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Reduction of Elemental Selenium by Samarium Diiodide: the Synthesis of Dithiodiselenides and Dithioselenides

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Abstract: The reduction of elemental selenium by samarium diiodide led to selective formation of selenolate anion species (Se^{2-}_2 and Se^{2-}), these nucleophilic species reacted readly with sodium alkyl thiosulfates to afford dithiodiselenides and dithioselenides in moderate to good yield under mild conditions.

Keywords: Synthesis, samarium diiodide, dithiodiselenides, dithioselenides.

Selenium is an essential element in living organism. It is reported that the selenosulfides have been transported *in vivo* in glutathione or coenzyme-A[1]. It is also discovered in low concentration in garlic[2]. In organic synthesis, selenosulfides are useful intermediates[3]. Several methods for the formation of sulfur-selenium bond have been reported. For example, the compounds including S-Se bond were prepared by chloroamination of thiols and selenols[4]; by heating the selenocyanate with thiols[5]; by refluxing a mixture of the diselenide and disufides in petroleum ether for 18h[6]; by the reaction of thiols with a selenium transfer reagent[7]. Samarium (II) diiodide (SmI_2) is of current interest in organic synthesis[8]. M. Sekjguchi, *et al*.[9] have reported the synthesis of diorganyl selenides and diselenides *via* the reduction of elemental selenium by SmI_2. Herein, we wish to report the preparation of dithiodiselenides and dithioselenides by samarium diiodide. To the best of our knowledge, there is no literature example for the preparation of dithiodiselenides. The results are list in **Table 1**.

Scheme 1

$$Se \xrightarrow{SmI_2} [\,Se_2^{2-}\,] \xrightarrow{R^1SSO_3Na} R^1SSeSeSR^1$$

$$Se \xrightarrow{SmI_2} [\,Se^{2-}\,] \xrightarrow{R^2SSO_3Na} R^2SSeSR^2$$

The reduction of elemental selenium by SmI_2 (1.1 equiv) proceeded very rapidly in THF at room temperature, and the subsequent reaction with sodium n-butyl thiosulfate in the presence of HMPA provided 66% yield of dithiodiselenide. Similar condition can be employed with benzyl group. In principle, if two equivalents of SmI_2 are used for the reduction of selenium, the Se^{2-} species would be generated *in situ*. Elevation of the

Table 1 The synthesis of dithiodiselenides and dithioselenides by SmI_2

Entry	R^1	R^2	Yield%[A]
1	nC_4H_9		66
2	nC_6H_{13}		68
3	nC_8H_{17}		70
4	$nC_{10}H_{21}$		76
5	$nC_{12}H_{25}$		71
6	$nC_{16}H_{33}$		63
7	$C_6H_5CH_2$		78
8	$p\text{-}NO_2C_6H_4CH_2$		74
9		$n\text{-}C_4H_9$	61
10		$C_6H_5CH_2$	76

a. isolated yield

temperature (refulxing temp. of THF) at the initial stage of the reaction improved the yield of dithioselenides. In our experiments, we have also found that about 10% disulfide as side product was obtained.

The present method for the preparation of dithiodiselenides and dithioselenides is more convenient than other methods[7] previously described.

Experimental

General procedure for the synthesis of dithiodiselenides

To a stirred purple solution of SmI_2 (1.1 mmol) in 10 mL THF and 1ml HMPA was added the amorphous selenium (1 mmol) under nitrogen atmosphere, the color of mixture was changed into brown and the reaction mixture was refluxed for 3 h. After the solution was cooled to room temperature, sodium alkyl thiosulfate (2 mmol) was added in one portion, the mixture was stirred continually at room temperature for 2 h. A dilute hydrochloric acid (2 $mol \cdot L^{-1}$ 5 mL) and ether (20 mL) were added. The organic layer was separated and the aqueous layer was extracted with ether (20 mL × 2). The combined organic layer was washed with saturated sodium thiosulfate, brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The residue was then purified by preparative TLC on silica gel (petroleum ether as eluent). The products were characterized by their ^1H NMR, IR and Mass spectra.

General procedure for the synthesis of dithioselenides

To a stirred purple solution of SmI_2 (2.2 mmol) in 20 mL THF and 1ml HMPA was added the amorphous selenium (1 mmol) under nitrogen atmosphere, and the mixture was stirred for 2 h under reflux. Sodium alkyl thiosulfate (2 mmol) was added in one portion, the mixture was continued for an additional 10 h. After the conventional work-up using preparative TLC on silica gel (petroleum ether as eluent). The products were characterized by their ^1H NMR, IR and Mass spectra.The spectral data of compounds **1-10** are as follows.

