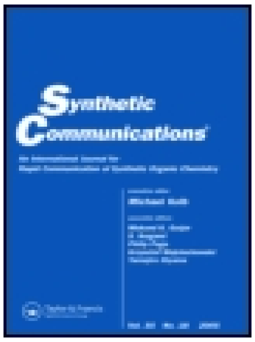

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REDUCTIVE CLEAVAGE OF THE Se-Se BOND BY THE Sm/CrCl$_3$ SYSTEM: A NOVEL ONE-POT METHOD FOR THE SYNTHESIS OF SELENOESTERS

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Abstract: Diaryl diselenides can react with acid chlorides or acid anhydrides in one-pot by the Sm/CrCl$_3$ system to give selenoesters in moderate to good yields under mild and neutral conditions.

Organoselenium compounds have received considerable attention as useful synthetic reagents and intermediates in organic synthesis.[1] For example, selenoesters are a type of activated esters due to their weaker C-Se bonds. They are very useful for the synthesis of naturally occurring macrocyclic lactones and lactams.[2] While there are many methods for the synthesis of selenoesters, the use of selenide anions reacting with acylating agents is especially convenient and common. Several methods for the synthesis of selenide anions have been recommended, the more important of which include the use of diselenide with

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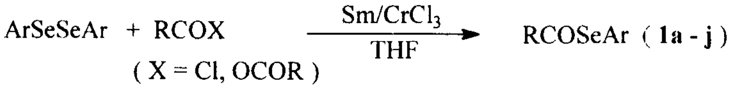
sodium borohydride,[3] reduction of the diselenide with sodium,[4] samarium diiodide[5] and lithium aluminium hydride.[6] Moreover, Grignard reagents also react with selenium to give selenide anions.[7]

Chromium(II) salts are widely used in organic synthesis as one-electron reducing agents.[8] The applications of chromium(II) salts to the reduction of alkyl halides, unsaturated systems, epoxides, acyloxyketones and nitro compounds have been reported.[9] Up to our knowledge, the use of chromium(II) salts to the reductive cleavage of diselenides has not been documented yet. The chromium(II) ion is readily prepared by the reduction of chromium(III) salts by zinc[9a] and $LiAlH_4$[10] in an inert atmosphere or direct use of anhydrous $CrCl_2$. However, the direct use of $CrCl_2$ is restricted due to its high hygroscopicity and sensitivity to air oxidation. Now we wish to describe a new method for preparation of the low valent chromium(II) reagent *in situ* from $Sm/CrCl_3/THF$ system, and use it to promote cleavage of the Se-Se bond to form a selenide anion. This species reacted with acid chlorides or acid anhydrides to afford selenoesters in moderate to good yields under mild and neutral conditions.. The results are summarized in **Table 1**.

Scheme 1



$$\underset{(\,X = Cl,\ OCOR\,)}{ArSeSeAr + RCOX} \xrightarrow[THF]{Sm/CrCl_3} RCOSeAr\ (\,\mathbf{1a-j}\,)$$

When anhydrous chromium(III) chloride suspended in THF was treated with samarium, the initial purple color of the reaction mixture darkened and finally turned dark brown after 20 min.. The color changes were similar to the

Table 1. Synthesis of selenoesters (1a-1j)

Entry	Ar	R	X	Temp.(°C)	Yield(%)[a]
1a	C_6H_5	C_6H_5	Cl	25	70
1b	C_6H_5	CH_3	Cl	25	84
1c	C_6H_5	n-$C_{11}H_{23}$	Cl	25	80
1d	C_6H_5	C_2H_5	$OCOCH_2CH_3$	25	75
1e	C_6H_5	n-C_3H_7	$OCO(CH_2)_2CH_3$	25	72
1f	*p*-$CH_3C_6H_4$	C_6H_5	Cl	40	65
1g	*p*-$CH_3C_6H_4$	CH_3	Cl	40	80
1h	*p*-$CH_3C_6H_4$	C_2H_5	$OCOCH_2CH_3$	40	71
1i	*p*-$CH_3C_6H_4$	n-C_3H_7	$OCO(CH_2)_2CH_3$	40	70
1j	*p*-ClC_6H_4	C_6H_5	Cl	40	87

[a] Yield of isolated product based on diselenides

changes in $CrCl_3/LiAlH_4$ system,[10] which indicated that low valent chromium(II) reagent was readily prepared. Treatment of a mixture of diselenides and acylating agents with the reagent produced selenoesters. We found that a mol ratio of 1.5 of $CrCl_3$: Sm was most effective for the reaction. It is interesting that catalytic amount of $CrCl_3$ (0.05mmol; samarium, 1mmol) was also practicable while it needed longer time(78% yield of **1b**, 20 hours). When substituting zinc for samarium, the reaction could also take place. However, the yield was much lower (40% yield of **1b**). We think it is probably because samarium has better reducing power(Sm^{3+}/Sm -2.41V) than that of zinc (Zn^{2+}/Zn -0.71V).

According to the experimental facts mentioned above, we herein propose a possible mechanism of catalytic $CrCl_3$ mediated cleavage of Se-Se bonds in diselenides as following.

