Heteroatom Chemistry
Volume 2, Number 3, 1991

Reduction of Elemental Selenium by Samarium Diiodide: Selective Synthesis of Diorganyl Selenides and Diselenides

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Received 21 September 1990.

ABSTRACT

The reduction of elemental selenium by samarium diiodide led to selective formation of selenolate anion species (Se^{2-} and Se_2^{2-}), the alkylation of which provided dialkyl selenides and diselenides, respectively, in excellent yields.

INTRODUCTION

Hydrogen selenide can be regarded as an important selenium source for the synthesis of organic selenium compounds, but the practical use has been limited because of its high toxicity and instability toward air. Instead, alkali metal salts (M_2Se, M_2Se_2, M = Li, Na, K) [1] or amine salts [2] of hydrogen selenide have been utilized as the synthetic equivalents, which can be prepared by the reduction of elemental selenium. However, there exist only very limited examples of the selective generation of Se^{2-} and Se_2^{2-} species, especially in aprotic solvents [3]. Herein we report that samarium diiodide (SmI_2) [4] reduces elemental selenium to Se^{2-} and Se_2^{2-} species with an excellent selectivity in an aprotic solvent such as tetrahydrofuran [5].

The reduction of elemental selenium by SmI_2 (1.1 equiv) proceeded very rapidly in THF at room temperature, and the subsequent alkylation with *n*-butyl bromide in the presence of HMPA provided a 94% yield of dibutyl diselenide, which clearly indicated the exclusive generation of the Se_2^{2-} species (Equation 1). Similar conditions can be employed with several organic halides, including those containing methoxycarbonyl and benzyl groups.

In principle, if two equivalents of SmI_2 are used for the reduction of selenium, the Se^{2-} species would be generated in situ. However, the main compound obtained was *n*-Bu_2Se_2 (77%) not *n*-Bu_2Se (3%), after alkylation with butyl bromide. Elevation of the temperature (refluxing THF) at the initial stage improved the yield of *n*-Bu_2Se (56%, cf. *n*-Bu_2Se_2, 13%), but not satisfactorily. The best result (Equation 2) was obtained by using HMPA, which is known to enhance the reducing ability of SmI_2 [4c]. It is of interest to note that the samarium salts of hydrogen selenide easily underwent alkylation with secondary alkyl halides, whereas the alkylation of M_2Se (M = Li, Na) with secondary alkyl halides hardly proceeds [3b].

The results shown in Equations 1 and 2 are highly suggestive of the wide range of organic halides that participate in this selective formation of selenides and diselenides. The present method has the following noteworthy features: (1) a first preparation of samarium salts of hydrogen selenide [7]; (2) an excellent selectivity for the generation of Se^{2-} and Se_2^{2-} species [8]; (3) high-yield preparation of diorganyl selenides and diselenides in an aprotic solvent; (4) a simple operation with safety [9].

It was also found that SmI_2 reduced organic diselenides smoothly to the corresponding anions. Thus, diphenyl diselenide was converted into an unsymmetrical selenide by the sequence of reduction followed by alkylation (Equation 3).

In summary, a highly selective method for

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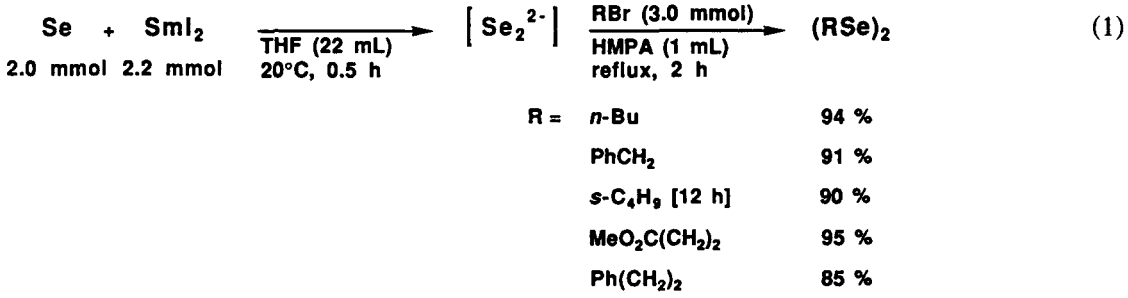
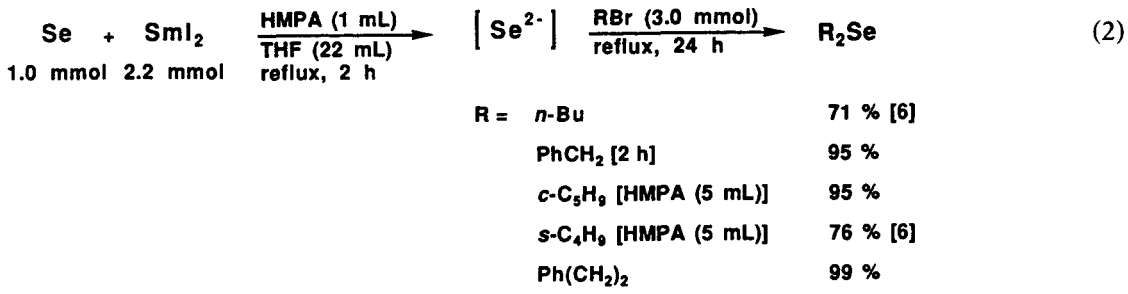


