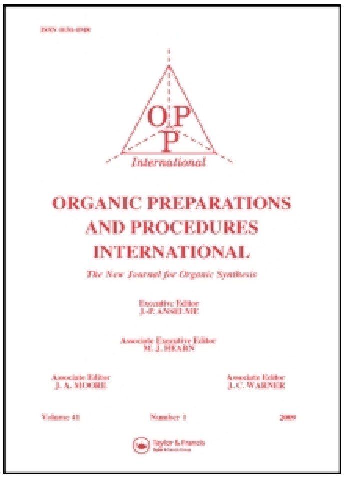

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A NOVEL METHOD FOR THE SYNTHESIS OF TELLUROESTERS

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11. Unpublished results from our laboratory.

12. Fisher reduced nickel powder, Cat. No. N-40 was employed.

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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 synthesis[4] 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 ($Sm^{3+}/Sm = -2.41V$) is comparable to that of magnesium ($Mg^{2+}/Mg = -2.37V$), superior to that of zinc ($Zn^{2+}/Zn = -0.71V$). 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.

$$\underset{\mathbf{1}}{\mathbf{RTeTeR}} \xrightarrow{Sm/ZrCl_4} \mathbf{[RTeSmCl_2]} \xrightarrow{R^1COX} \underset{\mathbf{2}}{\mathbf{RTeCOR^1}}$$

a) $R = C_6H_5, R^1 = C_6H_5$ b) $R = C_6H_5, R^1 = p\text{-}ClC_6H_4$ c) $R = C_6H_5, R^1 = p\text{-}BrC_6H_4$
d) $R = C_6H_5, R^1 = o\text{-}BrC_6H_4$ e) $R = p\text{-}MeC_6H_4, R^1 = C_6H_5$ f) $R = p\text{-}MeC_6H_4, R^1 = p\text{-}ClC_6H_4$
g) $R = C_6H_5, R^1 = CH_3$ h) $R = C_6H_5, R^1 = CH_3CH_2$ i) $R = C_6H_5, R^1 = CH_3$
j) $R = C_6H_5, R^1 = CH_3(CH_2)_{10}$ k) $R = n\text{-}C_4H_9, R^1 = C_6H_5$ l) $R = n\text{-}C_4H_9, R^1 = o\text{-}BrC_6H_4$

The formation and reaction of samarium aryltellurolates 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. ^{1}H NMR spectra were recorded on a Brucker 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})	^{1}H 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 temperature 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/$ZrCl_4$ and that the samarium aryltelluride ($ArTeSmCl_2$) 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 Na_2SO_4. 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

Submitted by (06/02/99)

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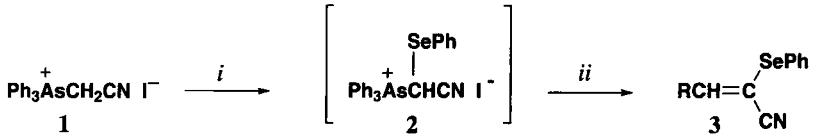
Functionalized vinyl selenides bearing α-electron-withdrawing groups such as the cyano group, have been found to be particularly useful radical acceptors, leading generally to fumaronitriles by treatment with a radical initiator, followed by dimerization and elimination of dialkyl diselenide.[1] Vinyl 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.



i) PhSeI, K_2CO_3, CH_3CN, RT *ii*) K_2CO_3, RCHO, RT or 60°

a) R= p-MeC_6H_4 b) R= p-$O_2NC_6H_4$ c) R= o-$O_2NC_6H_4$ d) R= m-$O_2NC_6H_4$
e) R= p-ClC_6H_4 f) R= p-BrC_6H_4 g) R= 2,4-$Cl_2C_6H_3$ h) R = $CH_3(CH_2)_2$
i) R = $CH_3(CH_2)_3$