1. $nC_4H_9SSeSeSC_4H_9$(-n) light yellow oil, ^1H NMR (CCl_4, δ ppm): 0.95 (t, 6H, J = 6Hz), 1.15-2.00 (m,8H), 2.80 (t, 4H, J=6Hz,); IR υ /cm^{-1} (KBr) 2970, 2940, 1470, 1380, 730;

MS (*m/z*) 338 (M^+, ^{80}Se).

2. $nC_6H_{13}SSeSeSC_6H_{13}$(n) light yellow oil, ^1H NMR (CCl_4, δ ppm): 0.90 (t, 6H, J = 6Hz,), 1.10-1.90 (m,16H), 2.85 (t, 4H, J = 6Hz,); IR υ /cm^{-1} (KBr) 2980, 2940, 1475, 1380, 740; MS(*m/z*) 394 (M^+,^{80}Se).

3. $nC_8H_{17}SSeSeSC_8H_{17}$ (n) light yellow oil, ^1H NMR (CCl_4, δ ppm): 0.95 (t, 6H, J = 6Hz,), 1.15-1.97 (m,24H), 2.75 (t, 4H, J = 6Hz,); IR υ /cm^{-1} (KBr) 2975, 2940, 1475, 1380, 730; MS (*m/z*) 450 (M^+,^{80}Se).

4. $nC_{10}H_{21}SSeSeSC_{10}H_{21}$ (n) light yellow oil, ^1H NMR(CCl_4, δ ppm): 0.95 (t, 6H, J = 6Hz,), 1.10-2.06 (m,32H), 2.80 (t, 4H, J = 6Hz,); IR υ /cm^{-1} (KBr) 2975, 2940, 1475, 1380, 740; MS (*m/z*) 506 (M^+,^{80}Se).

5. $nC_{12}H_{25}SSeSeSC_{12}H_{25}$ light yellow oil, ^1H NMR (CCl_4, δ ppm): 0.93(t, 6H, J = 6Hz,), 1.15-2.06 (m, 40H), 2.80 (t, 4H, J = 6Hz,); IR υ /cm^{-1} (KBr) 2980, 2940, 1475, 1380, 740; MS (*m/z*) 562 (M^+,^{80}Se).

6. $nC_{16}H_{33}SSeSeSC_{16}H_{33}$ (n) light yellow crystal, m.p.35-37°C ^1H NMR (CCl_4, δ ppm): 0.92 (t, 6H, J = 6Hz,), 1.15-2.00 (m,56H), 2.75 (t, 4H, J = 6Hz,); υ /cm^{-1} (KBr) 2980, 2940, 1475, 1380, 740.

7. $C_6H_5CH_2SSeSeSCH_2C_6H_5$ light yellow oil, ^1H NMR (CCl_4, δ ppm) 7.06-7.60 (m,10H), 3.92 (s,4H); IR υ /cm^{-1} (KBr) 3340, 3020, 2970, 2940, 1510, 1460, 1385, 1240, 1205, 1070, 1030, 910, 700, 660; MS (*m/z*) 406 (M^+, ^{80}Se).

8. p-$NO_2C_6H_4CH_2SSeSeSCH_2C_6H_4(NO_2$-p) deep yellow crystal, m.p.105-107°C ^1H NMR ($CDCl_3$, δ ppm) 8.30 (d, 4H, J = 8Hz,), 7.46 (d, 4H, J = 8Hz,), 3.70 (s,4H); IR υ /cm^{-1} (KBr) 3070, 3035, 2830, 2780, 1720, 1710, 1650, 1600, 1530, 1470, 1420, 1270, 1210, 1100, 960, 800, 790, 760, 620, 490.

9. $nC_4H_9SSeSC_4H_9$ (-n) light yellow oil, ^1H NMR (CCl_4, δ ppm): 0.92 (t, 6H, J = 6Hz,), 1.17-2.05 (m,8H), 2.85 (t, 4H, J = 8Hz,); IR υ /cm^{-1} (KBr) 2980, 2940, 1475, 1380, 710; MS (*m/z*) 258 (M^+,^{80}Se).

10. $C_6H_5CH_2SSeSCH_2C_6H_5$ light yiellow oil, ^1H NMR (CCl_4, δ ppm): 3.95 (s,4H), 7.00-7.73 (m,10H); IR υ /cm^{-1} (KBr) 3350, 3020, 2970, 2940, 1510,1470, 1385, 1240, 1205, 1070, 1030, 930, 700; MS (*m/z*) 326 (M^+,^{80}Se).

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