

Reductive Cleavage of the Te—Te Bond in Diphenyl Ditelluride by the Sm/CrCl₃(cat.) System: Preparation of Telluroesters and Unsymmetrical Phenyltellurides

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The reduction of diphenyl ditelluride by the Sm/CrCl₃(cat.) system led to a telluride anion. This species reacted with acid chlorides, alkyl halides, and α,β -unsaturated enoates or α,β -unsaturated ene nitriles to afford telluroesters and unsymmetrical phenyltellurides, respectively, in moderate to good yields under mild and neutral conditions.

Keywords diphenyl ditelluride, samarium/chromium(III) chloride(cat.) system, acid chlorides, alkyl halides, α,β -unsaturated enoates, α,β -unsaturated ene nitriles, telluroesters, unsymmetrical phenyltelluride

Organotellurium compounds have recently attracted considerable interest both as reagents and intermediates in organic synthesis.¹ A number of synthetic methods for organotellurium derivatives have been found. A convenient and general method to introduce a tellurium moiety into organic molecules is the reaction of telluride anions with appropriate electrophiles.²

Samarium diiodide is a powerful one-electron transfer reductant. It has been widely employed as a useful reagent in organic synthesis.³ Our previous work on the reductive cleavage of the S—S, Se—Se, Te—Te, S—Si, and Se—Si bonds by SmI₂ has been reported.⁴ In recent years, we have been focusing our efforts on direct use of the more convenient and cheaper samarium metal as a reductant instead of samarium diiodide. Our ongoing interest in the Sm⁰/MCl_n systems⁵ leads us to explore

Sm⁰/CrCl₃ system and its application in organic synthesis.

Meanwhile, chromium(II) salts are widely used in organic synthesis as one-electron reducing agents. The applications of chromium(II) salts to the reduction of alkyl halides, unsaturated systems, epoxides, acyloxy ketones and nitro compounds have been achieved.⁶ However, to our knowledge, the use of chromium(II) salts to the reductive cleavage of ditellurides has not been reported yet.

Our previous work on the reductive cleavage of the Se—Se bond by the Sm/CrCl₃ system⁷ led us to further investigate the reductive cleavage of a Te—Te bond. We found that diphenyl ditelluride could be easily reduced by the Sm/CrCl₃ system to afford a phenyl telluride anion. This species reacted with acid chlorides, alkyl halides, and α,β -unsaturated enoates or α,β -unsaturated enenitriles to afford telluroesters and unsymmetrical phenyltellurides, respectively, in moderate to good yields under mild and neutral conditions, as shown in Scheme 1. Moreover, in our experiment, we have been more interested in using only a catalytic amount of CrCl₃ due to the disadvantage of its toxicity. The results are summarized in Table 1.

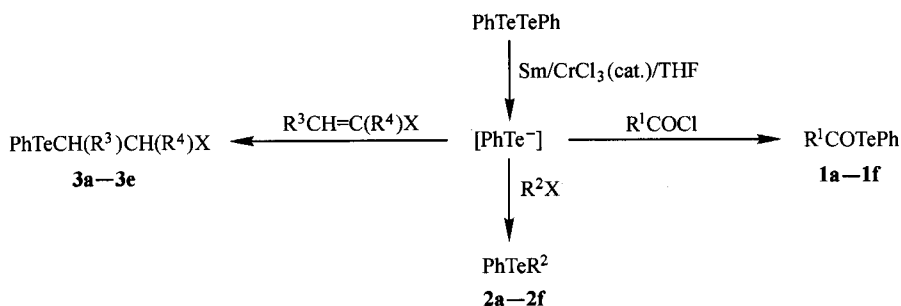
When diphenyl ditelluride was added to a mixture of samarium powder and anhydrous chromium(III) chlo-

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Scheme 1



R¹: C₆H₅; *p*-Cl C₆H₄; *p*-Br C₆H₄; Me; Et; *n*-C₁₁H₂₃. R²: *n*-C₆H₁₃; *n*-C₈H₁₇; *n*-C₁₂H₂₅; CH₂CO₂Et; CH₂CO₂Me; CH₃CHCO₂Et. R³: H. R⁴: H; Me. X: CO₂Me; CO₂Et; CO₂Bu-*n*; CO₂Me; CN

ride (10 mol% based on samarium) in THF under an inert atmosphere of nitrogen, the initial purple color of the reaction mixture darkened. After stirring for about 2 h, the samarium powder was almost completely consumed and the mixture turned dark brown which showed that phenyl telluride anion was readily generated. This species reacted smoothly with acid chlorides to afford telluroesters (Entries 1—6) easily in good yields. When alkyl halides were used, the corresponding alkylphenyl

tellurides (Entries 7—9) or α -phenyltelluroesters (Entries 10—12) were produced. Besides, the Michael addition of this species to α,β -unsaturated enoates (ene nitriles) took place readily to give β -phenyltelluroesters (nitriles) (Entries 13, 14) in moderate to good yields. To avoid polymerization of α,β -unsaturated enoates (ene nitriles), stoichiometric quantities of *t*-BuOH were added to the solution.

