C=); MS: *m/z* 368 (M + 2, 1.1), 366 (M^+, 0.8), 209 (M - SePh, 100), 103 (34), 77 (26 %).

3d: a pale yellow oil, IR(film): ν/cm^{-1} 1690, 1640; δ_H ($CDCl_3$): 7.10-7.40 (m, 5H, Ph), 6.76 (dt, J_d = 16 Hz, J_t = 6.5 Hz , 1H, *H*C=), 6.00 (d, J = 16 Hz ,1H, *H*C=), 2.25 (m, 2H), 0.80 - 1.60 (m, 7H); MS: *m/z* 268 (M^+, 0.9), 111 (M - SePh, 100), 55 (45 %).Calc. for $C_{13}H_{16}OSe$: C, 58.43; H, 6.03.Found: C, 58.71; H, 6.07 %.

3e: a pale yellow oil, IR(film): ν/cm^{-1} 1705, 1640; δ_H ($CDCl_3$): 7.05-7.50 (m, 5H, Ph), 6.80 (dt, J_d = 16 Hz, J_t = 6.5 Hz , 1H, *H*C=), 6.03 (d, J = 16 Hz ,1H, *H*C=), 2.15 (m, 2H), 0.70 - 1.60 (m, 9H); MS: *m/z* 283 (M + 1, 9.3), 282 (M^+, 1.2), 125 (M - SePh, 100), 55 (15 %). Calc. for $C_{14}H_{18}OSe$: C, 59.79; H, 6.45.Found: C, 59.45; H, 6.43 %.

3f: a pale yellow solid, Mp 84-85 °C (lit.[11] 83-85 °C). IR (KBr): ν/cm^{-1} 1688, 1620; δ_H ($CDCl_3$): 7.60 (d, J=16Hz, 1H, *H*C=), 7.20-7.60 (m, 9H, Ph), 6.70 (d, J=16Hz, 1H, *H*C=); 2.16 (s, 3H, C*H*$_3$); MS: *m/z* 302 (M^+, 35), 211 (M – 4-MeC_6H_4, 6.8), 131 (M - 4-MeC_6H_4Se, 100), 91 (54), 55 (27 %).

3g: a pale yellow oil, IR(film): ν/cm^{-1} 1690, 1640; δ_H ($CDCl_3$): 7.20-7.40 (m, 4H, C_6H_4), 6.80 (dt, J_d = 16 Hz, J_t = 6.5 Hz , 1H, *H*C=), 6.05 (d, J = 16 Hz ,1H, *H*C=), 2.26 (s, 3H, C*H*$_3$), 2.20 (m, 2H), 0.80 - 1.60 (m, 7H); MS: *m/z* 282 (M^+, 4.2), 111 (M - 4-MeC_6H_4Se, 100), 109 (13), 55 (50 %). Calc. for $C_{14}H_{18}OSe$: C, 59.79; H, 6.45. Found: C, 60.03; H, 6.47 %.

3h: a pale yellow oil, IR(film): ν/cm^{-1} 1700, 1640; δ_H ($CDCl_3$): 7.10-7.40 (m, 4H, C_6H_4), 7.00 (dt, J_d = 16 Hz, J_t = 6.5 Hz , 1H, *H*C=), 6.00 (d, J = 16 Hz ,1H, *H*C=), 2.28 (s, 3H, C*H*$_3$), 2.25 (m, 2H), 0.80 - 1.60 (m, 9H); MS: *m/z* 297 (M + 1, 20.4), 125 (M - 4-MeC$_6$H$_4$Se, 100), 89 (3.2), 55 (18.8 %). Calc. for $C_{15}H_{20}OSe$: C, 61.01; H, 6.83. Found: C, 60.83; H, 6.87 %.

