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Samarium Diiodide Induced Reductive Cleavage of the Te–Si Bond in Phenyltellurotrimethylsilane: A Novel Method for the Synthesis of Alkylphenyl Tellurides, Telluroesters, and β-Phenyltelluro Esters (Nitriles)

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ABSTRACT: *Phentyltellurotrimethylsilane (***1***) was reduced by samarium diiodide in tetrahydrofuran (THF) to produce samarium phenyltellurolate. This new tellurolate anion reacted smoothly with alkyl and benzyl halides to give alkyl and benzyl-phenyl tellurides in good yields under mild and neutral conditions. The samarium tellurolate also reacted with acyl halides or anhydrides to give telluroesters, and the 1,4-addition of samarium tellurolate to α, β-unsaturated esters (nitriles) gave β-phenyltelluro esters (nitriles).* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 471–474, 1999

INTRODUCTION

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 tellurosilane **1** was synthesized in 1980 [3], but very few reports about reactivity have been published [1]. Based on the weak Te–Si bond and the high nucleophilicity of the PhTe group, it is anticipated that it will be a promising reagent for organotelluration.

Samarium diiodide is a powerful one-electron transfer reductant. It has widely been applied in organic synthesis [4]. Our previous work on the reductive cleavage of the S–S, Se–Se, Te–Te, S–Si and Se–Si bonds by SmI_2 [5a–d] led us to investigate the reductive cleavage of the Te–Si bond by SmI_2.

We now report that samarium diiodide reduces phenyltellurotrimethylsilane to samarium phenyltellurolate under a nitrogen atmosphere. This new tellurolate species reacts with alkyl, benzyl, and acyl halides, and also anhydrides and α,β-unsaturated esters (nitriles) to give alkyl, benzyl, phenyltellurides, telluroesters, and β-phenyltelluro esters (nitriles), respectively.

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RESULTS AND DISCUSSION

We first examined whether the Te–Si bond in tellurosilane **1** could be cleaved by SmI_2. The cleavage of the S–Si or Se–Si bond in phenylthiotrimethylsilane and phenylselenotrimethylsilane, respectively, by SmI_2 has been reported to give samarium phenylthiolate ($PhSSmI_2$) and samarium phenylselenolate ($PhSeSmI_2$) species [5b,5c]. Similarly, addition of tellurosilane **1** to a deep blue solution of SmI_2 in tetrahydrofuran (TH_P) resulted in a change of color of the solution to dark brown, indicating that the Te–Si bond was reductively cleaved by SmI_2, and that samarium phenyltellurolate ($PhTeSmI_2$) was formed [1] (Scheme 1). The samarium phenyltellurolate was never isolated but reacted smoothly with acyl halides or anhydrides to afford telluroesters easily in good yields (Table 1).

The halogen moiety of an alkyl halide was displaced by the phenyltellurolate ion of the samarium salt successfully to give the corresponding alkyl or phenyltelluride (Scheme 2); some results are summarized in Table 2.

The Michael addition of samarium phenyltellurolate to α,β-unsaturated esters (nitriles) took place readily to give β-phenyltelluro esters (nitriles) as shown in Scheme 3. To avoid polymerization of α,β-unsaturated esters (nitriles), stoichiometric quantities of *t*-BuOH were added to the solution. The results are summarized in Table 3.

EXPERIMENTAL

Melting points were obtained on an electrothermal melting point apparatus and were uncorrected. ^1H 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 an HP5989B mass spectrometer. Elemental analyses were carried out using a Carlo Erba 1106 instrument.

Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl before use. All organic halides, anhydrides, and α,β-unsaturated esters (nitriles) were commercially available and were used without further purification. Tellurosilane **1** was prepared by the reaction of phenyltellurolate with trimethylsilyl chloride [1b]. All reactions were performed in a Schlenk type glass apparatus and under a nitrogen atmosphere.

