SHORT PAPER

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A novel method for synthesis of β-telluroesters(and nitriles)

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The Te–Te bond in ditellurides was reduced by the $Zn/ZrCl_4$ system in THF to produce tellurium anions, which then react with α,β-unsaturated esters and α,β-unsaturated nitriles to give β-telluroesters (and nitriles).

Keywords: zinc, zirconium(IV) chloride, β-telluroesters(and nitriles)

Metallic zinc has been employed as an efficient, inexpensive and highly reactive reagent in Barbier-type reductive coupling and Reformatsky reactions. Our work on the reductive cleavage of the Se–Se bond with the $Zn/ZrCl_4$ system[1] has led us to investiage the reductive cleavage of the Te–Te bond with the $Zn/ZrCl_4$ system. Although to the best of our knowledge, there are no report on the use of zinc in the preparation of β-telluroesters (and nitriles), other methods have been described for the synthesis of β-telluroesters (and nitriles). For example, tellurides react with α,β-unsaturated esters and α,β-unsaturated nitriles with carbon monoxide (1–30atm) in the presence of a palladium(II) salt such as Li_2PdCl_4, $PdCl_2$ or $Pd(OAC)_2$[2] or using SmI_2,[3], $Sm/TiCl_4$,[4] $Sm/ZrCl_4$[5] or $Sm/CrCl_3$[6] as reductant, to give β-telluroesters (and nitriles). Unfortunately, most of these reactions suffer from significant problems including the use of strong base, high pressure and expensive starting materials. Herein, we report that the $Zn/ZrCl_4$ system reduces ditellurides to give telluride anions, which then react with α,β-unsaturated esters and α,β-unsaturated nitriles to afford β-telluroesters (and nitriles). The advantages of the present method are availability of starting cheap materials, a single product, simple manipulation, the mild and neutral conditions.

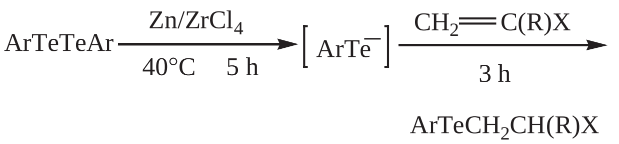

Table 1

Entry	Ar	$CH_2C(R)X$	Yield/%
1	Ph	CH_2CHCO_2Me	70
2	Ph	CH_2CHCO_2Et	69
3	Ph	CH_2CHCO_2Bu-*n*	65
4	Ph	CH_2CHCN	51
5	Ph	$CH_2C(CH_3)CO_2Me$	57
6	*p*-$CH_3C_6H_4$	CH_2CHCO_2Me	66
7	*p*-$CH_3C_6H_4$	CH_2CHCO_2Et	60
8	*p*-$CH_3C_6H_4$	CH_2CHCO_2Bu-*n*	68
9	*p*-$CH_3C_6H_4$	CH_2CHCN	57
10	*p*-$CH_3C_6H_4$	$CH_2C(CH_3)CO_2Me$	54

All products are yellow oil liquids.

Experimental

Melting points are uncorrected. IR spectra were obtained on a PE-683 infrared spectrophotometer. ^{1}H NMR Spectra were recorded on a PMX-60 MHz instrument in CCl_4 using TMS as internal standard. Metallic zinc was activated before use.[7] 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 nitrogen gas atmosphere.

General procedure: Under an inert atmosphere of nitrogen gas, zinc power (1.5mmol), Zirconium (IV) chloride (0.2mmol) and diaryl tellurides (0.5mmol) were placed in a well-dried two neck round bottom flask containing a magnetic stirrer bar. Freshly distilled, dry THF (10ml) was added through a rubber septum by a syringe. The resulting mixture was stirred at 40°C for about 5h by which time the zinc power had almost completely disappeared; cleavage of the Te–Te bond was indicated by the dissipation of the red colour in the reaction mixture. Then the α,β-unsaturated esters (1.5mmol) and α,β-unsaturated nitriles (1.5mmol) in THF (1ml) and n-BuOH (1mmol) were added by a syringe to the mixture and stirred for 3h (TLC as monitored). Then the whole solution was poured into dilute HCl (1.2mol/l, 20ml) and the mixture was extracted with ether (15ml × 3). The organic layer was washed with saturated NaCl and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, the residue was then purified by preparative TLC on silica gel (light petroleum/ether as eluent) to give pure products. Some results were summarised in Table 1.

