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# A novel synthesis of unsymmetrical selenides via the cleavage of Se–Se bond by Sm/cat.$CoCl_2$ system

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Promoted by Sm/cat. $CoCl_2$ system, the Se–Se bond of diaryldiselenides was easily cleaved to form a “living” intermediate, which reacted readily with alkyl halides to afford unsymmetrical alkylarylselenides in good yields under mild and neutral reaction conditions.

**Keywords:** Sm/$CoCl_2$ system, Se–Se bond cleavage, diaryldiselenides, unsymmetrical alkylarylselenides

Samarium diiodide is a powerful single electron transfer(SET) reductant and has widely been applied in organic synthesis.[1-3] However, its storage is difficult because samarium diiodide is very sensitive to air and water. On the other hand, metallic samarium is stable to air and has a strong reducing power ($Sm^{3+}/Sm = -2.41V$) similar to that of magnesium ($Mg^{2+}/Mg = -2.37V$). These properties prompted us to use the more convenient and cheaper metallic samarium directly as a reductant instead of $SmI_2$.

Organoselenium compounds have received considerable attention as useful synthetic reagents in organic synthesis.[4] Among the methods for the introduction of selenium-substituents into organic molecules, aryl selenide anions are especially convenient. Several methods for the synthesis of selenide anions have been recommended, including the reduction of diphenyl diselenides with sodium borohydride,[5] with sodium,[6] samarium diiodide[7] or lithium aluminium hydride.[8] Alternatively, sodium phenylselenide may be obtained from the selenol by using sodium hydride or even by treatment with aqueous sodium hydroxide under certain conditions.[9]

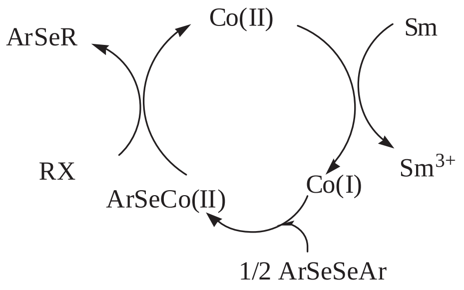
In previous work we reported the reductive cleavage of Se–Se bond with the aid of $SmI_2$.[7] Recently, the cobalt (II) assisting cleavage of S–S bond was reported.[10] Herein we wish to report that the Sm/cat. $CoCl_2$ system promotes the cleavage of Se–Se bond of diaryldiselenides. When this is followed by reaction with alkyl halides it affords unsymmetrical alkylarylselenides (Scheme 1). The results were summarised in Table 1. According to Table 1, it was found that diaryldiselenides could be easily cleaved by Sm/cat. $CoCl_2$ system to form a “living” intermediate (ArSeCo(II)), which reacted readily with active alkyl halides (RX) to afford the corresponding unsymmetrical alkylarylselenides (ArSeR) in good yields under mild conditions. Less reactive halides such as *n*-butyl bromide and benzyl chloride, required a higher temperature (65°C). Unfortunately, in the case of *n*-butyl chloride, no product can be isolated even at higher temperature and a longer time (entry h).

$$\text{ArSeSeAr} + \text{RX} \xrightarrow[\text{THF, 45-65 }^0\text{C}]{\text{Sm / cat. CoCl}_2} \text{ArSeR}$$

**Scheme 1**

Control experiments revealed that Se–Se bond could not be cleaved by metallic samarium in the absence of $CoCl_2$. Therefore, according to the relative report[10] we proposed the following mechanism as shown in Scheme 2: (a) one electron was transferred from metallic samarium to cobalt(II) to form Co(I) and Sm(III), respectively; (b) the active intermediate Co(I) reacted readily with diarydiselenides to produce ArSeCo(II) *in situ*. This is followed by reaction with the alkyl halide (RX) to afford the unsymmetrical alkylarylselenides and the recovery of Co(II). A catalytic amount of $CoCl_2$ can be used for this reaction (Scheme 2). However, the exact mechanism is not clear and a more detailed study is in progress in our laboratory.