Reaction of Tellurosilane 1 *with an Acyl Chloride or Anhydrides Mediated by SmI_2*

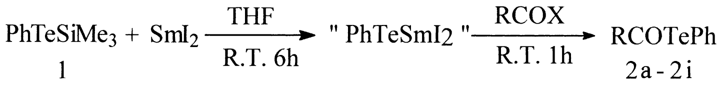
General Procedure. Samarium powder (0.33 g, 2.2 mmol, 99.9%) was placed in a well dried three-necked round bottom flask containing a magnetic stir bar. The flask was flushed with nitrogen several times. Tetrahydrofuran (10 mL) was added through a rubber septum by use of a syringe. Iodine (0.55 g, 2.2 mmol) was added to the flask under the protection of nitrogen. The mixture was stirred at room temperature until the solution became deep blue and homogeneous (1–2hours). This solution of SmI_2 was ready for subsequent use. To the THF solution of SmI_2 was added tellurosilane **1** (0.28 g, 1 mmol) by syringe at room temperature under a nitrogen atmosphere. The deep blue solution gradually became brown within 6 hours, which showed that the Te–Si bond had been reductively cleaved by SmI_2 and that the samarium phenyltellurolate ($PhTeSmI_2$) had been generated. Acyl halides (1.5 mmol) or anhydrides (1.5 mmol) in THF (1 mL) were then added by syringe, and the mixture was stirred at room temperature for 1hour. A dilute solution of HCl (20 mL) and diethyl ether (50 mL) was added. The organic layer was washed twice with water (20 mL) 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:ethyl acetate = 100:1 as eluent).

Reaction of Tellurosilane 1 *with Alkyl Halides Mediated by SmI_2*

The preparation of samarium phenyltellurolate ($PhTeSmI_2$) was the same as described previously. Each alkyl halide (1 mmol) in THF (1 mL) was then added by syringe, and the mixture was stirred at room temperature for 10 hours. A dilute solution of HCl (20 mL) and diethyl ether (50 mL) was added. The organic layer was washed twice with water (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo. The crude product was purified by preparative TLC on a silica gel (cyclohexane:ethyl acetate = 100:1 as the eluent).

Reaction of Tellurosilane 1 *with α,β-Unsaturated Esters (Nitriles) Mediated by SmI_2*

The solution of samarium phenyltellurolate ($PhTeSmI_2$) was prepared as described previously. Each α,β-unsaturated ester (nitrile) (1.5 mmol) and *t*-BuOH (1 mmol) in THF (1 mL) were then added by syringe, and the mixture was stirred at room temperature for 2 hours. Dilute HCl (20 mL) and diethyl ether (50 mL) were added. The organic layer was washed twice with water (20 mL) 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:ether = 5:1 as the eluent).



$$\underset{1}{PhTeSiMe_3} + SmI_2 \xrightarrow[\text{R.T. 6h}]{\text{THF}} \text{" PhTeSmI2 "} \xrightarrow[\text{R.T. 1h}]{\text{RCOX}} \underset{2a-2i}{RCOTePh}$$

SCHEME 1

TABLE 1 SmI_2 Mediated Reaction of Tellurosilane **1** with Acyl Halides or Anhydrides

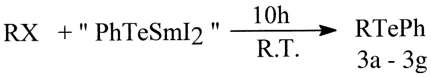
Entry	*RCOX*	*Product* (**2**)	*Yield*^{a} (*%*)
a	PhCOCl	PhTeCOPh	82
b	*p*-Cl-C_6H_4COCl	*p*-Cl-$C_6H_4COTePh$	81
c	*p*-Br-C_6H_4COCl	*p*-Br-$C_6H_4COTePh$	80
d	*o*-Br-C_6H_4COCl	*o*-Br-$C_6H_4COTePh$	78
e	CH_3COCl	$CH_3COTePh$	76
f	$CH_3(CH_2)_{10}COCl$	$CH_3(CH_2)_{10}COTePh$	68
g	$(CH_3CO)_2O$	$CH_3COTePh$	74
h	$(CH_3CH_2CO)_2O$	$CH_3CH_2COTePh$	72
i	$(CH_3)_2CHCOCl$	$(CH_3)_2CHCOTePh$	68

^{a}Isolated yield based on PhTe-$SiMe_3$.