Table 1 Synthesis of telluroesters and unsymmetrical phenyltellurides

Entry	R ¹ COCl	R ² X	R ³	R ⁴	X	T (h)	Product	Yield (%) ^a
1	C ₆ H ₅					2	1a	80
2	<i>p</i> -ClC ₆ H ₄					2	1b	79
3	<i>p</i> -BrC ₆ H ₄					2	1c	79
4	CH ₃					2	1d	75
5	CH ₃ CH ₂					2	1e	73
6	CH ₃ (CH ₂) ₁₀					2	1f	70
7		CH ₃ (CH ₂) ₅ Br				8	2a	72
8		CH ₃ (CH ₂) ₇ Br				8	2b	68
9		CH ₃ (CH ₂) ₁₁ Br				8	2c	64
10		BrCH ₂ CO ₂ Et				8	2d	76
11		BrCH ₂ CO ₂ Me				8	2e	75
12		CH ₃ CHBrCO ₂ Et				8	2f	68
13			H	H	CO ₂ Me	3	3a	75
14			H	H	CO ₂ Et	3	3b	81
15			H	H	CO ₂ Bu- <i>n</i>	3	3c	74
16			H	CH ₃	CO ₂ Me	3	3d	62
17			H	H	CN	3	3e	58

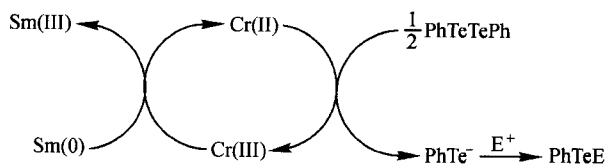
^aYield of isolated product based on diphenyl ditelluride.

The possible mechanism of Sm/CrCl₃(cat.) system mediated cleavage of Te—Te bond may be similar to the one of cleavage of Se—Se bond⁷ (Scheme 2).

In conclusion, we have found that the Sm/CrCl₃(cat.) system is an effective method for cleaving the Te—Te bond in diphenyl ditelluride under mild condi-

tions. The notable advantages of this reaction are easy availability of starting materials, neutral reaction conditions, simple operation and moderate to good yields.

Scheme 2



Experimental

Melting points were uncorrected. IR spectra were recorded on a PE-683 spectrometer. ¹H NMR spectra were obtained with a Bruker AC 80 MHz spectrometer in CDCl₃ solution using TMS as the internal standard. MS spectra were obtained on a HP 5989 mass spectrometer. The reactions were performed in a Schlenk-type glass apparatus under a nitrogen atmosphere. THF was freshly distilled from sodium-benzophenone ketyl prior to use.

General procedure for the synthesis of telluroesters

Under an inert atmosphere of nitrogen, metallic samarium powder (0.15 g, 1.0 mmol), CrCl₃ (0.016 g, 0.1 mmol) and THF (8 mL) were placed in a three-necked reaction flask with a reflux condenser. The initial purple mixture darkened after being magnetically stirred at room temperature for 5 min. Then diphenyl ditelluride (0.20 g, 0.5 mmol) was added to the mixture and the resulting mixture was magnetically stirred for another 2 h at the same conditions until the powdered samarium was almost consumed. Finally the mixture turned dark brown which showed that phenyl telluride anion was readily generated. An acyl halide (1.2 mmol) was then added by syringe, and the mixture was stirred at room temperature for 2 h. A dilute aqueous solution of HCl (0.5 mol/L, 20 mL) and diethyl ether (50 mL) was added. The organic layer was washed twice with water (20 mL) and dried over anhydrous Na₂SO₄. The solvent was removed *in vacuo*. The crude product was purified by preparative TLC on silica gel (light petroleum ether: ethyl acetate = 100:1 as eluent).

Reaction of phenyl telluride anion with alkyl halides

The preparation of phenyl telluride anion was the same as described above. Each of alkyl halides (1.2 mmol) in THF (1 mL) was then added by syringe, and the mixture was stirred at room temperature for 8 h. The further treatment of the mixture and the purifying procedure was the same as mentioned above.