(1)



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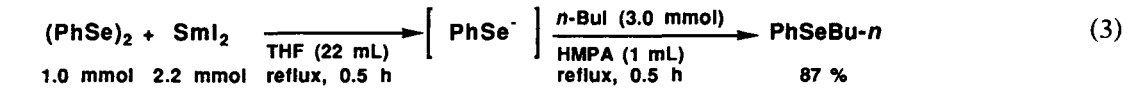

(3)

forming Se^{2-} and Se_2^{2-} has been discovered. The alkylation of the resulting samarium selenolates appears to be among the most practical methods for synthesis of organic selenides and diselenides in terms of high yield, excellent selectivity, and simple operation.

EXPERIMENTAL

Instruments and Materials

^1H NMR spectra were recorded on a JEOL JNM-GSX-270 (270 MHz) spectrometer using $CDCl_3$ as the solvent with Me_4Si as an internal reference. ^{13}C NMR spectra were taken on a JEOL JNM-GSX-270 (68 MHz) spectrometer. IR spectra were determined on a Perkin Elmer Model 1600 spectrometer. Melting points were determined on a Yanagimoto micro melting point apparatus. Mass spectra were obtained on a JEOL JMS-DX303 spectrometer in the analytical section of our department.

Unless otherwise noted, materials were obtained from commercial sources and purified by distillation. Samarium powder in oil (99.9%) was purchased from High Purity Chemicals, and was used after washing with dry pentane, followed by drying for 4 h under reduced pressure. Samarium diiodide (SmI_2) was prepared by the reaction of samarium powder with 1,2-diiodoethane in freshly distilled (from sodium/benzophenone ketyl) THF [4a], and the concentration (0.1 M) was determined by adding 1 mL of the solution to 0.01 N of iodine in 15 mL of Et_2O, followed by back titration with a standard sodium thiosulfate solution (0.1 N). Amorphous selenium was prepared by reduction of selenium dioxide with SO_2 (generated from Na_2SO_3 and 12 N HCl) and dried for 5 h under reduced pressure [10]. Diphenyl diselenide was prepared according to the literature [11] and purified by recrystallization from *n*-hexane.

A Representative Procedure for the Synthesis of Diselenides

The blue solution of SmI_2 (2.2 mmol) in THF (22 mL) was added with a syringe to amorphous selenium (2.0 mmol) [12] in a 30 mL glass vessel filled with argon. The solution gradually turned to brown within 0.5 h along with deposition of a pale yellow precipitate [13]. To the mixture was added successively HMPA (1 mL) [14] and the desired organic halide (3.0 mmol). The solution was stirred under reflux for 2 h. The reaction mixture was diluted with Et_2O (60 mL) and the solution was washed three times with water (40 mL × 3). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. Purification by MPLC (silica gel, 25–40 μm, length 310 mm, i.d. 25 mm, eluent *n*-hexane) or flash chromatography (silica gel, 63–180 nm, length 300 mm, i.d. 25 mm) provided the expected diorganyl diselenide.

Di(n-*butyl*) *Diselenide:* 94% (253 mg); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.93 (t, 6H, J = 7.3 Hz), 1.42 (sextet, 4H), 1.72 (quintet, 4H), 2.92 (t, 4H, J = 7.3 Hz); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 13.59, 22.62, 29.94 ($^1J_{Se-C}$ = 71.6 Hz), 33.10; IR (NaCl) 2957, 2926, 2870, 1463, 1378, 1253, 1188 cm^{-1}; MS (m/e) 274 (M^+, 6).

Dibenzyl Diselenide: 91% (311 mg); mp 90–91°C (lit., [15] 92°C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.81 (s, 4H), 7.19–7.31 (m, 10H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 32.58 ($^1J_{Se-C}$ = 68.3 Hz), 127.05 (p), 128.40, 128.98, 138.99 (ipso); IR (KBr) 3065, 3019, 2963, 2904, 1598, 1493, 1453, 1262, 1176, 1097, 1064, 1030, 802, 759, 693 cm^{-1}; MS (CI, m/e) 343 (M^+ + 1, 66).

