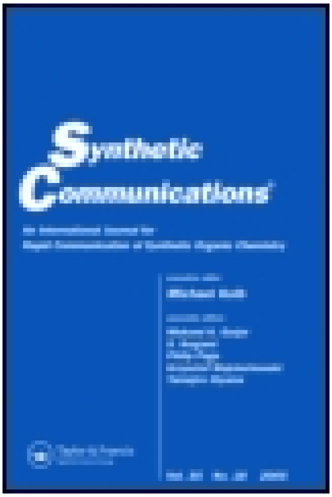

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Reductive Cleavage of Te-Te Bond in Ditellurides by Sm / $ZrCl_4$ System : a Novel Method for the Synthesis of β-Telluroesters (and Nitriles)

Songlin Zhang [a] & Yongmin Zhang [a]
[a] Department of Chemistry , Zhejiang University at Xi Xi Campus , Hangzhou, 310028, P.R., China

To cite this article: Songlin Zhang & Yongmin Zhang (2000) Reductive Cleavage of Te-Te Bond in Ditellurides by Sm / $ZrCl_4$ System : a Novel Method for the Synthesis of β-Telluroesters (and Nitriles), Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 30:2, 285-292, DOI: 10.1080/00397910008087320

To link to this article: http://dx.doi.org/10.1080/00397910008087320

SYNTHETIC COMMUNICATIONS, 30(2), 285–292 (2000)

REDUCTIVE CLEAVAGE OF Te-Te BOND IN DITELLURIDES BY Sm / $ZrCl_4$ SYSTEM : A NOVEL METHOD FOR THE SYNTHESIS OF β-TELLUROESTERS (AND NITRILES)

Songlin Zhang and Yongmin Zhang*

Department of Chemistry, Zhejiang University at Xi Xi Campus,
Hangzhou, 310028 P. R. China

ABSTRACT: Diaryl ditellurides were conveniently reduced by a system consisting of samarium and zirconium tetrachloride in tetrahydrofuran to produce samarium aryltellurolates. This new tellurolate anion species reacted smoothly with α,β-unsaturated esters (and nitriles) to give β-telluroesters (and nitriles) in good yields.

Organotellurium compounds have recently attracted considerable interest as reagents and intermediates in organic synthesis.[1] A number of synthetic methods have been found to prepare organotellurium derivatives. A convenient and general method to introduce a tellurium moiety into organic molecules is the reaction of metal tellurolates with appropriate eletrophiles.[2] The use of ditellurides and

---

*To whom correspondence should be addressed.

samarium diiodide in THF/HMPA has also recently been reported to give the telluride anion.[3]

As a powerful, verastile and ether-soluble one-electron transfer reductive agent, SmI_2 has played an ever-increasing role in organic synthesis since its introduction by H. B. Kagan and his group.[4] Samarium diiodide promotes a number of important individual reactions which were found useful in organic synthesis.[5] Though SmI_2 is a useful reagent, storage is difficult because it is very sensitive to air oxidation. On the other hand, metallic samarium is stable in air and its strong reducing power ($Sm^{3+} / Sm = -2.41V$) is similar to that of magnesium ($Mg^{2+} / Mg = -2.37V$) and superior to that of zinc ($Zn^{2+} / Zn = -0.71V$). These properties prompted us to use the more convenient and cheaper metallic samarium directly instead of samarium (II) iodide. Recently, there are some reports on the direct use of Sm in organic synthesis.[6] Herein, we wish to report that reductive cleavage of the Te-Te bond in ditellurides by the Sm / $ZrCl_4$ system led to the tellurolate anion species, which react with α,β-unsaturated esters (and nitriles) to give β-telluroesters (and nitriles) in good yields under mild and neutral conditions.

Results and discussion

The formation and reaction of samarium aryltellurolates, which formed *in situ* from the cleavage of the corresponding ditellurides with the Sm / $ZrCl_4$ reductive system, are shown in the **Scheme**.

$$\mathrm{ArTeTeAr} \xrightarrow{\mathrm{Sm/ZrCl_4}} \text{"}\mathrm{ArTeSmCl_2}\text{"} \xrightarrow{\mathrm{RCH{=}C(R_1)X}} \mathrm{ArTe(R)CHCH(R_1)X}$$

(a-k)

Scheme

The formation of tellurolate anion species with Sm / $ZrCl_4$ is similar to that with SmI_2 .[3] The results of our experiments are summarized in the **Table**.

