J. Chem. Research (S),
1999, 634–635†

Synthesis of α,β-Unsaturated Selenoesters by the Reaction of Acylzirconene Chlorides with ArSeBr†

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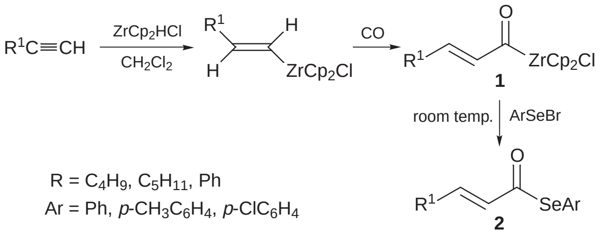
α,β-Unsaturated selenoesters are prepared in good yields by the reaction of ArSeBr with acylzirconene chlorides.

Selenoesters are useful synthetic intermediates having been employed,[1] for example, as mild acyltransfer reagents,[2] building blocks for heterocyclic compounds (axaze)[3] and precursors of acyl radicals.[4] Recently we have revealed that the selenocarbonylation addition reaction of selenoesters to nonactivated terminal alkynes under the catalysis of CuX produces (*Z*) arylseleno α,β-unsaturated ketones in high selectivity and high yields.[5] In addition, Byeon[6] reported that α,β-unsaturated selenoesters served as dienophiles in Diels–Alder reactions with a variety of 1,3-dienes with reverse regioselectivity. In contrast to their growing utility in organic synthesis, the preparative methods are limited: they have usually been prepared by conventional methods based on the reaction of selenolate anions with carboxylic acids and their derivatives,[7] and other methods, such as alkylation of selenocarboxylates,[8] reaction of carboxylic acid with tributylphosphine,[9] $Co_2(CO)_8$ mediated carbonylation of diselenides,[10] reaction of esters or aldehydes with $Bu^n_2AlSeBu^n$.[11]

As an extension of our study on the addition of selenoesters to terminal acetylene, we needed a practical and convenient preparative method for selenoesters other than arylselenoester sources. Here we report a new convenient synthesis of α,β-unsaturated selenoesters from the reaction of acylzirconene chlorides with the electrophilic selenium bromides (ArSeBr) as shown in Scheme 1.



Scheme 1

Acylzirconene chloride derivatives **1**, which are used as an "unmasked" acyl anion for organic synthesis, can be conveniently prepared through sequential treatment of alkynes with zirconene hydrochloride (Schwarts reagent) and carbon monoxide.[12] Here, we have investigated the reactivity of **1** with ArSeBr. When **1** was added to ArSeBr in CH_2Cl_2, the α,β-unsaturated carboxylate selenoesters **2** were obtained immediately (see Table 1).

As the data in Table 1 show this method affords a variety of α,β-unsaturated selenoesters in good yield and more importantly the reaction can be performed rapidly at room temperature. The configuration of the products could be confirmed by the analysis of the coupling constant data in the ^1H NMR spectra ($J = 16-17$ Hz). Only the *E* isomer was observed due to the hydrozirconation and insertion reaction of CO with retention of configuration

In conclusion, a new convenient synthetic method for α,β-unsaturated selenoesters has been developed by the reaction of acylzirconene chlorides with ArSeBr. Compared to other reported methods, this method has the advantages of mild reaction conditions, available reagents, high yield and a lower reaction time. Further work on addition of α,β-unsaturated selenoesters to terminal acetylenes is in progress.

Experimental

^1H NMR spectra were recorded on PMX-60 spectrometer using $CDCl_3$ as the solvent with TMS as an internal standard. *J* Values are given in Hz. IR spectra were obtained on a PE-683 spectrophotometer. Mass spectra were obtained on an HP 5989A spectrometer. Melting points were uncorrected. Elemental analyses were conducted using a Yanaco MT-3CHN elemental analyser. All reactions were carried out in pre-dried glassware (150 °C, 4 h) and cooled under a stream of dry nitrogen. CH_2Cl_2 was distilled over CaH_2.

General Procedure for the Synthesis of **2a**–**2i**.—To a suspension of $[Cp_2ZrHCl]$ (512 mg, 2.0 mmol) in CH_2Cl_2 (8 ml) was added terminal acetylene (2.0 mmol), and the resulting mixture was stirred for 30 min at ambient temperature. After the mixture had been stirred under an atmosphere of CO for 2 h the mixture was added to ArSeBr[13] (2.0 mmol) in CH_2Cl_2 *via* syringe at room temperature and stirred for 10 min. After reaction, the mixture was treated with aqueous NH_4Cl and extracted with ether (3 × 10 ml), the combined ethereal extracts were dried over $MgSO_4$ and concentrated under reduced pressure, the crude product was purified by preparative TLC on silica gel using CCl_4 as eluant.

2a: Oil. ν_{max}/cm^{-1}: 1709 (C=O). δ_H 0.82–1.70 (7H, m, $CH_2CH_2CH_3$), 2.25 (2H, m, CH_2), 6.06 (1H, d, *J* 16 Hz), 6.80 (1H, dt, *J* 16, 6.5 Hz), 7.15–7.50 (5H, m, C_6H_5). MS(EI) *m/z*: 269 (M + 1, 5%), 111 (M − SePh, 100%). Found: C, 58.39; H, 6.07. Calc. for $C_{13}H_{16}OSe$: C, 58.43; H, 6.03%.