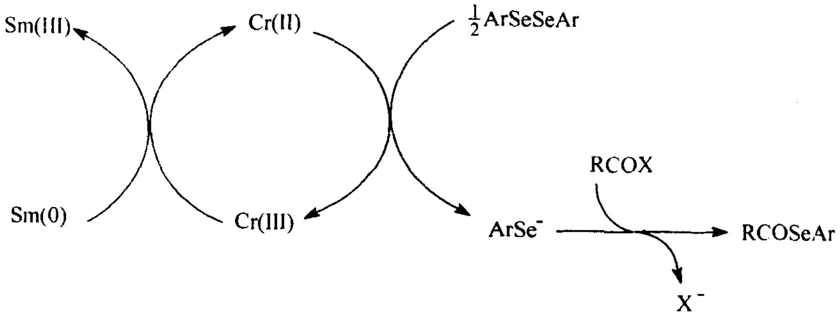


Figure 1

As mentioned in the beginning of the article, there have been many methods of synthesizing selenoesters. However, most of these methods have certain disadvantages such as harsh reaction conditions, using dangerous reagents, or obtaining lower yields. The present method has the advantages of easy availability of starting materials, neutral reaction conditions, simple operation and moderate to good yields.

Experimental Section

Melting points were uncorrected, Mass spectra were obtained on a HP 5989B mass spectrometer, IR spectra were recorded on a PE-683 spectrometer, ^{1}H NMR spectra were obtained with a JEOL PMX 60 SI spectrometer in CCl_4 solution using TMS as internal standard. The reactions were performed in a schlenk type glass apparatus under a nitrogen atmosphere. THF was freshly distilled from sodium-benzophenone ketyl prior to use.

General procedure for the synthesis of selenoesters in one-pot: Under an inert atmosphere of nitrogen, metallic samarium powder (0.15g, 1 mmol), CrCl$_3$ (0.24g, 1.5 mmol), diaryl diselenide (0.5 mmol), acid chloride or acid anhydride (1.2 mmol), THF (15 ml) were placed in a three-necked reaction flask with a reflux condenser. The mixture was magnetically stirred at 25-40 °C for 5 hours .When the reaction was complete, dilute hydrochloric acid (0.1M, 5 ml) was added to quench the reaction and the mixture was extracted with diethyl ether (2×20 ml). The extracts were washed with brine, dried over anhydrous MgSO$_4$, filtered, and the solvent was removed under reduced pressure; the residue was then purified by preparative TLC on silica gel to give pure product.

1a[11]. m.p. 34-36 °C(lit, 35-37 °C); ^{1}H NMR, 8.02-7.73(m, 2H), 7.63-7.20(m, 8H) ppm; IR (C=O), 1695 cm^{-1}.

1b[2]. oil (lit, b.p. 80 °C /0.5 mmHg); ^{1}H NMR, 7.52-7.10 (m, 5H), 2.30 (s, 3H) ppm; IR (C=O), 1740cm^{-1}.

1c[12]. oil; ^{1}H NMR 7.56-7.15 (m, 5H), 2.60 (t, 3H), 1.52-1.14 (m, 18H), 0.85 (t, 3H); IR (C=O), 1740 cm^{-1}; m/z, 340 (M$^+$).

1d[13]. oil; (lit, b.p. 122-126°C/18 mmHg); 7.52-7.08 (m, 5H), 2.58 (q, 2H), 1.10 (t, 3H) ppm; IR (C=O), 1740 cm^{-1}.

1e[14] oil (lit, b.p. 125-128 °C/80 mmHg); ^{1}H NMR, 7.60-7.10 (m, 5H), 2.56 (t, 2H), 2.04-1.30 (m, 2H),0.92 (t, 3H) ppm; IR (C=O), 1740 cm^{-1}.

1f[15]. m.p. 71-72 °C (lit, 70-71 °C); ^{1}H NMR, 8.02-7.20 (m. 9H), 2.33 (s. 3H) ppm; IR (C=O), 1700 cm^{-1}.

1g[16]. oil; ^{1}H NMR, 7.40-6.84 (m, 4H), 2.32 (s, 3H), 2.20 (s, 3H) ppm; IR (C=O), 1735 cm^{-1}; m/z, 214 (M$^+$).

1h[17]. oil; ^{1}H NMR, 7.42-6.90 (m, 4H), 2.64 (q, 2H), 2.30 (s, 3H), 1.10 (t, 3H) ppm; IR (C=O), 1735 cm^{-1}; m/z, 228 (M$^+$).

1i[17]. oil. ^{1}H NMR 7.40-6.86 (m, 4H), 2.58 (t, 2H), 2.30 (s, 3H), 2.02-1.30 (m, 2H), 0.92 (t, 3H) ppm; IR (C=O), 1740 cm^{-1}; m/z, 242 (M$^+$).

1j[15]. m.p. 72-74 °C (lit, 74-75 °C); ^{1}H NMR, 8.00-7.70 (m, 2H), 7.60-7.12 (m, 7H) ppm; IR (C=O), 1710 cm^{-1}.

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