In conclusion, we have demonstrated Sm/cat. $CoCl_2$ system can be used for the preparation of unsymmetrical alkylaryl-



**Scheme 1**

**Table 1** The condition and results of the preparation of ArSeR

| Entry | Ar | RX | t/h | T/°C | Product | Yield*/% |
|---|---|---|---|---|---|---|
| a | Ph | $CH_2$=$CHCH_2Br$ | 4 | 45 | **1** $PhSeCH_2CH$=$CH_2$ | 76 |
| b | Ph | $PhCH_2Br$ | 3 | 45 | **2** $PhSeCH_2Ph$ | 81 |
| c | Ph | $PhCH_2Cl$ | 5 | 65 | **2** $PhSeCH_2Ph$ | 60 |
| d | Ph | $PhCOCH_2Br$ | 3 | 45 | **3** $PhSeCH_2COPh$ | 78 |
| e | Ph | $BrCH_2CO_2Et$ | 3 | 45 | **4** $PhSeCH_2CO_2Et$ | 80 |
| f | Ph | $BrCH_2CO_2Me$ | 3 | 45 | **5** $PhSeCH_2CO_2Me$ | 73 |
| g | Ph | n-BuBr | 6 | 65 | **6** *n*-BuSePh | 51 |
| h | Ph | n-BuCl | 10 | 65 | **6** *n*-BuSePh | – |
| i | Ph | $BrCH_2CN$ | 4 | 45 | **7** $PhSeCH_2CN$ | 69 |
| j | *p*-$MeC_6H_4$ | $CH_2$=$CHCH_2Br$ | 3 | 45 | **8** *p*-$MeC_6H_4SeCH_2CH$=$CH_2$ | 78 |
| k | *p*-$MeC_6H_4$ | $BrCH_2CO_2Et$ | 3 | 45 | **9** *p*-$MeC_6H_4SeCH_2CO_2Et$ | 65 |
| l | *p*-$MeC_6H_4$ | $BrCH_2CN$ | 4 | 45 | **10** *p*-$MeC_6H_4SeCH_2CN$ | 75 |

*Isolated yields

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selenides *via* the cleavage of the Se–Se bond. The advantages of this method are the mild neutral conditions, simple operation and good yields.

## Experimental

Metallic samarium and other chemicals were purchased from commercial sources and used without purification. Tetrahydrofuran (THF) was distilled from sodium/benzophenone immediately prior to use. All reactions were carried on under a dry nitrogen atmosphere. Infrared spectra were recorded on a Perkin-Elmer 683 spectrometer. $^1$H NMR spectra were determined on a Bruker AC-400 instrument. All NMR samples were measured in $CDCl_3$ using TMS as internal standard. MS spectra were recorded on a Finnigen MAT GC-MS mass spectrometer. High Resolution Mass Spectra (HRMS) were measured with JEOL JMS-DX303.

*General procedure*: Under nitrogen atmosphere, to a three-necked reaction flask was added metallic samarium powder (1.0 mmol), cobalt(II) chloride (0.2 mmol), diaryldiselenide (0.5 mmol), and THF (10 ml) successively. Alkyl halide (1.2 mmol) was then added to the mixture and the reaction was stirred for the time indicated in Table 1. The reaction was quenched by diluted HCl aqueous and extracted with diethyl ether (3 × 30 ml). The organic layer was washed with water, brine and dried over anhydrous $Na_2SO_4$. The solvent was removed in *vacuo*. The residue was purified by preparative TLC on silica gel using cyclohexane/ethyl acetate (10:1) as eluent to give the corresponding product as an oil.

**1**[11]: Oil; $^1$H NMR($CDCl_3$) $\delta_H$: 3.31(2H, d, *J* = 6.8 Hz), 4.79(2H, d, *J* = 15.6 Hz), 5.66–6.05 (1H, m), 7.06–7.56 (5H, m); IR(neat): 3095, 2940, 1645, 1485, 985, 910, 730, 685 cm$^{-1}$.