Experimental

^{1}H NMR spectra were recorded with a Brucker 80 MHz instrument, with carbon tetrachloride used as the solvent and tetramethylsilane as an internal standard. IR spectra were determined on a PE-683 spectrometer. MS spectra were obtained on HP5989B mass spectrometer. Elemental analyses were carried out using a Carlo Erba 1106 instrument.

Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl before use. α,β-unsaturated esters (and nitriles) are commercially available and were used without further purification. The reactions were proceeded in a Schlenk type glass apparatus and under a nitrogen atmosphere.

General procedure:

Samarium powder (0.15g, 1mmol, 99.9 %), zirconium tetrachloride (0.04g, 0.2mmol) and ditelluride (0.5mmol) were placed in a well-dried three-necked round bottom flask containing a magnetic stirrer bar. The flask was flushed with nitrogen several times. Tetrahydrofuran (10ml) was added through a rubber

Table : Sm / $ZrCl_4$ Mediated Michael Reaction of ditellurides with α,β-Unsaturated Esters (and Nitriles)

Entry	Ar	$RCH = C(R_1)X$	Product	Yield[a] (%)
a	Ph	CH_2=$CHCO_2Me$	$PhTeCH_2CH_2CO_2Me$	82
b	Ph	CH_2=$CHCO_2Et$	$PhTeCH_2CH_2CO_2Et$	85
c	Ph	CH_2=$CHCO_2Bu$-*n*	$PhTeCH_2CH_2CO_2Bu$-*n*	84
d	Ph	CH_3CH=$CHCO_2Et$	$PhTeCH(CH_3)CH_2CO_2Et$	63
e	Ph	CH_2=$C(CH_3)CO_2Me$	$PhTeCH_2CH(CH_3)CO_2Me$	75
f	Ph	CH_2=$CHCN$	$PhTeCH_2CH_2CN$	63
g	4-MeC_6H_4	CH_2=$CHCO_2Me$	4-$MeC_6H_4TeCH_2CH_2CO_2Me$	85
h	4-MeC_6H_4	CH_2=$CHCO_2Et$	4-$MeC_6H_4TeCH_2CH_2CO_2Et$	93
i	4-MeC_6H_4	CH_2=$C(CH_3)CO_2Me$	4-$MeC_6H_4TeCH_2$-$CH(CH_3)CO_2Me$	81
j	4-MeC_6H_4	CH_2=$CHCO_2Bu$-*n*	4-$MeC_6H_4TeCH_2CH_2CO_2Bu$-*n*	89
k	4-MeC_6H_4	CH_2=$CHCN$	4-$MeC_6H_4TeCH_2CH_2CN$	69

a isolated yield base on ditelluride

septum by a syringe. The mixture was stirred at room temperature under the atmosphere of nitrogen, the red solution gradually became brown within 2h, which showed that the Te-Te bond had been reductively cleaved by Sm/$ZrCl_4$ and that the samarium aryltellurolate ($ArTeSmCl_2$) had been generated. α,β-unsaturated esters (and nitriles) (1.5mmol) and t-BuOH (1mmol) in THF (1ml) were then added by syringe and stirred at room temperature for 2h. A dilute HCl (20ml) and diethyl ether (50ml) were added. The organic layer was washed with water (20ml × 2) and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo. The crude product was purified by preparative TLC on silica gel (light petroleum : ether = 5 : 1 as eluent.)