Di(s-*butyl*) *Diselenide:* Alkylation with *s*-butyl bromide was carried out using 1 mL of HMPA for 12 h. 90% (244 mg); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.98 (t, 6H, J = 7.3 Hz), 1.43 (d, 6H, J = 6.8 Hz), 1.60 (dq, 2H), 1.74 (dq, 2H), 3.02 (sextet, 2H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 12.44, 22.11, 22.14, 30.70, 41.60 ($^1J_{Se-C}$ = 69.4 Hz), 41.63 ($^1J_{Se-C}$ = 69.4 Hz); IR (NaCl) 2962, 2916, 2872, 1453, 1376, 1285, 1272, 1193, 1138, 1004, 996, 786 cm^{-1}; MS (m/e) 274 (M^+, 5).

Bis(2-*methoxycarbonylethyl*) *Diselenide:* 95% (314 mg); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.83 (t, 4H, J = 7.1 Hz), 3.11 (t, 4H, J = 7.1 Hz), 3.71 (s, 6H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 23.20 ($^1J_{Se-C}$ = 48.5 Hz), 35.68, 51.85, 172.49; IR (NaCl) 2995, 2951, 2844, 1728, 1436, 1347, 1220, 1162, 1130, 1011, 977, 807 cm^{-1}; MS (CI, m/e) 335 (M^+ + 1, 40).

Di(2-*phenylethyl*) *Diselenide:* 85% (313 mg); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.02 (m, 4H), 3.13 (m, 4H), 7.24 (m, 10H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 30.64 ($^1J_{Se-C}$ = 73.7 Hz), 37.48, 126.31, 128.42, 128.45, 140.70; IR (NaCl) 3025, 2927, 1602, 1495, 1452, 750, 698 cm^{-1}; MS (m/e) 370 (M^+, 3).

A Representative Procedure for the Synthesis of Selenides

SmI_2 (2.2 mmol) in THF (22 mL) was added to a mixture of amorphous selenium (1.0 mmol) and HMPA (1 mL) contained in a 30 mL glass vessel filled with argon, and the mixture was stirred for 2 h under reflux. A given organic halide (3.0 mmol) was added to the resulting mixture, and the reaction was continued for an additional 24 h [16]. The reaction mixture was diluted with Et_2O (60 mL) and the solution was washed with water (40 mL × 3). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. Purification by MPLC (silica gel, 25–40 mm, length 310 mm, i.d. 25 mm, eluent *n*-hexane) or flash chromatography (silica gel, 63–180 nm, length 300 mm, i.d. 25 mm) provided the expected diorganyl selenide.

Di(n-*butyl*) *Selenide:* 71% (137 mg); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.92 (t, 6H, J = 7.3 Hz), 1.40 (sextet, 4H), 1.65 (quintet, 4H), 2.55 (t, 4H, J = 7.3 Hz); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 13.62, 23.11, 23.66 ($^1J_{Se-C}$ = 60.6 Hz), 32.84; IR (NaCl) 2957, 2927, 2872, 1464, 1377, 1257, 1194 cm^{-1}; MS (m/e) 194 (M^+, 10).

Dibenzyl Selenide: Alkylation was complete after 2 h. 95% (249 mg); mp 43–43.5°C (lit., [17] 45.5°C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.70 (s, 4H), 7.16–7.30 (m, 10H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 27.55 ($^1J_{Se-C}$ = 61.7 Hz), 126.68 (p), 128.46, 128.95, 139.16 (ipso); IR (NaCl) 3082, 3060, 3026, 2926, 1600, 1493, 1452, 1179, 1067, 1029, 758, 696 cm^{-1}; MS (m/e) 262 (M^+, 8).

Di(*cyclopentyl*) *Selenide:* Alkylation with cyclopentyl bromide was carried out using 5 mL of HMPA. 95% (205 mg); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.47–1.90 (m, 12H), 1.93–2.20 (m, 4H), 3.25 (quintet, 2H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 23.97, 33.85, 36.52 ($^1J_{Se-C}$ = 65.0 Hz); IR (NaCl) 2955, 2866, 1448, 1217, 734 cm^{-1}; MS (m/e) 218 (M^+, 5).

