SHORT PAPER

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Convenient one-pot synthesis of α-selenonitriles, α-selenoesters and asymmetrical selenides by a Sm/ZnCl$_2$ system in DMF-H$_2$O[†]

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α-Selenonitriles, α-selenoesters, and asymmetrical selenides can be readily obtained from the one-pot reaction of diselenides and active organic halides by a Sm/ZnCl$_2$ system in DMF-H$_2$O.

Keywords: α-selenonitriles, α-selenoesters, asymmetrical selenides

Organoselenium compounds are important synthetic reagents and intermediates in organic synthesis.[1] The reaction of RSe species with many electrophilic reagents is one of the synthetic methods for organoselenium compounds. There have been many methods for the preparation of the nucleophilic reagent (RSe$^-$). Some of the important examples include the reduction of diselenides with sodium,[2] sodium borohydride,[3] samarium diiodide[4], lithium aluminium hydride[5] and the cleavage of Se–Si bond by SmI$_2$,[6] *etc*.

Recently, metal-mediated organic reactions in aqueous media have attracted considerable interest. These reactions offer a number of advantages over conventional organometallic reactions in an organic solvent.[7] For example, no special drying of solvents, reagents, glassware is required. Our group has reported reductive cleavage of Se–Se bond in diselenides by a Sm/HgCl$_2$ system.[8] These methods, however, suffer from some disadvantages in terms of anhydrous reaction conditions. Herein, we wish to report a convenient one-pot method for the preparation of α-selenonitriles, α-selenoesters and asymmetrical selenides by a Sm/ZnCl$_2$ system in DMF-H$_2$O using diselenides. The results are summarized in Table 1.

$$\underset{\mathbf{1}}{R^1SeSeR^1} + \underset{\mathbf{2}}{R^2X} \xrightarrow[\text{DMF–H}_2\text{O, rt}]{\text{SmZnCl}_2} \underset{\mathbf{3}}{R^1SeR^2}$$

$$(R^2X{:}ClCH_2CN,\ BrCH_2CO_2CH_2CH_3,\ BrCH_2Ph)$$

Scheme 1

In our experiments, it has been found that diaryl diselenides react smoothly with active organic halides such as chloroethyl nitrile, ethyl bromoacetate and benzyl bromide to give products in good yield at 45°C. With the less active dialkyl diselenides, the reaction should be carried out at elevated reaction temperature in a longer reaction time.

The results of our experiments indicated that when Sm powder alone or zinc dichloride alone was used only a very small amount of product was obtained even with a longer reaction time. In our experiments, we also found the formation of activated zinc (black suspension), but the possible reaction mechanism is still under study in our laboratory.

Table 1 Preparation of α-selenonitriles, α-selenoesters and asymmetrical selenides via Sm/ZnCl$_2$ system

Entry	R^1	R^{2}X	Reaction condition		Yield/%[a]
			T/°C	t/h	
a	Ph	ClCH$_2$CN	45	2	78
b	PhCH$_2$	ClCH$_2$CN	45	2	62
c	*p*-ClC$_6$H$_4$	C1CH$_2$CN	45	2	82
d	*n*-C$_4$H$_9$	ClCH$_2$CN	70	3	70
e	Ph	BrCH$_2$CO$_2$C$_2$H$_5$	45	2	72
f	*p*-ClC$_6$H$_4$	BrCH$_2$CO$_2$C$_2$H$_5$	45	2	76
g	PhCH$_2$	BrCH$_2$CO$_2$C$_2$H$_5$	45	2	71
h	Ph	BrCh$_2$Ph	45	2	84
i	PhCH$_2$	BrCH$_2$Ph	45	2	78
j	*n*-C$_4$H$_9$	BrCH$_2$Ph	70	3	54
k	*n*-C$_6$H$_{13}$	BrCH$_2$Ph	70	3	58

[a]isolated yield. Reaction conditions, diselenide (0.5mmol) R^{2}X (1.1mmol), Sm powder (2mmol), ZnCl$_2$·H$_2$O(2mmol), DMF(8ml), H$_2$O(1ml).

In conclusion, it has been found that the Sm/ZnCl$_2$ system in DMF-H$_2$O is an effective method for the cleavage of Se–Se bonds in diselenides. The notable advantages of the method are simple operation, good yields and it being a one-pot method.

Experimental

^{1}H NMR spectra were recorded on a Bruker AC-80 instrument. All NMR samples wre measured in CCl$_4$ using TMS as internal standard. IR spectra were obtained on a Perkin-Elmer 683 spectrophotometer as liquid films.