TABLE 2 SmI_2 Mediated Reaction of Tellurosilane **1** with Alkyl or Benzyl Halides

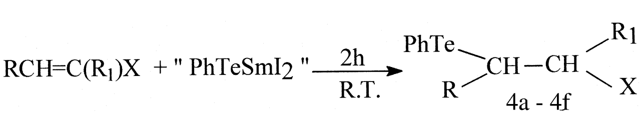
Entry	*RX*	*Product* (**3**)	*Yield*^{a} (*%*)
a	$PhCH_2Cl^b$	$PhTeCH_2Ph$	78
b	$CH_3(CH_2)_5Br$	$PhTe(CH_2)_5CH_3$	71
c	$CH_3(CH_2)_7Br$	$PhTe(CH_2)_7CH_3$	69
d	$CH_3(CH_2)_9Br$	$PhTe(CH_2)_9CH_3$	65
e	$CH_3(CH_2)_{11}Br$	$PhTe(CH_2)_{11}CH_3$	68
f	$CH_3(CH_2)_{15}Br$	$PhTe(CH_2)_{15}CH_3$	70
g	$(CH_3)_2CHBr$	$PhTeCH(CH_3)_2$	53

^{a}Isolated yield based on PhTe-$SiMe_3$.
^{b}Room temperature, 4 hrs.



$$RX + \text{" PhTeSmI2 "} \xrightarrow[\text{R.T.}]{\text{10h}} \underset{3a-3g}{RTePh}$$

SCHEME 2



SCHEME 3

TABLE 3 SmI_2 Mediated Michael Reaction of Tellurosilane **1** with α,β-Unsaturated Esters (Nitriles)

Entry	*RCH = C(R$_1$)X*	*Product* (**4**)	*Yield*^{a} (*%*)
a	$CH_2=CHCO_2Me$	$PhTeCH_2CH_2CO_2Me$	75
b	$CH_2=CHCO_2Et$	$PhTeCH_2CH_2CO_2Et$	82
c	$CH_2=CHCO_2Bu$-n	$PhTeCH_2CH_2CO_2Bu$-n	79
d	$CH_3CH=CHCO_2Et$	$PhTeCH(CH_3)CH_2CO_2$	60
e	$CH_2=C(CH_3)CO_2Me$	$PhTeCH_2CH(CH_3)CO_2Me$	69
f	$CH_2=CHCN$	$PhTeCH_2CH_2CN$	60

^{a}Isolated yield based on tellurosilane **1**.

DATA OF PRODUCTS

2a[6]. M.p. 70–71°C, ^{1}H NMR (δ_H): 7.02–8.03 (m); IR ν_{max}/cm^{-1}: 3080, 3040, 1685, 1600, 1590, 1480, 1280, 1200, 1170, 1010, 1000, 850, 760, 740, 680, 650.

2b[7]. M.p. 69–72°C, ^{1}H NMR (δ_H) 7.20–7.75 (m); IR ν_{max}/cm^{-1}: 3080, 3050, 1690, 1600, 1580, 1490, 1440, 1250, 1200, 1160, 1085, 1010, 1000, 850, 780, 750, 680.

2c[8]. M.p. 76–78°C, ^{1}H NMR(δ_H): 7.20–7.70 (m); IR ν_{max}/cm^{-1}: 3100, 3080, 1690 1595, 1580, 1530, 1490, 1250, 1200, 1170, 1070, 1010, 850, 780, 750, 680.

2d[6]. M.p. 64–66°C, ^{1}H NMR (δ_H): 7.10–7.70 (m); IR ν_{max}/cm^{-1}: 3080, 3050, 1685, 1600, 1575, 1440, 1250, 1020, 850, 750, 680.

2e and 2g[6]. Oil, ^{1}H NMR (δ_H): 2.40(3H,s), 7.00–7.33(3H,m), 7.51–7.80(2H,m); IR ν_{max}/cm^{-1}: 3090, 3085 2980, 1740, 1580, 1520, 1480, 1440, 1350, 1250, 1080, 1020, 1000, 760, 680.

2f[9]. Oil, ^{1}H NMR (δ_H): 0.89(3H,t), 1.40(18H,m), 2.50(2H,t), 7.00–7.21(3H,m). 7.50–7.71(2H,m); IR ν_{max}/cm^{-1}: 3080, 3075, 2985, 2960, 2890–2860, 1720, 1580, 1560, 1480, 1440, 1380, 1250, 1020, 1000, 740, 680.