Di(s-*butyl*) *Selenide:* Alkylation with *s*-butyl bromide was carried out using 5 mL of HMPA. 76% (145 mg); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.99 (t, 6H, J = 7.3 Hz), 1.42 (d, 6H, J = 6.8 Hz), 1.50 (m, 4H), 2.93 (sextet, 2H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 12.18, 12.26, 22.31, 22.38, 31.19, 35.94 ($^1J_{Se-C}$ = 61.7 Hz); IR (NaCl) 2965, 2918, 2873, 1454, 1377, 1196, 1139, 996, 790 cm^{-1}; MS (m/e) 194 (M^+, 7).

Di(2-*phenylethyl*) *Selenide:* 99% (289 mg); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.76 (m, 4H), 2.93 (m, 4H), 7.22 (m, 10H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 24.90 ($^1J_{Se-C}$ = 63.4 Hz), 37.11, 126.23, 128.26, 128.37, 141.15; IR (NaCl) 3025, 2928, 1602, 1495, 1452, 751, 698 cm^{-1}; MS (m/e) 290 (M^+, 35).

Reduction of Diphenyl Diselenide with SmI_2

A THF solution (22 mL) of SmI_2 (2.2 mmol) was added to diphenyl diselenide (1.0 mmol) contained in a 30 mL glass vessel, and the mixture was refluxed for 0.5 h. The solution turned to red along with deposition of a pale yellow precipitate. To the mixture was added successively HMPA (1 mL) and *n*-butyl iodide (3.0 mmol). The solution was stirred under reflux for 0.5 h, and a workup procedure similar to that described above yielded 368 mg of *n*-butyl phenyl selenide (87%): ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.89 (t, 3H, J = 7.3 Hz), 1.41 (sextet, 2H), 1.67 (quintet, 2H), 2.89 (t, 2H, J = 7.6 Hz); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 13.54, 22.93, 27.59 ($^1J_{Se-C}$ = 60.6 Hz), 32.24, 126.53 (p), 128.93 (m), 130.75 (ipso), 132.35 (o, $^2J_{Se-C}$ = 9.9 Hz); IR (NaCl) 3071, 3058, 2958, 2929, 2871, 1579, 1478, 1439, 1258, 1200, 1074, 1022, 734, 690 cm^{-1}; MS (m/e) 214 (M^+, 49).

ACKNOWLEDGMENT

This research was supported by a Grant in Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan. Thanks are due to the Instrumental Analysis Center, Faculty of Engineering, Osaka University for assistance in obtaining Mass spectra on a JEOL JMS-DX303 spectrometer.

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[2] We have recently developed the reduction of some functional groups using the Se–CO–H_2O reaction system, where amine salts of hydrogen selenide act as the active reducing species, see: Y. Nishiyama, Y. Makino, S. Hamanaka, A. Ogawa, N. Sonoda, *Bull. Chem. Soc. Jpn., 62,* 1989, 1682, and refs. therein.

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[5] This work was presented at the 58th Annual Meeting of the Chemical Society of Japan, 1989.

[6] NMR yields of *n*- and *s*-Bu_2Se were 92% and 87%, respectively.

[7] Samarium salts of butaneselenol were reported to be synthesized by the reaction of hexamethylsamarium triamide with butaneselenols, see: Y. F. Rad'kov, E. A. Fedorova, S. Y. Khorshev, G. S. Kalinina, M. N. Bochkarev, G. A. Razuvaev, *Zh. Obshch. Khim., 55,* 1985, 2153.

[8] The alkylation of samarium diselenide with several organic halides provided diorganyl diselenides essentially as the sole product. Contrary to this, the alkylation of samarium selenide involved the formation of small amounts of diorganyl diselenide (<5%), most probably via mono-alkylation of Se^{2-} to RSe^-, followed by oxidation during workups. However, diorganyl diselenides formed as a byproduct can be removed easily by MPLC or column chromatography on silica gel.

[9] Some of the known methods require cumbersome manipulation of liq. NH_3 or alkali metals.

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[11] H. J. Reich, J. M. Renga, I. L. Reich, *J. Am. Chem. Soc., 97,* 1975, 5434.

[12] Metallic selenium was also usable for the synthesis of diselenides. For example, the reaction of metallic selenium (2.0 mmol) with SmI_2 (2.2 mmol) in the presence of HMPA (1 mL) at 67°C for 10 h, followed by alkylation with *n*-BuBr (3.0 mmol) at 67°C for 24 h provided 71% of *n*-Bu_2Se_2 along with 15% of *n*-Bu_2Se.

[13] An attempt to isolate samarium selenide by filtration of the precipitate failed, since samarium selenide is much too sensitive to air.

[14] Alkylation in the absence of HMPA takes a longer reaction time.

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[16] In the case of the Se^{2-} species, a longer reaction time is required for the alkylation. A similar observation was reported on the alkylation of M_2Se (M = Li, Na, K) [3b].

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