A Novel Method for the Synthesis of Telluroesters

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Diaryl ditellurides were conveniently reduced by a system consisting of cerium trichloride and samarium intetrahydrofuran to produce the aryltellurolates. This “living” tellurolate anion species reacted smoothly with acid chlorides and acid anhydrides to afford telluroesters in good yields under mild and neutral conditions.

Keywords: Ditellurides; Samarium; $CeCl_3$; Reductive; Aryltelluroester.

INTRODUCTION

Organotellurium compounds have attracted considerable interest recently as reagents and intermediates in organic synthesis.[1] Considering that the C-Te bond of the telluroesters is weak and very easily broken, telluroesters have been employed as mild acyltransfer reagents,[2] precursors of acyl radicals,[3] or anions.[4] And the findings of its liquid crystal properties have also been attractive.[5]

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 electrophiles.[6] It can be prepared by the reaction of a benzoyl chloride with NaTeAr.[7] The use of ditellurides and samarium diiodide in THF/HMPA,[8] $Sm/ZrCl_4$,[9] $Sm/CrCl_3$ (Cat.)[10] have also recently been reported to give the telluride anions.

In 1980, Kagan and cowoekers[11] published a seminal paper on the usage of samarium diiodide. Following the pioneering work of Kagan, a number of important individual reactions induced by SmI_2 have been found useful in organic synthesis.[12] Although SmI_2 is a useful reagent, its sensitivity to air limits its application in organic synthesis. 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 ($Zn^{2+}/Zn = -0.71$). These properties encouraged us and other workers to use the more convenient and cheaper metallic samarium directly instead of samarium diiodide.[13]

In our previous work, we investigated the reductive cleavage of Se-Se bond by a new reductive system $CeCl_3/Sm$ to afford organic seleno compounds.[14] And we also reported the $CeCl_3/Sm$ system promoted pinacolic coupling of aromatic aldehydes and ketones to afford 1,2-diols.[15] In continuing our research in this area, herein we wish to report the $CeCl_3/Sm$ system promoted reductive cleavage of Te-Te bond in ditellurides to produce aryltellurolates, which reacted with acid chlorides and acid anhydrous to afford telluroesters.

EXPERIMENTAL SECTION

Melting points were uncorrected. IR spectra were obtained on a PE-683 infrared spectrophotometer. ^1H NMR spectra were recorded on a JEOL-90Q NMR instrument in carbon tetrachloride as solvent and tetramethylsilane as an internal standard. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl before use. Acyl halides and anhydrides were commercially available and were used without further purification. The reaction was performed in a Schlenk type apparatus and under a nitrogen atmosphere.

GENERAL PROCEDURE

Under nitrogen atmosphere, metallic samarium powder (3 mmol), cerium trichloride (1 mmol) and ditelluride (0.5 mmol) were placed in a three-necked reaction flask and THF (10 mL) was added in one portion. The resulting mixture was magnetically stirred at 30 °C for 4 h, and the cleavage of the Te-Te bond was indicated by the dissipation of the red color of the mixture due to ditelluride. To the mixture was added successively the acid chloride (1.5 mmol) or the acid anhydride (1.5 mmol) and stirred for given times (see Table 1, TLC as monitored). When the reaction was finished, dilute HCl (0.1 M, 10 mL) and diethyl ether (50 mL) were added. The organic layer was washed with water (20 mL × 2) and

Table 1. Synthesis of the Telluroesters

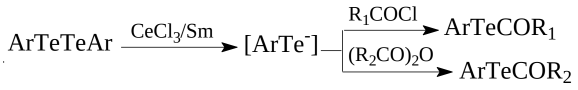
Entry	Ar	R_1	R_2	Time (h)	Yield (%)[a]
1	Ph	Ph		2	70
2	P-MeC_6H_4	Ph		2	72
3	Ph	P-ClC_6H_4		2	75
4	Ph	o-BrC_6H_4		2	67
5	Ph	P-BrC_6H_4		2	73
6	P-MeC_6H_4	P-BrC_6H_4		2	75
7	Ph		CH_3	3	68
8	Ph	CH_3CH_2		2	71

[a] Isolated yields based on ditelluride.

dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure; the residue was then purified by preparative TLC on Silica gel with light petroleum and ethyl acetate (100:1) as eluent to give the products.

In summary, a novel method for the preparation of telluroesters has been provided. The advantages of which are easily available and cheap materials, single product, simple manipulation, and mild and neutral conditions.

Scheme I



DATA OF THE PRODUCTS

1[16] PhCOTePh m.p. 70-71 °C (lit. 71-72 °C); IR ν_{max} (cm^{-1}) 3080, 3040, 1685, 1600, 1590, 1480, 1280, 1200, 1170, 1010, 1000, 850, 760, 740, 680, 650; ^{1}H NMR 7.02-8.03 (m).

2[17] PhCOTeC_6H_4Me-p m.p. 64-66 °C (lit. 65-67 °C); IR ν_{max} (cm^{-1}) 3100, 3080, 2980, 2880, 1680, 1595, 1580, 1530, 1490, 1385, 1250, 1200, 1170, 1070, 1010, 850, 780, 750, 690; ^{1}H NMR 2.35 (3H, s), 6.90-7.10 (2H, m), 7.30-7.70 (5H, m), 7.90-8.15 (2H, m).

3[2] p-ClC_6H_4COTePh m.p. 69-72 °C (lit. 71-72 °C); IR ν_{max} (cm^{-1}) 3080, 3050, 1690, 1600, 1580, 1490, 1440, 1250, 1200, 1160, 1085, 1010, 1000, 850, 780, 750, 680; ^{1}H NMR 7.20-7.75 (m).

4[16] o-BrC_6H_4COTePh m.p. 64-66 °C (lit. 65-67 °C); IR ν_{max} (cm^{-1}) 3080, 3050, 1685, 1600, 1575, 1440, 1250, 1020, 850, 750, 680; ^{1}H NMR 7.10-7.70 (m).

5[17] p-BrC6H$_4$COTePh m.p. 76-78 °C (lit. 79 °C); IR ν_{max} (cm^{-1}) 3100, 3080, 1690, 1595, 1580, 1530, 1490, 1250, 1200, 1170, 1070, 1010, 850, 780, 750, 680; ^{1}H NMR 7.20-7.70 (m).

6[17] p-BrC_6H_4COTeC_6H_4Me-p m.p.110-112 °C (lit. 111-112 °C); IR ν_{max} (cm^{-1}) 3100, 3080, 2980, 2880, 1670, 1595, 1580, 1530, 1490, 1385, 1250, 1200, 1170, 1070, 1010, 850, 780, 750, 680; ^{1}H NMR 2.35 (3H, s), 6.90-7.20 (2H, m), 7.40-7.90 (6H, m).

7[16] CH_3COTePh oil; IR ν_{max} (cm^{-1}) 3090, 3085, 2980, 1740, 1580, 1520, 1480, 1440, 1350, 1250, 1080, 1020, 1000, 760, 680; ^{1}H NMR 2.40 (3H, s), 7.00-7.33 (3H, m), 7.51-7.80 (2H, m).

8[16] CH_3CH_2COTePh oil; IR ν_{max} (cm^{-1}) 3080, 3075, 2985, 2960, 2890-2860, 1720, 1560, 1480, 1480, 1440, 1380, 1250, 1020, 1000, 740, 680; ^{1}H NMR 1.16 (3H, t), 2.50 (2H, q), 7.00-7.30 (3H, m), 7.40-7.73 (2H, m).

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