SHORT PAPER

J. Chem. Research (S),
2000, 118–119

Synthesis of α, β-unsaturated tellurolesters by the reaction of acylzirconocene chlorides with ArTeI[†]

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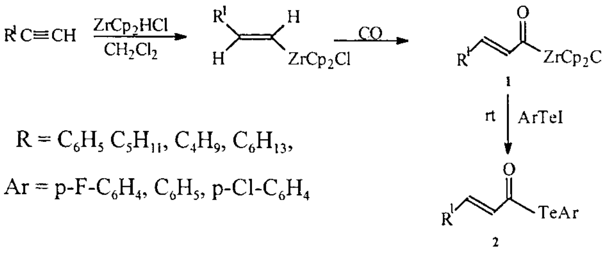
α, β-unsaturated tellurolesters have been prepared in good yield by the reaction of ArTeI with acylzirconocene chlorides.

Tellurolesters are useful synthetic intermediates,[1] having been employed, for example, as mild acyltransfer reagents,[2] precursors of acyl radical[3] or anion.[4] In spite of the growing interest in new organic transformations of these compounds, preparative methods available are still limited: they have usually been prepared by conventional methods based on the reaction of lithium or sodium tellurolate anions with carboxylic acid chlorides or anhydrides,[5] and by the reaction of phenyltellurotrimethylsilane with acyl chlorides.[2] In addition, a new method based on the reaction of aldehydes with diisobutylaluminium tellurate has been described recently.[6] To our knowledge, only syntheses of aryl- or alkyl-carboxylate tellurolesters has been reported before, there is no report of syntheses of vinylcarboxylate tellurolesters. Herein, we report stereoselective syntheses of α,β-unsaturated carboxylate tellurolesters by the reaction of acylzirconocene chlorides with the electrophilic tellurium iodides (ArTeI) as shown in Scheme 1.



Scheme 1

Table 1 Synthesis of α, β-unsaturated tellurolesters **2a–2j**

Products	R^1	Ar	Yields[*](%)
2a	C_6H_5	*p*-F-C_6H_4	59
2b	C_6H_5	*p*-ClC_6H_4	67
2c	C_5H_{11}	C_6H_5	55
2d	C_5H_{11}	*p*-F-C_6H_4	61
2e	C_5H_{11}	*p*-Cl-C_6H_4	69
2f	C_4H_9	*p*-F-C_6H_4	58
2g	C_4H_9	*p*-Cl-C_6H_4	65
2h	C_6H_{13}	C_6H_5	57
2i	C_6H_{13}	*p*-F-C_6H_4	60
2j	C_6H_{13}	*p*-Cl-C_6H_4	66

Isolated yields based on ATeI.

Acylzirconocene chloride derivatives **1**, which are used as an ‘unmasked’ acyl anion for organic synthesis, can be conveniently prepared through sequential treatment of alkynes with zirconocene hydrochloride (Schwarts reagent) and carbon monoxide.[7] Here, we have investigated the reactivity of **1** with ArTeI. When **1** (1.2equiv) was added to ArTeI in THF at room temperature, and stirring for half an hour, the α,β-unsaturated tellurolesters **2** were obtained (see Table 1).

As the data in Table 1 show, this method affords a variety of α,β-unsaturated tellurolesters in good yields and more importantly the reaction can be performed at room temperature immediately. The configuration of the products could be confirmed by the analysis of the coupling constant data in the ^{1}H NMR spectra (*J*=16 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 of α,β-unsaturated tellurolesters has been developed by the reaction of acylzirconocene chlorides with ArTeI. This method has the advantages of mild reaction conditions, available reagents, good yield.

Experimental

^{1}H NMR spectra were recorded on PMX-60 spectrometer, using $CDCl_3$ as the solvent with TMS as an internal standard. *J* values were given in Hz. IR spectra was determined on a PE-683 spectrophotometer. Mass spectra were obtained on an HP 5989A spectrometer. Melting points were uncorrected. Elemental analysis was conducted using a Yanaco MT-3CHN elemental analyser. All reaction were carried out in pre-dried glass ware (150°C, 4h) 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] (310 mg, 1.2 mmol) in CH_2Cl_2 (5 ml) was added terminal acetylene (1.2 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 2h, then the mixture was added to ArTeI (1.0 mmol) in THF (prepared *in situ*) via syringe at room temperature and stirred for 30 min at this temperature. 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 cyclohexane-ethyl acetate as eluent.

2a: Mp 71–73 °C. ν_{max}/cm^{-1}: 1670 (C=O). δ_H 6.57 (1H, d, *J* 16), 6.83–7.9 (10H, m). MS(EI) *m/z*: 131 (M^+-TeC_6H_4-p-F, 100%), 103 (42.95%), 77 (26.55%). Found: C 50.85, H 3.10. Calc. for $C_{15}H_{11}FOTe$: C 50.92, H 3.13%.