Metallic samarium and other chemicals were purchased from commercial sources and used without purification. Diselenides wre prepared by the known methods.[10]

General procedure for the preparation of α-selenonitriles © Samarium powder (0.30g, 1mmol), diselenide (0.5mmol), zinc dichloride (1mmol), ClCH$_2$CN (1.1mmol) were placed in a reaction flask. Then DMF (8ml) and H$_2$O (1ml) were added and the mixture was magnetically stirred for 4h at 45°C until the yellow solution had become almost colourless. When the reaction was complete (monitored by TLC), 5ml 1NHCl and 20ml diethyl ether was added, and then the organic layer was separated. The aqueous layer was extracted with diethyl ether (20ml). The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, and the solvent was removed under reduced pressure. The residue was then purified by preparative TLC on silica gel to give a pure product. The products were identified by elemental analyses, IR and ^{1}H NMR spectra.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

3a: oil, IR (film): 3010, 3000, 2965, 2250, 1580, 1480, 1450, 1020, 880, 740,690cm^{-1}. ^{1}H NMR: 7.10–7.70(m,5H), 3.15(s,2H). Found: C,48.95; H,3.63; N,7.36, C_8H_7NSe, requires C,48.73; H,3.55; N.7.11%

3b: oil, IR (film): 3030, 3010, 3000, 2965, 2250, 1600, 1500, 1460, 1030, 765, 690cm^{-1}. ^{1}H NMR: 7.30(s,5H), 2.86(s,2H), 3.20(s,2H). Found: C,51.21; H,4.19; N,6.79, C_9H_9NSe, requires C,51.18; H,4.27; N,6.64%

3c: oil, IR (film): 3080, 2950, 2255, 1600, 1500, 1410, 1020, 800, 670, 490cm^{-1}. ^{1}H NMR: 7.10–7.65(q,4H), 3.20(s,2H). Found: C,41.52; H,2.81; N,6.17, C_8H_6ClNSe, requires C,41.47; H,2.59; N,6.05%

3d: oil, IR (film): 2980, 2960, 2870, 2240, 1475, 1405, 935, 810 cm^{-1}. ^{1}H NMR: 3.10(s,2H), 2.8(t,2H,*J*=6.9Hz), 1.85–1.10(m,4H), 0.80(t,3H,*J*=6.7Hz). Found: C,40.85; H,6.31; N,8.04, $C_6H_{11}NSe$, requires C,40.68; H,6.22; N.7.91%

3e: oil[11], IR (film): 3080, 3000, 2965, 2835, 1745, 1490, 1450, 1280, 1170, 1120, 1070, 880, 740, 690^{-1}. ^{1}H NMR: 7.10–7.70(m,5H), 4.06(q,2H), 3.30(s,2H), 1.20(t,3H,*J*=7.1Hz).

3f: oil[11], IR (film): 3080, 3010, 2960, 2840, 1760, 1495, 1450, 1380, 1175, 1120, 1075, 880, 800, 670 cm^{-1}. ^{1}H NMR: 7.06–7.60(q,4H), 4.10(q,2H), 3.30(s,2H), 1.20(t,3H,*J*=7.1Hz).

3g: oil[11], IR (film): 3080, 3000, 2965, 2835, 1750, 1490, 1450, 1380, 1170, 1070, 880, 740, 690^{-1}. ^{1}H NMR: 7.10–7.70(m,5H), 4.15(q,2H), 3.06(s.2H), 3.30(s,2H), 1.16(t,3H,*J*=7.1Hz).

3h: oil[12], IR (film): 3100, 3080, 3040, 2950, 1610, 1590, 1500, 1485, 1460, 1400, 1180, 1020, 1000, 910, 760, 740 cm^{-1}. ^{1}H NMR: 6.90–7.50(m,10H), 3.83(s,2H).

3i: oil[13], IR (film): 3100, 3085, 3045, 2950, 1610, 1590, 1500, 1485, 1460, 1440, 1180, 1080, 1010, 910, 760 cm^{-1}. ^{1}H NMR: 6.95–7.26(m,10H), 3.50(s,4H).

3j: oil[12], IR (film): 3100, 3080, 3040, 2950, 1610, 1580, 1505, 1485, 1460, 1440, 1380, 1180, 1020, 1000, 910 cm^{-1}. ^{1}H NMR: 6.90–7.40(m,5H), 3.60(s,2H), 2.30(t,2H,*J*=6.8Hz) 1.00–1.80 (m, 4H), 0.80(t, 3H,*J*=6.6Hz).

3k: oil[12], IR (film): 3105, 3085, 3040, 2950, 1615, 1590, 1500, 1485, 1460, 1440, 1180, 1020, 1000, 910, 760 cm^{-1}. ^{1}H NMR: 7.10–7.35(m,5H), 3.60(s,2H), 2.30(t,2H,*J*=6.8Hz), 1.05–1.85(m,8H), 0.80(t,3H,*J*=6.5Hz).

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