Data of Products

a[7].oil, ^{1}HNMR (δ_H) 2.75-3.30(4H,m), 3.50(3H,s), 7.00-7.20(3H,m), 7.50-7.73(2H,m); IR ν_{max} /cm^{-1} 3090, 3070, 2980, 2960,2890, 2860, 1750, 1580, 1560, 1460, 1440, 1380, 1250, 1220, 1020, 1000, 740, 685.

b[7]. oil, ^{1}HNMR(δ_H) 1.18(3H,t), 2.63-3.13(4H,m), 3.99(2H,q), 7.03-7.23(3H,m), 7.53-7.78(2H,m); IR ν_{max} /cm^{-1} 3080, 3070, 2990, 2960, 2940, 2890, 2860, 1750, 1580, 1480, 1440, 1380, 1200, 1020, 1000, 730, 680, 650.

c[8]. oil, ^{1}HNMR(δ_H) 0.89(3H,t), 1.14-1.70(4H,m), 2.67-3.04(4H,m), 3.96(2H,t), 7.00-7.30(3H,m), 7.50-7.80(2H,m); IR ν_{max} /cm^{-1} 3090, 3080, 2980, 2950, 2890, 2870, 1750, 1580, 1560, 1480, 1440, 1380, 1250, 1200, 1160, 1020, 740, 690.

d[8]. oil, ^{1}HNMR(δ_H) 1.04-1.64(6H,m), 2.64(2H,d), 3.24-3.64(1H,m), 3.96(2H,q), 6.90-7.21(3H,m), 7.50-7.77(2H,m); IR ν_{max}/cm^{-1} 3090, 3080, 3000-2960, 2880, 1750, 1580, 1480, 1440, 1380, 1360, 1200, 1100, 1020, 1000, 970, 850, 730, 690, 650.

e^7. oil, ^{1}HNMR(δ_H) 1.50(3H,d), 2.57-3.10(3H,m), 3.50(3H,s), 6.90-7.24(3H,m), 7.52-7.77(2H,m); IR ν_{max}/cm^{-1} 3090, 3080, 2990-2940, 2890, 1750, 1580, 1480, 1460, 1440, 1380, 1300, 1200, 1100, 1020, 1000, 900, 850, 730, 690, 650.

f^7. oil, ^{1}HNMR (δ_H) 2.50-3.10(4H,m), 7.07-7.30(3H,m), 7.60-7.80(2H,m); IR ν_{max}/cm^{-1} 3080, 3060, 2980-2940, 2860, 2225, 1580, 1480, 1440, 1300, 1250, 1170, 1060, 1020, 1000, 900, 850, 730, 690, 650.

g. oil, ^{1}HNMR(δ_H) 2.25 (3H, s) 2.60-3.10(4H,m), 3.50(3H,s), 6.73-6.90(2H,m), 7.40-7.60(2H,m); IR ν_{max}/cm^{-1} 3090, 3070, 2980, 2960, 2890, 2860, 1745, 1580, 1560, 1460, 1440, 1380, 1250, 1220, 1020, 1000, 910, 880, 800; m / z (M^+), 308; Anal. Calc. for $C_{11}H_{14}O_2Te$: C 43.20, H 4.61; Found C 43.33, H 4.68.

h. oil, ^{1}HNMR (δ_H) 1.18(3H,t), 2.25 (3H, s), 2.60-3.10(4H,m), 3.99(2H,q), 6.73-6.90(2H,m), 7.40-7.60(2H,m) ; IR ν_{max}/cm^{-1} 3090, 3070, 2980, 2960, 2890, 2860, 1745, 1580, 1560, 1460, 1440, 1380, 1250, 1220, 1020, 1000, 910, 880, 800. m / z (M^+), 322; Anal. Calc. for $C_{12}H_{16}O_2Te$: C 45.06, H 5.06; Found C 45.00, H 5.06.

i. oil, ^{1}HNMR (δ_H) 1.50(3H,d), 2.25 (3H, s), 2.57-3.10(3H,m), 3.50(3H,s), 6.73-6.90(2H,m), 7.40-7.60(2H,m); IR ν_{max}/cm^{-1} 3090, 3080, 2990-2940, 2890, 1750, 1580, 1480, 1460, 1440, 1380, 1300, 1200, 1100, 1020, 1000, 910, 880, 800. m / z (M^+), 322; Anal. Calc. for $C_{12}H_{16}O_2Te$: C 45.06, H 5.06; Found C 45.16, H 5.07.