2b: Oil. ν_{max}/cm^{-1}: 1720 (C=O). δ_H 0.80–1.70 (7H, m, $CH_2CH_2CH_3$), 1.90–2.30 (2H, m, CH_2), 6.00 (1H, d, *J* 16.3 Hz), 6.90 (1H, dt, *J* 16.3, 6.5 Hz), 7.35 (4H, m, C_6H_4). MS(EI) *m/z*: 303 (M + 1, 2%), 111 (M − *p*-ClPhSe), 100%). Found: C, 51.63; H, 4.97. Calc. for $C_{13}H_{15}ClOSe$: C, 51.76; H, 5.01%.

Table 1 Synthesis of α,β-unsaturated selenoesters **2a**–**2i**

Products	R¹	Ar	Yields[a] (%)
2a	C_4H_9	C_6H_4	75
2b	C_4H_9	*p*-ClC_6H_4	79
2c	C_4H_9	*p*-$CH_3C_6H_5$	82
2d	C_5H_{11}	C_6H_4	83
2e	C_5H_{11}	*p*-$CH_3C_6H_4$	76
2f	C_5H_{11}	*p*-ClC_6H_4	84
2g	Ph	C_6H_4	84
2h	Ph	*p*-$CH_3C_6H_4$	80
2i	Ph	*p*-ClC_6H_4	85

[a] Isolated yields based on ArSeBr.

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† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

2c: Oil. ν_{max}/cm^{-1}: 1700 (C=O). δ_H 0.80–1.70 (7H, m, $CH_2CH_2CH_3$), 1.87–2.45 (5H, m), 6.10 (1H, d, J 16 Hz), 6.90 (1H, dt, J 16, 6.5 Hz), 7.20 (4H, m, C_6H_4). MS(EI) m/z: 283 (M + 1, 1.3%), 111 (M−p-CH_3PhSe, 100%). Found: C, 59.82; H, 6.41. Calc. for $C_{14}H_{18}OSe$: C, 59.79; H, 6.45%.

2d: Oil. ν_{max}/cm^{-1}: 1703 (C=O). δ_H 0.67–1.67 (9H, m, $CH_2CH_2CH_2CH_3$), 2.05 (2H, m, CH_2), 6.04 (1H, d, J 16 Hz), 6.84 (1H, dt, J 16, 6.5 Hz), 7.34 (5H, m, C_6H_5). MS(EI) m/z: 283 (M + 1, 5%), 125 (M−PhSe, 100%). Found: C, 59.87; H, 6.41. Calc. for $C_{14}H_{18}OSe$: C, 59.79; H, 6.45%.

2e: Oil. ν_{max}/cm^{-1}: 1705 (C=O). δ_H 0.67–1.67 (9H, m, $CH_2CH_2CH_2CH_3$), 1.86–2.45 (5H, m, $CH_2 + CH_3$), 6.03 (1H, d, J 16 Hz), 6.87 (1H, dt, J 16, 7.0 Hz), 7.20 (4H, m, C_6H_4). MS(EI) m/z: 297 (M + 1, 6.5%), 125 (M−p-CH_3PhSe, 100%). Found: C, 60.86; H, 6.75. Calc. for $C_{15}H_{20}OSe$: C, 61.01; H, 6.83%.

2f: Oil. ν_{max}/cm^{-1}: 1717 (C=O). δ_H 0.67–1.67 (9H, m, $CH_2CH_2CH_2CH_3$), 2.10 (2H, m, CH_2), 6.03 (1H, d, J 16 Hz), 6.87 (1H, dt, J 16, 7.0 Hz), 7.36 (4H, m, C_6H_4). MS(EI) m/z: 317 (M + 1, 1.5%), 125 (M − p-ClPhSe), 100%). Found: C, 53.13; H, 5.36. Calc. for $C_{14}H_{17}ClOSe$: C, 53.26; H, 5.43%.

2g: Mp 79–81 °C (lit[14] 79–91 °C). ν_{max}/cm^{-1}: 1700 (C=O). δ_H 6.70 (1H, d, J 16 Hz), 7.30–7.73 (11H, m, $C_6H_5 + C_6H_5 + 1H$).

2h: Mp 83–85 °C (lit[14] 83–85 °C). ν_{max}/cm^{-1}: 1709 (C=O). δ_H 2.33 (3H, s, CH_3), 6.60 (1H, d, J 16.5 Hz), 7.15–7.5 (10H, m, $C_6H_4 + C_6H_5 + 1H$).

2i: Mp 92–94 °C. ν_{max}/cm^{-1}: 1709 (C=O). δ_H 6.43 (1H, d, J 16.5 Hz), 7.30–7.70 (10H, m, $C_6H_4 + C_6H_5 + 1H$). MS(EI) m/z: 323 (M + 1, 1%), 131 (M − p-ClPhSe), 100%). Found: C, 55.91; H, 3.37. Calc. for $C_{15}H_{11}ClOSe$: C, 56.01; H, 3.45%.

Received, 28th June 1999; Accepted, 15th July 1999
Paper E/9/05158I

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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