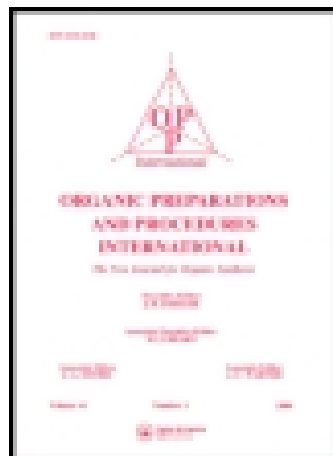


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A NOVEL METHOD FOR THE SYNTHESIS OF TELLUROESTERS

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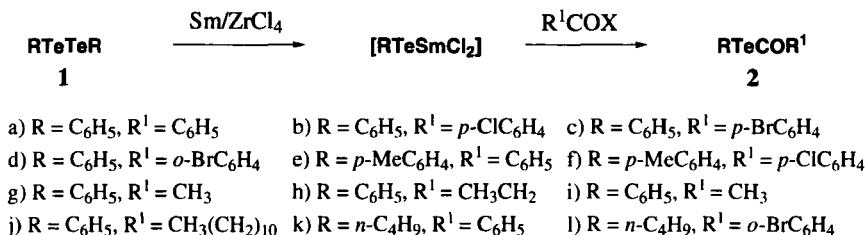
11. Unpublished results from our laboratory.
12. Fisher reduced nickel powder, Cat. No. N-40 was employed.

A NOVEL METHOD FOR THE SYNTHESIS OF TELLUROESTERS

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Organotellurium compounds have attracted considerable interest as reagents and intermediates in organic synthesis recently.¹ From a number of methods, a convenient and general method to introduce a tellurium moiety into organic molecules is the reaction of metal tellurides with appropriate electrophiles.² The use of ditellurides and samarium diiodide in THF/HMPA has also been reported recently to give telluride anions.³ As a powerful, versatile and ether-soluble one-electron transfer reducing agent, SmI_2 has played an ever-increasing role in organic synthesis⁴ since its introduction by Kagan and his group.⁵ Though SmI_2 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 ($\text{Sm}^{3+}/\text{Sm} = -2.41\text{V}$) is comparable to that of magnesium ($\text{Mg}^{2+}/\text{Mg} = -2.37\text{V}$), superior to that of zinc ($\text{Zn}^{2+}/\text{Zn} = -0.71\text{V}$). These properties prompted us to use it directly instead of samarium (II) iodide.⁶ Herein, we report that reductive cleavage of Te-Te bond in ditellurides by Sm/ZrCl_4 system led to telluride anion species, which react with acyl halides or anhydrides to give telluroesters in good yields under mild and neutral conditions.



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

formation of telluride anion species with Sm/ZrCl_4 is similar to that with SmI_2 .³ The results of our experiments are summarized in the **Table**. In summary, we have developed a novel method for the preparation of telluroesters as single product by simple manipulation under mild and neutral conditions.

EXPERIMENTAL SECTION

Melting points were obtained on a electrothermal melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a Bruker 80 MHz instrument in carbon tetrachloride as the solvent and tetramethylsilane as an internal standard. IR spectra(KBr) were determined on a PE-683 spectrometer. 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 glass apparatus and under a nitrogen atmosphere.

TABLE. Yields, Physical Constants and Spectral Data of **2**

Entry	Yield (%)	mp. (°C)	lit. mp., bp. ^b (°C, °C/torr)	IR (CO) (cm ⁻¹)	^1H NMR (δ)
2a	87	70-71	70-72 ⁷	1685	7.02-8.03 (m)
2b	84	69-72	71-72 ⁸	1690	7.20-7.75 (m)
2c	82	76-78	77-79 ⁹	1690	7.20-7.70 (m)
2d	79	64-66	65-68 ⁷	1685	7.10-7.70 (m)
2e	93	64-66	65-67 ¹¹	1680	2.35 (3H, s), 6.90-7.10 (2H, m), 7.30-7.70 (5H, m), 7.90-8.15 (2H, m)
2f	90	110-112	111-112 ¹¹	1670	2.35 (3H, s), 6.90-7.20 (2H, m), 7.40-7.90 (6H, m)
2g^a	72	oil	105-110/0.3 ⁷	1720	2.40 (3H, s), 7.00-7.33 (3H, m), 7.51-7.80 (2H, m)
2h^a	76	oil	108-110/0.3 ⁷	1720	0.86 (3H, t), 2.50(2H, q), 7.00-7.30 (3H, m), 7.40-7.73 (2H, m)
2i	80	oil	105-110/0.3 ⁷	1740	2.40 (3H, s), 7.00-7.33 (3H, m), 7.51-7.80 (2H, m)
2j	70	oil	140-144/0.3 ¹⁰	1720	0.89 (3H, t), 1.40 (18H, m), 2.50 (2H, t), 7.00-7.21 (3H, m), 7.50-7.71 (2H, m)
2k	75	oil	136/3 ⁷	1676	0.90 (3H, t), 1.15-1.96 (4H, m), 2.85 (2H, t), 7.20-7.90 (5H, m)
2l	70	oil	165/3 ¹²	1680	0.90 (3H, t), 1.16-1.98 (4H, m), 2.75 (2H, t), 6.95-7.70 (4H, m)