2b: Mp 76–78 °C. ν_{max}/cm^{-1}: 1675 (C=O). δ_H 6.50 (1H, d, *J* 16), 7.13–7.77 (10H, m). MS(EI) *m/z*: 131 (M^+-TeC_6H_4-p-Cl, 100%), 103 (39.97%), 77 (22.40%). Found: C 48.60, H 2.95. Calc. for $C_{15}H_{11}ClOTe$: C 48.65, H 2.99%.

2c: Oil. ν_{max}/cm^{-1}: 1718 (C=O). δ_H 0.63–1.50 (9H, m), 1.93–2.33 (2H, m), 6.10 (1H, d, *J* 16), 6.50-7.00 (1H, dt, *J* 16; 7), 7.13-7.48 (3H, m), 7.67–7.9(2H, m). MS(EI) *m/z*: 332 (M^++2, 0.78%), 330 (M^+,0.74%), 125 (100%). Found: C 50.91, H5.45. Calc. for $C_{14}H_{18}OTe$: C 50.97, H 5.50%.

2d:Oil. ν_{max}/cm^{-1}: 1710 (C=O). δ_H 0.67–1.57 (9H, m), 1.93–2.37 (2H, m), 6.03 (1H, d, *J* 16), 6.5-7.3 (3H, m.), 7.6–7.97 (2H, m). MS(EI) *m/z*: 350 (M^++2, 0.25%), 348(M^+, 0.26%), 125 (100%). Found: C 48.28, H 4.98. Calc. for $C_{14}H_{17}FOTe$: C 48.34, H 4.93%.

2e:Oil. ν_{max}/cm^{-1}: 1695 (C=O). δ_H 0.7–1.8 (9H, m), 1.9–2.3 (2H, m), 5.93 (1H, d, *J* 16), 6.7 (1H, dt, *J* 16; 7.0), 7.15–7.9 (4H, m). MS

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

(EI) *m/z*: 366 (M^++2, 0.35%), 364(M^+, 0.30%), 125 (100%). Found: C 46.07, H 4.66 Calc. for $C_{14}H_{17}ClOTe$: C46.15, H 4.70 %.

2f:Oil. ν_{max}/cm^{-1}: 1700 (C=O). δ_H 0.67–1.57 (7H, m), 1.97–2.37 (2H, m), 5.97 (1H, d, *J* 16), 6.47–7.27 (3H, m), 7.5–7.9 (2H, m). MS(EI) *m/z*: 336 (M^++2, 0.38%), 334(M^+, 0.35%), 111 (100%). Found: C 46.71, H 4.50. Calc. for $C_{13}H_{15}FOTe$: C 46.77, H 4.53 %.

2g: Oil. ν_{max}/cm^{-1}: 1697 (C=O). δ_H 0.67–1.77 (7H, m,), 1.93–2.37 (2H, m), 5.98 (1H, d, *J* 16), 6.47–7.00 (3H, m), 7.2–7.8 (2H, m). MS(EI) *m/z*: 352 (M^++2, 1.84%), 350(M^+, 1.48%), 111 (100%). Found: C 44.48, H 4.28. Calc. for $C_{13}H_{15}ClOTe$: C 44.57, H 4.32%.

2h:Oil. ν_{max}/cm^{-1}: 1720 (C=O). δ_H 0.77–1.67 (11H, m), 1.97–2.37 (2H, m), 6.07 (1H, d, *J* 16), 6.53-7.03 (1H, dt, *J* 16;7), 7.27–7.53 (3H, m), 7.73–7.93(2H, m). MS(EI) *m/z*: 346 (M^++2, 0.78%), 344(M^+, 0.74%), 139 (100%). Found: C52.30, H 5.84. Calc. for $C_{15}H_{20}OTe$: C 52.39, H 5.86%.

2i:Oil. ν_{max}/cm^{-1}: 1700 (C=O). δ_H 0.67–1.57 (11H, m), 1.93–2.33 (2H, m), 6.02 (1H, d, *J* 16), 6.5–7.3 (3H, m), 7.6–7.96 (2H, m). MS(EI) *m/z*: 364 (M^++2, 0.30%), 362(M^+, 0.31%), 139 (100%). Found: C 49.71, H 5.23 Calc. for $C_{15}H_{19}FOTe$: C49.78, H 5.29. %.

2j: Oil. ν_{max}/cm^{-1}: 1700 (C=O). δ_H 0.67–1.57 (11H, m), 1.9–2.33 (2H, m), 5.9 (1H, d, *J* 16), 6.3-6.87 (1H, dt, *J* 16; 7), 7.07–7.77 (4H, m). MS(EI) *m/z*: 380 (M^++2, 0.38%), 378(M^+, 0.35%), 139 (100%). Found: C 47.49, H 5.01, Calc. for $C_{15}H_{19}ClOTe$: C 47.42, H 5.06%.

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.

Received 9 November 1999; accepted 26 January 2000
Paper 99/45

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