**2**[12]: Oil; $^1$H NMR($CDCl_3$) $\delta_H$: 3.95 (2H, s), 7.05–7.45 (10H, m); IR(neat): 3090, 2980, 1580, 1490, 1440, 1150, 940, 740, 690 cm$^{-1}$.

**3**[7]: Oil; $^1$H NMR($CDCl_3$) $\delta_H$: 4.05 (2H, s), 7.00–7.95 (10H, m); IR (neat): 3085, 2960, 1682, 1600, 1590, 1480, 1410, 1275, 1180, 925, 735, 700, 680 cm$^{-1}$.

**4**[13]: Oil; $^1$H NMR($CDCl_3$) $\delta_H$: 1.12 (3H, t, *J*=7.2 Hz), 3.29 (2H, s), 3.96 (2H, q, *J*=7.2 Hz), 7.01–7.65 (5H, m); IR(neat): 3070, 2960, 1750, 1590, 1485, 1460, 1350, 1220, 1170, 935, 740, 690 cm$^{-1}$.

**5**[14]: Oil; $^1$H NMR ($CDCl_3$) $\delta_H$: 3.60 (3H, s), 3.66 (2H, s), 7.10–7.65 (5H, m); IR (neat): 3100, 3030, 2960, 1750, 1490, 1450, 1270, 1010, 888, 740, 690 cm$^{-1}$.

**6**[15]: Oil; $^1$H NMR ($CDCl_3$)$\delta_H$: 0.80 (3H, t, *J*=6.4 Hz), 1.00–1.85 (4H, m), 2.70 (2H, t, *J*=6.8 Hz), 6.95–7.55 (5H, m); IR(neat): 3050, 2950, 1590, 1470, 1420, 1370, 1220, 1115, 920, 735 cm$^{-1}$.

**7**[14]: Oil; $^1$H NMR ($CDCl_3$)$\delta_H$: 3.40 (2H, s), 7.16–7.70 (5H, m); IR(neat): 3010, 3000, 2960, 2250, 1580, 1480, 1450, 1020, 880, 740, 690 cm$^{-1}$.

**8**[11,16]: Oil; $^1$H NMR ($CDCl_3$) $\delta_H$: 2.22 (3H, s), 3.31 (2H, d, *J*=7.2 Hz), 4.77 (2H, d, *J*=15.6 Hz), 5.53–5.90 (1H, m), 6.73–7.50 (4H, m); IR(neat): 3080, 2965, 2870, 1642, 1510, 1380, 990, 830 cm$^{-1}$.

**9**: Oil; $^1$H NMR ($CDCl_3$) $\delta_H$: 1.10 (3H, t, *J*=6.4 Hz), 2.30 (3H, s), 3.30 (2H, s), 4.02 (2H, q, *J*=6.4 Hz), 6.96 (2H, d, *J*=6.8 Hz), 7.38 (2H, d, *J*=6.8 Hz); IR(neat): 3030, 3000, 2940, 2870, 1748, 1600, 1450, 1260, 1020, 880, 800, 660 cm$^{-1}$; MS (EI) *m/z* 258($^{80}$Se–M$^+$, base), 256. HRMS(EI) Calcd for $C_{11}H_{14}O_2Se$ (M$^+$)258.0159. Found: 258.0165.

**10**: Oil; $^1$H NMR ($CDCl_3$) $\delta_H$: 2.16 (3H, s), 3.0 (2H, s), 6.91 (2H, d, *J*=7.0 Hz), 7.28 (2H, d, *J*=7.0 Hz); IR(neat): 3080, 3030, 3000, 2960, 2870, 2240, 1600, 1500, 1450, 1400, 1010, 90 cm$^{-1}$; MS (EI) *m/z* 211($^{80}$Se-M$^+$, base), 209. HRMS(EI) Calcd for $C_{11}H_{14}O_2Se$ (M$^+$)210.9900. Found: 210.9935.

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