a) From anhydride. b) Lit. data given in references.

General Procedure.- Samarium powder (0.15g, 1mmol, 99.9%), zirconium tetrachloride (0.04g, 0.2mmol) and the ditelluride (0.5mmol) were placed in a well-dried, three-necked round bottom flask containing a magnetic stir bar. The flask was flushed with nitrogen several times. Tetrahydrofuran (10mL) was added through a rubber septum by a syringe. The mixture was stirred at room tempera-

ture under an atmosphere of nitrogen, the red solution gradually became brown within 2h, indicating that the Te-Te bond had been reductively cleaved by Sm/ZrCl₄ and that the samarium aryltelluride (ArTeSmCl₂) had been generated. Acyl halides or anhydrides (1.5 mmol) were then added by syringe and stirred at room temperature for 1h. A 0.1 N HCl (20mL) and diethyl ether (50mL) were added. The organic layer was washed with water (20mL x 2) and dried over anhydrous Na₂SO₄. The solvent was removed in vacuum. The crude product was purified by preparative TLC on silica gel (100:1 light petroleum-ethyl acetate as eluent for all products).

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AN EFFICIENT ONE-POT SYNTHESIS OF α -PHENYLSELENO- α,β -UNSATURATED NITRILES *via* ARSONIUM SALTS

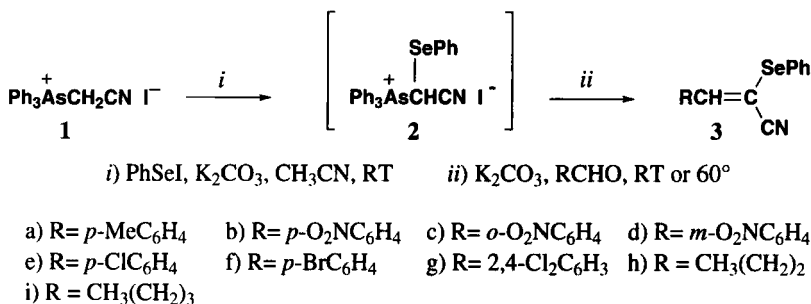
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Functionalized vinyl selenides bearing α -electron-withdrawing groups such as the cyano group, have been found to be particularly useful radical acceptors, leading generally to fumaronitriles by treatment with a radical initiator, followed by dimerization and elimination of dialkyl diselenide.¹ Vinyl selenides and ethylenes bearing electron-withdrawing groups, undergo [2+2]-cycloaddition to afford selenocyclobutanes.² The selenyl group may readily be replaced by various groups to afford substituted unsaturated compounds.^{3,4}

α -Phenylseleno- α,β -unsaturated nitriles have only been prepared by the addition of phenylselenenyl chloride, bromide or amide to the respective α,β -unsaturated nitriles, followed by elimination of hydrogen halide albeit in low overall yields.⁵ This has greatly stimulated our



interest in exploring an efficient one-pot synthesis of α -phenylseleno- α,β -unsaturated nitriles *via* the readily available arsonium salt **1** under mild condition in good yields. The arsonium iodide **1** reacted with phenylselenenyl iodide in the presence of anhydrous potassium carbonate at room temperature to produce the α -selenoarsonium iodide **2** which, without isolation, was treated with aromatic aldehydes to produce α -phenylseleno- α,β -unsaturated nitriles **3** in good yields; however, the yields were low with aliphatic aldehydes. The results are compiled in Table 1.