2h[6]. Oil, ^{1}H NMR (δ_H): 0.86(3H,t), 2.50(2H,q), 7.00–7.30(3H,m), 7.40–7.73(2H,m); IR ν_{max}/cm^{-1}: 3080, 3075, 2985, 2960, 2890–2860, 1720, 1580, 1560, 1480, 1440, 1380, 1250, 1020, 1000, 740, 680.

2i. Oil, ^{1}H NMR (δ_H): 1.10(6H,d), 2.30–2.80(1H,m), 7.00–7.21(3H,m), 7.50–7.70(2H,m); IR ν_{max}/cm^{-1}: 3080, 3075, 2985, 2960, 2890–2860, 1720, 1580, 1560, 1480, 1440, 1380, 1250, 1020, 1010, 745, 690; *m/z* (M^+), 278; Anal. calc. for $C_{10}H_{12}OTe$: C, 43.55; H, 4.38; Found: C, 43.42; H 4.49.

3a[10]. M.p. 33–34°C, ^{1}H NMR (δ_H): 3.95(2H,s), 6.80–7.70(10H,m); IR ν_{max}/cm^{-1}: 3080, 3050, 2950, 1580, 1560, 1500, 1480, 1250, 1160, 1020, 760, 740, 690.

3b[11]. Oil, ^{1}H NMR (δ_H): 0.83(3H,t), 1.10–

1.40(8H,m), 2.73(2H,t), 6.90–7.16(3H,m), 7.40–7.66(2H,m); IR ν_{max}/cm^{-1}: 3085, 3070, 2980, 2960, 2860, 1580, 1480, 1450, 1440, 1380, 1300, 1150, 1060, 1020, 1000, 720, 685, 650.

3c[11]. Oil, ^{1}H NMR (δ_H): 0.83(3H,t), 1.20–1.41(12H,m), 2.74(2H,t), 6.85–7.18(3H,m), 7.42–7.70(2H,m); IR ν_{max}/cm^{-1}: 3080, 3070, 2980, 2960, 2860, 1580, 1480, 1450, 1380, 1300, 1150, 1060, 1020, 1000, 725, 685, 650.

3d[10]. Oil, ^{1}H NMR (δ_H): 0.83(3H,t), 1.20–1.40(16H,m), 2.73(2H,t), 6.90–7.16(3H,m), 7.40–7.66(2H,m); IR ν_{max}/cm^{-1}: 3085, 3070, 2980, 2960, 2860, 1580, 1480, 1460, 1440, 1380, 1300, 1150, 1060, 1020, 1000, 720, 685, 650.

3e[12]. Oil, ^{1}H NMR (δ_H): 0.81(3H,t), 1.05–1.45(20H,m), 2.75(2H,t), 6.95–7.15(3H,m), 7.45–7.78(2H,m); IR ν_{max}/cm^{-1} 3085, 3065, 2980, 2960, 2870, 1585, 1560, 1475, 1460, 1440, 1380, 1020, 1000, 720, 685, 650.

3f[11]. m.p. 32–33°C, ^{1}H NMR (δ_H): 0.80(3H,t), 1.06–1.45(28H,m), 2.74(3H,t). 6.95–7.15(3H,m), 7.45–7.78(2H,m); IR ν_{max}/cm^{-1}: 3080, 3065, 2980–2960, 2870, 1585, 1560, 1480, 1440, 1380.

3g[5b]. Oil, ^{1}H NMR (δ_H): 1.30(6H,d), 3.50–3.70(1H,m), 7.10–7.30(3H,m), 7.40–7.60(2H,m); IR ν_{max}/cm^{-1}: 3085, 3070, 2980, 2960, 2860, 1580, 1480, 1450, 1440, 1380, 1300, 1250, 1140, 1070, 1020, 1000, 720, 690, 650.

4a[13]. Oil, ^{1}H NMR (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.

4b[13]. Oil, ^{1}H NMR (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.

4c[14]. Oil, ^{1}H NMR (δ_H): 0.89(3H,t), 1.14–1.70(4H,m), 2.67–3.04(4H,m), 3.96(2H,q), 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.

4d[12]. Oil, ^{1}H NMR (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.

4e[13]. Oil, ^{1}H NMR (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.

4f[13]. Oil, ^{1}H NMR (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, 880, 730, 690, 650.

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