3i: a pale yellow solid, Mp 93-94 °C (from methanol). IR (KBr): ν/cm^{-1} 1700, 1630, 1485; δ_H (CDCl$_3$): 7.48 (d, J=16Hz, 1H, *H*C=), 7.00-7.45 (m, 9H, Ph), 6.58 (d, J=16Hz, 1H, *H*C=); MS: *m/z* 322 (M$^+$, 0.1), 131 (M - 4-ClC$_6$H$_4$Se, 100), 103 (41), 77 (22 %). Calc. for $C_{15}H_{11}ClOSe$: C, 56.01; H, 3.45. Found: C, 56.32; H, 3.47 %.

3j: a pale yellow oil, IR(film): ν/cm^{-1} 1700, 1640; δ_H (CDCl$_3$): 7.00-7.35 (m, 4H, Ph), 6.70 (dt, J_d = 16 Hz, J_t = 6.5 Hz , 1H, *H*C=), 6.00 (d, J = 16 Hz ,1H, *H*C=), 2.20 (m, 2H), 0.90 - 1.55 (m, 7H); MS: *m/z* 302 (M$^+$, 0.6), 111 (M – 4-ClC$_6$H$_4$Se, 100), 55 (43 %).Calc. for $C_{13}H_{15}ClOSe$: C, 51.76; H, 5.01.Found: C, 51.99; H, 5.04 %.

3k: a pale yellow oil, IR(film): ν/cm^{-1} 1700, 1600; δ_H (CDCl$_3$): 6.95-7.30 (m, 4H, Ph), 6.65 (dt, J_d = 16 Hz, J_t = 6.5 Hz, 1H, *H*C=), 6.00 (d, J = 16 Hz, 1H, *H*C=), 2.10 (m, 2H), 0.90 - 1.50 (m, 9H); MS: *m/z* 316 (M$^+$, 0.8), 125 (M - 4-ClC$_6$H$_4$Se, 100), 55 (56 %). Calc. for $C_{14}H_{17}ClOSe$: C, 53.26; H, 5.43. Found: C, 53.52; H, 5.41 %.

3l: a pale yellow solid, Mp 119-120 °C (from methanol). IR (KBr): ν/cm^{-1} 1695, 1650, 1570; δ_H (CDCl$_3$): 7.72 (d, J=16.2 Hz, 1H, *H*C=), 7.10-7.55 (m, 9H, Ph), 6.33 (d, J=16.2 Hz, 1H, *H*C=); MS: *m/z* 368 (M + 2, 3), 131 (M - 4-BrC$_6$H$_4$Se, 100), 103 (37), 77 (27), 55 (42 %). Calc. for $C_{15}H_{11}BrOSe$: C, 49.21; H, 3.03. Found: C, 49.02; H, 3.04 %.

The synthesis of (*E*)-1,5-diphenyl-1-penten-3-one 4: To a solution of compound **3a** (1 mmol) in CH$_2$Cl$_2$ (8 ml) was added styrene (1 mmol) and n-Bu$_3$SnH (1 mmol). After the mixture being stirred at room temperature for 4 h, it was purified by preparative TLC on silica gel eluting with light petroleum and ether (10 : 1) to afford the compound **4** in 7 %.

4: a pale yellow solid, Mp 53-54 °C (lit.[13] 54-54.5 °C); IR (KBr): ν/cm^{-1} 1685, 1615, 1500; δ_H(CDCl$_3$): 7.50 (d, J=16Hz, 1H, *H*C=), 7.30-7.10 (m, 10H, Ph), 6.55 (d, 1H, J=16Hz, 1H, *H*C=), 3.10 (t, J=7.6 Hz, 2H), 2.70 (t, J=7.6 Hz, 2H); Calc. for $C_{17}H_{16}O$: C, 86.41; H, 6.82; Found: C, 86.67; H, 6.85 %.

Acknowledgment: Project 29772007 was supported by the National Nature Science Foundation of China and this work was also supported by The National Nature Science Foundation of Zhejiang Province.

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(Received in Japan 7 June 1999)