Data for products: $PhTeCH_2CH_2CO_2Me$[5]: Oil, ν_{max}(cm^{-1}), 3068, 3050, 2993, 2842, 1737, 1575, 1475, 1434, 1359, 1341, 1206, 1141, 1018, 998, 734, 693. ^{1}H NMR 7.50–7.72 (2H, m), 7.00–7.18 (3H, m), 3.51 (3H, s), 2.74–3.30 (4H, m).

$PhTeCH_2CH_2CO_2Et$[5]: Oil, ν_{max}(cm^{-1}), 3068, 3050, 2980, 2917, 2853, 1734, 1575, 1475, 1434, 1372, 1334, 1200, 1138, 1037, 998, 733, 693, 668. ^{1}H NMR 7.50–7.66 (5H, m), 7.00–7.24 (3H, m), 4.00 (2H, q), 2.62–3.15 (4H, m), 1.17 (3H, t).

$PhTeCH_2CH_2CO_2Bu$–n[5]: Oil, ν_{max}(cm^{-1}), 3065, 3050, 2960, 2933, 2874, 1733, 1572, 1473, 1341, 1197, 1137, 1061, 1023, 733, 693. ^{1}H NMR 7.48–7.77 (2H, m), 7.02–7.31 (3H, m), 3.99 (2H, q), 2.66–3.03 (4H, m), 0.86 (3H, t).

$PhTeCH_2CH_2CN$[5]: Oil, ν_{max}(cm^{-1}), 3057, 2960, 2923, 2954, 2223, 1540, 1458, 1377, 1265, 1114, 1045, 738, 716, 657. ^{1}H NMR 7.57–7.80 (2H, m), 7.06–7.30 (3H, m), 2.49–3.12 (4H, m).

$PhTeCH_2CH(CH_3)CO_2Me$[5]: ν_{max}(cm^{-1}), 3070, 3050, 2960, 2925, 2855, 1735, 1575, 1525, 1459, 1373, 1066, 942, 770, 705. ^{1}H NMR 7.50–7.78 (2H, m), 6.90–7.20 (3H, m), 3.95 (2H, q), 3.20–3.60 (1H, m), 2.63 (2H, d), 1.01–1.62 (6H, m).

p-$CH_3C_6H_4TeCH_2CH_2CO_2Me$[5]: Oil, ν_{max}(cm^{-1}), 3050, 2960, 2924, 2854, 1740, 1653, 1559, 1436, 1339, 1208, 1013, 799, 668. ^{1}H NMR 7.40–7.58 (2H, m), 6.75–6.90 (2H, m), 3.50 (3H, s), 2.60–3.10 (4H, m), 2.24(3H, s).

p-$CH_3C_6H_4TeCH_2CH_2CO_2Et$[5]: Oil, ν_{max}(cm^{-1}), 3052, 2950, 2923, 2854, 1735, 1635, 1559, 1506, 1457, 1198, 799, 668. ^{1}H NMR 7.40–7.59 (2H, m), 6.74–6.91 (2H, m), 3.98 (3H, s), 2.60–3.10 (4H, m), 2.25(3H, s).

p-$CH_3C_6H_4TeCH_2CH_2CO_2Bu$-n[5]: Oil, ν_{max}(cm^{-1}), 3050, 2960, 2922, 2868, 1732, 1594, 1486, 1464, 1330, 1276, 1196, 1007, 799, 689. ^{1}H NMR 7.38–7.62 (2H, m), 6.72–6.90 (2H, m), 3.95 (2H, t), 2.58–3.09 (4H, m), 2.24 (3H, s), 1.15–1.70 (4H, m), 0.88 (3H, t)

p-$CH_3C_6H_4TeCH_2CH_2CN$[5]: Oil, ν_{max}(cm^{-1}), 3059, 2970, 2924, 2854, 2225, 1599, 1462, 1377, 1068, 810, 782, 738. ^{1}H NMR 7.40–7.60 (2H, m), 6.72–6.90 (2H, m), 2.50–3.10(4H, m), 2.24(3H, s).

p-$CH_3C_6H_4TeCH(CH_3)CH_2CO_2Me$[5]: Oil, ν_{max}(cm^{-1}), 3050, 2961, 2925, 2855, 1741, 1540, 1459, 1373, 1066, 943, 846, 770, 701. ^{1}H NMR 7.38–7.59 (2H, m), 6.72–6.88 (2H, m), 3.48 (3H, s), 2.55–3.08 (4H, m), 2.24 (3H, s), 1.50 (3H, s).

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