Michael addition of phenyl telluride anion to α, β -unsaturated enoates (ene nitriles)

The procedure of the generation of phenyl telluride anion was the same as mentioned above. Each of α, β -unsaturated enoates (ene nitriles) (1.2 mmol) and *t*-BuOH (1 mmol) in THF (1 mL) were then added by syringe, and the mixture was stirred at room temperature for 3 h. The further treatment of the mixture and the purifying procedure was the same as mentioned above.

1a m.p. 71–73 °C (lit.⁸ 70–72 °C); ¹H NMR (CDCl₃, 80 MHz) δ : 8.02–7.05 (m); IR (KBr) ν : (1685 C=O) cm⁻¹.

1b m.p. 68–71 °C (lit.⁹ 65 °C); ¹H NMR (CDCl₃, 80 MHz) δ : 7.78–7.24 (m); IR (KBr) ν : 1690 (C=O) cm⁻¹.

1c m.p. 76–78 °C (lit.⁸ 77–79 °C); ¹H NMR (CDCl₃, 80 MHz) δ : 7.72–7.18 (m); IR (KBr) ν : 1690 (C=O) cm⁻¹.

1d oil (lit.¹⁰); 7.78–7.52 (m, 2H), 7.34–7.02 (m, 3H), 2.40 (s, 3H); IR (film/CCl₄) ν : 1740 (C=O) cm⁻¹; MS *m/z* (%): 250 (Te¹³⁰ – M⁺, 53), 248 (Te¹²⁸ – M⁺, 49).

1e oil (lit.¹⁰); ¹H NMR (CDCl₃, 80 MHz) δ : 7.75–7.40 (m, 2H), 7.32–7.00 (m, 3H), 2.51 (q, *J* = 7.0 Hz, 2H), 0.86 (t, *J* = 7.0 Hz, 3H); IR (film/CCl₄) ν : 1720 (C=O) cm⁻¹; MS *m/z* (%): 264 (Te¹³⁰ – M⁺, 48), 262 (Te¹²⁸ – M⁺, 44).

1f oil (lit.¹¹); ¹H NMR (CDCl₃, 80 MHz) δ : 7.72–7.50 (m, 2H), 7.23–7.00 (m, 3H), 2.50 (t, *J* = 7.0 Hz, 2H), 1.54–1.12 (m, 18H), 0.89 (t, *J* = 7.0 Hz, 3H); IR (film/CCl₄) ν : 1720 (C=O) cm⁻¹; MS *m/z* (%): 390 (Te¹³⁰ – M⁺, 37), 388 (Te¹²⁸ – M⁺, 33).

2a oil (lit.¹²); ¹H NMR (CDCl₃, 80 MHz) δ : 7.66–7.42 (m, 2H), 7.18–6.90 (m, 3H), 2.74 (t, *J* = 7.0 Hz, 2H), 1.40–1.10 (m, 8H), 0.84

(t, $J = 7.0$ Hz, 3H); IR (film/ CCl_4) ν : 3085, 3070, 2980, 2960, 2860, 1580, 1480, 1450, 1440, 1380, 1150, 1060, 1020, 1000, 720, 685, 650 cm^{-1} ; MS m/z (%): 292 ($\text{Te}^{130} - \text{M}^+$, 50), 290 ($\text{Te}^{128} - \text{M}^+$, 46).

2b oil (lit¹²); ^1H NMR (CDCl_3 , 80 MHz) δ : 7.70—7.40 (m, 2H), 7.20—6.86 (m, 3H), 2.74 (t, $J = 7.0$ Hz, 2H), 1.40—1.21 (m, 12H), 0.83 (t, $J = 7.0$ Hz, 3H); 3080, 3070, 2980, 2960, 2860, 1580, 1480, 1450, 1380, 1300, 1150, 1060, 1020, 725, 685, 650 cm^{-1} ; MS m/z (%): 320 ($\text{Te}^{130} - \text{M}^+$, 45), 318 ($\text{Te}^{128} - \text{M}^+$, 42).

2c oil (lit¹³); ^1H NMR (CDCl_3 , 80 MHz) δ : 7.78—7.46 (m, 2H), 7.14—6.94 (m, 3H), 2.75 (t, $J = 7.0$ Hz, 2H), 1.45—1.05 (m, 20H), 0.82 (t, $J = 7.0$ Hz, 3H); IR (film/ CCl_4) ν : 3085, 3065, 2980, 2960, 2870, 1585, 1560, 1475, 1460, 1440, 1380, 1020, 1000, 720, 685, 650 cm^{-1} ; MS m/z (%): 376 ($\text{Te}^{130} - \text{M}^+$, 43), 374 ($\text{Te}^{128} - \text{M}^+$, 40).

