Reductive cleavage of the Te-Te bond in ditellurides by CeCl₃/Sm system: A novel method for the synthesis of β-telluroesters (and nitriles)

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Diaryl ditellurides are conveniently reduced by a system consisting of CeCl₃/Sm in tetrahydrofuran to produce aryltellurolates. This new tellurolate anion species reacts smoothly with α,β-unsaturated esters (and nitriles) to give β-telluroesters (and nitriles) in moderate to good yields.

Organotellurium compounds have recently attracted considerable interest as reagents and intermediates in organic synthesis since it's increasing role in organic synthesis. A convenient and general method to introduce tellurium moiety into organic molecules is the reaction of metal tellurolates with appropriate electrophiles. The use of ditellurides and samarium diiodide in THF/HMPA and Sm/ZrCl₄ system have also recently been reported to give the telluride anions.

As a powerful, versatile and ether-soluble one-electron transfer reducing agent, SmI₂ has played an ever-increasing role in organic synthesis since its introduction by Kagan and his group. Though SmI₂ is a useful reagent, its 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 (Sm³⁺/Sm = -2.41V) is comparable to that of magnesium (Mg²⁺/Mg = -2.37V), superior to that of zinc (Zn²⁺/Zn = -0.71V). These properties promoted us and other workers to use the more convenient and cheaper metallic samarium directly instead of samarium diiodide.

In continuing our research in this area, we investigated the cleavage of Te-Te bond induced by CeCl₃/Sm system since cerium trichloride is a very cheap, nontoxic, and water tolerant reagent and has emerged as a Lewis acid imparting high regio- and chemo-selectivity in various chemical transformations. One of the remarkable features of CeCl₃ is its efficient activity in combination with sodium iodide, MeLi⁸, and n-BuLi⁹ to form organic cerium reagents which can be used as selective organic magnesium reagents and the reductive system of NaBH₄-CeCl₃ has been widely used in organic synthesis.

Experimental Section

Melting points were uncorrected. IR spectra (max in cm⁻¹) were obtained on a PE-683 infrared spectrophotometer, ¹H NMR spectra on a JEOL-90Q NMR instrument measured in CCl₄ using TMS as internal standard (chemical shifts in ppm) and mass spectra on Agilent 5973 Spectrometer(EI at 70ev). The solvent THF was freshly distilled from sodium/benzophenone ketyl prior to use. The α, β-unsaturated esters (and nitriles) are commercially available and were used without further purification. The reactions were performed in a Schlenk type glass apparatus under a nitrogen atmosphere.

General procedure

Under nitrogen atmosphere, metallic samarium powder (3mmole), cerium trichloride (1mmole), THF (10mL) and ditelluride (0.5mmole) were placed in a three necked reaction flask. The resulting mixture was magnetically stirred at 30°C for 4hr, and the cleavage of the Te-Te bond was indicated by the dissipation of the yellow color of the mixture due to ditelluride. The α,β-unsaturated esters (or nitriles) (1.5mmole) and t-BuOH(1mmole) in THF(1mL) were then added by syringe and stirred at room temperature for 4hr. A dilute solution of HCl (10mL) and diethyl ether (50mL) were added. The organic layer was washed with water (20mL×2) and dried over anhydrous Na₂SO₄. The solvent was removed in vacuo and the residue was then purified by preparative TLC on silica gel with light petroleum: ether (5:1) as eluent. The results are reported in Table I.

In summary, a novel method for the preparation of the β-telluroesters (and nitriles) has been provided, the advantages of which are easily available and...
Data of the products

Methyl 3-(phenyltelluro) propanate 2a: Oil\textsuperscript{i}; \textsuperscript{1}H NMR: \textsuperscript{2}2.75-3.30(4H, m), 3.50(3H, s), 7.00-7.20(3H, s), 7.50-7.73(2H, m); IR: 1745, 1580, 1480, 1440, 1380, 1250, 1220, 1020, 1000, 910, 880, 800; MS: m/z 308(M\textsuperscript{+}).

Ethyl 3-(phenyltelluro) propanate 2b: Oil\textsuperscript{i}; \textsuperscript{1}H NMR: \textsuperscript{2}1.18(3H, t), 2.63-3.13(4H, m), 3.99(2H, q), 6.73-6.90(2H, m); IR: 1745, 1580, 1480, 1460, 1440, 1380, 1250, 1220, 1020, 1000, 910, 880, 800; MS: m/z 322(M\textsuperscript{+}).

Butyl 3-(phenyltelluro) propanate 2c: Oil\textsuperscript{i}; \textsuperscript{1}H NMR: \textsuperscript{2}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: 3080, 3070, 2910, 2890, 2870, 1750, 1580, 1480, 1440, 1380, 1250, 1200, 1160, 1020, 740, 690, 650; MS: m/z 336(M\textsuperscript{+}).

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\textbf{References}