j. oil, ^{1}HNMR(δ_H) 0.89(3H,t), 1.14-1.70(4H,m), 2.25 (3H, s), 2.60-3.10(4H,m), 3.96(2H,t), 6.73-6.90(2H,m), 7.40-7.60(2H,m); IR ν_{max}/cm^{-1} 3090, 3080, 2980, 2950, 2890, 2870, 1750, 1580, 1560, 1480, 1440, 1380, 1250, 1200, 1160, 1020, 910, 880, 800. m / z (M^+), 350; Anal. Calc. for $C_{14}H_{20}O_2Te$: C 48.33, H 5.80; Found C 48.60, H 5.90.

k. oil, ^{1}HNMR (δ_H) 2.25 (3H, s), 2.50-3.10(4H,m), 6.73-6.90(2H,m), 7.40-7.60(2H,m); IR ν_{max}/cm^{-1} 3080, 3060, 2980-2940, 2860, 2225, 1580, 1480, 1440, 1300, 1250, 1170, 1060, 1020, 1000, 910, 880, 800. m / z (M^+), 275; Anal. Calc. for $C_{10}H_{11}NTe$: C 44.03, H 4.06, N 5.14; Found C 44.25, H 4.11, N 5.06.

In summary, a novel method for the preparation of β-telluroesters (and nitriles) has been provided. The advantages of the present procedure are simple manipulation, and mild and neutral conditions.

Acknowledgement

We are grateful to the National Natural Science Foundation of China (Project . No. 294938004 and 29872010), the NSF of Zhejiang Province, China and the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, for financial support.

References

1 (a) Patai, S. and Rappoport, Z., ***The Chemistry of Organic Selenium and Tellurium Compounds***, John Wiley, Chichester, Vol.1, **1986.** (b) . Schiesser, C. H. and Skidmore, M. A., ***J. Chem. Soc., Perkin Trans.1***, **1997**, 2689.

2 (a) Uemura, S. and Fukuzawa, S., ***J. Am. Chem. Soc.***, **1980**, *102*, 4438. (b) Sasaki, K., Aso, Y., Otsubo T. and Ogura, F., ***Tetrahedron Lett.***, **1985**, ***26***, 453. (c) Barton, D. H. R., Bridon, D. and Zard, S. Z., ***Tetrahedron Lett.***, **1984** , *25*, 5777.

3 (a) Fukuzawa, S., Niiomoto, Y., Fujinami, T., and Sakai, S., ***Heteroatom Chemistry***, **1990**, *1*, 492. (b) Zhang, Y., M., Yu, Y. P. and Lin, R. H., ***Synth. Commun.***, **1993**, *23*, 189.

4 (a) Girard, P., Namy, J. L. and Kagan, H. B., ***J. Am. Chem. Soc.***, **1980**, *102*, 2693. (b) Kagan, H. B. and Namy, J. L., ***Tetrahedron***, **1986**, *42*, 6573.

5. (a) Molander, G. A., ***Chem. Rev.***, **1992**, *92*, 29. (b) Molander, G. A., ***Organic Reactions***, **1994**, *46*, 211. (c) Molander, G. A. and Harris, C. R., ***Chem. Rev.***, **1996**, *96*, 307. (d) Zhang, S. L. and Zhang, Y. M., ***J. Chem. Res.***, **1998**, 350. (e) Zhang, S. L. and Zhang, Y. M., ***Synth. Commun.*** , **1998**, *28*, 3999. (f) Zhang, S. L. and Zhang, Y. M., ***J. Chem. Res.***, **1998**, 48.

6. Yanada, R., Negoro, N., Tanada, K. and Fujita, T., ***Tetyahedron Lett.***, **1997**, 3271 and references cited therein.

7. Jiang, H. and Zhang,Y. M., ***You Ji Hua Xue***, **1994**, *14*, 307.

8. Sasaki, K., Aso, Y., Otsubo, T. and Ogura, F., ***Chem. Lett.***, **1989**, *4*, 607.

Received in the UK 5 February 1999