2d oil (lit¹⁴); ^1H NMR (CDCl_3 , 80 MHz) δ : 7.92—7.78 (m, 2H), 7.32—7.16 (m, 3H), 4.00 (q, $J = 7.8$ Hz, 2H), 3.48 (s, 2H), 1.17 (t, $J = 7.8$ Hz, 3H); IR (film/ CCl_4) ν : 1717 (C=O) cm^{-1} ; MS m/z (%): 294 ($\text{Te}^{130} - \text{M}^+$, 50), 292 ($\text{Te}^{128} - \text{M}^+$, 46).

2e oil (lit¹⁴); ^1H NMR (CDCl_3 , 80 MHz) δ : 7.96—7.82 (m, 2H), 7.40—7.22 (m, 3H), 3.58 (s, 3H), 3.50 (s, 2H); IR (film/ CCl_4) ν : 1715 (C=O) cm^{-1} ; MS m/z (%): 280 ($\text{Te}^{130} - \text{M}^+$, 50), 278 ($\text{Te}^{128} - \text{M}^+$, 47).

2f oil (lit¹⁵); ^1H NMR (CDCl_3 , 80 MHz) δ : 7.90—7.76 (m, 2H), 7.34—7.20 (m, 3H), 3.98 (q, $J = 8.0$ Hz, 2H), 3.80 (q, $J = 7.8$ Hz, 1H), 1.58 (d, $J = 8.0$ Hz, 3H), 1.17 (t, $J = 7.8$ Hz, 3H); IR (film/ CCl_4) ν : 1717 (C=O) cm^{-1} ; MS m/z (%): 308 ($\text{Te}^{130} - \text{M}^+$, 42), 306 ($\text{Te}^{128} - \text{M}^+$, 39).

3a oil (lit¹⁶); ^1H NMR (CDCl_3 , 80 MHz) δ : 7.72—7.52 (m, 2H), 7.20—7.01 (m, 3H), 3.52 (s, 3H), 3.31—2.76 (m, 4H); IR (film/ CCl_4) ν : 1750 (C=O) cm^{-1} ; MS m/z (%): 294 ($\text{Te}^{130} - \text{M}^+$, 45), 292 ($\text{Te}^{128} - \text{M}^+$, 42).

3b oil (lit¹⁶); ^1H NMR (CDCl_3 , 80 MHz) δ : 7.78—7.52 (m, 2H), 7.23—7.01 (m, 3H), 3.99 (q, $J = 7.8$ Hz, 2H), 3.12—2.62 (m, 4H), 1.17 (t, $J = 7.8$ Hz, 3H); IR (film/ CCl_4) ν : 1750 (C=O) cm^{-1} ; MS m/z (%): 308 ($\text{Te}^{130} - \text{M}^+$, 46),

306 ($\text{Te}^{128} - \text{M}^+$, 43).

3c oil (lit¹⁷); ^1H NMR (CDCl_3 , 80 MHz) δ : 7.79—7.52 (m, 2H), 7.30—7.00 (m, 3H), 3.96 (t, $J = 7.8$ Hz, 2H), 3.05—2.66 (m, 4H), 1.71—1.14 (m, 4H), 0.88 (t, $J = 7.0$ Hz, 3H); IR (film/ CCl_4) ν : 1750 (C=O) cm^{-1} ; MS m/z (%): 336 ($\text{Te}^{130} - \text{M}^+$, 37), 334 ($\text{Te}^{128} - \text{M}^+$, 34).

3d oil (lit¹⁷); ^1H NMR (CDCl_3 , 80 MHz) δ : 7.76—7.52 (m, 2H), 7.24—6.91 (m, 3H), 3.50 (s, 3H), 3.12—2.57 (m, 3H), 1.50 (d, $J = 8.0$ Hz, 3H); IR (film/ CCl_4) ν : 1750 (C=O) cm^{-1} ; MS m/z (%): 308 ($\text{Te}^{130} - \text{M}^+$, 34), 306 ($\text{Te}^{128} - \text{M}^+$, 31).

3e oil (lit¹⁶); ^1H NMR (CDCl_3 , 80 MHz) δ : 7.81—7.62 (m, 2H), 7.3—7.07 (m, 3H), 3.10—2.51 (m, 4H); IR (film/ CCl_4) ν : 3080, 3060, 2980, 2940, 2860, 2225, 1580, 1480, 1440, 1300, 1250, 1170, 1060, 1020, 1000, 900, 880, 730, 690, 650 cm^{-1} ; MS m/z (%): 261 ($\text{Te}^{130} - \text{M}^+$, 47), 359 ($\text{Te}^{128} - \text{M}^+$, 44).

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