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Selective Synthesis of Organic Sulfides and Disulfides by the Reduction of Elemental Sulfur with Samarium Diiodide

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ABSTRACT: *Elemental sulfur can be reduced to the corresponding thiolate anion species (S^{2-} and S_2^{2-}) selectively by samarium diiodide in the presence and absence of HMPA, respectively. The subsequent alkylation of the thiolate anion species provides a useful synthetic route to dialkyl sulfides and disulfides.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9: 581–584, 1998

Organic sulfides and disulfides are widely accepted as key parent organosulfur compounds, and a number of preparative methods have been developed hitherto [1]. Among these, one of the most straightforward routes to organic sulfides and disulfides is the alkylation of metal sulfides (M_2S) or metal disulfides (M_2S_2) (M = Na, Li, etc.). Sodium sulfide (Na_2S) is commercially available, and sodium disulfide (Na_2S_2) can be generated by the reaction of Na_2S with elemental sulfur [2]. Lithium sulfide and disulfide (Li_2S and Li_2S_2) can be generated in situ by the reduction of elemental sulfur with lithium triethylborohydride in THF [3]. However, the alkylation of metal sulfides and disulfides sometimes suffers from contamination with R-S_n-R (n = 1, 2, 3 . . .).

Recently, we have found that elemental selenium can be reduced by samarium diiodide (SmI_2) [4] to generate samarium selenide [$(I_2Sm)_2Se$] and samarium diselenide [$(I_2Sm)_2Se_2$] selectively, depending upon reaction stoichiometry and conditions [5]. These results suggest that it might be possible to generate samarium sulfide [$(I_2Sm)_2S$] and disulfide [$(I_2Sm)_2S_2$] from elemental sulfur [6,7]. Herein, we report selective formation and alkylation of samarium sulfide and disulfides.

When the reduction of elemental sulfur (1 mmol) with SmI_2 (2.2 equiv) in the presence of HMPA [8] (1 mL) in refluxing THF (22 mL) for 2 hours was conducted (Scheme 1) and then the resulting samarium sulfide species was treated with 3 equiv of butyl iodide, both dibutyl sulfide and disulfide were formed almost equally in 51% and 49% yields, respectively. However, the use of excess amounts of HMPA (4 mL) dramatically improved the product selectivity: Dibutyl sulfide was obtained predominantly, as shown in entry 1 of Table 1.

In principle, if equimolar amounts of SmI_2 are used for the reduction of sulfur, samarium disulfide would be generated in situ. Thus, the reduction of elemental sulfur (2 mmol) with SmI_2 (2.2 mmol) in THF (22 mL) was carried out at 20°C for 0.5 hour in

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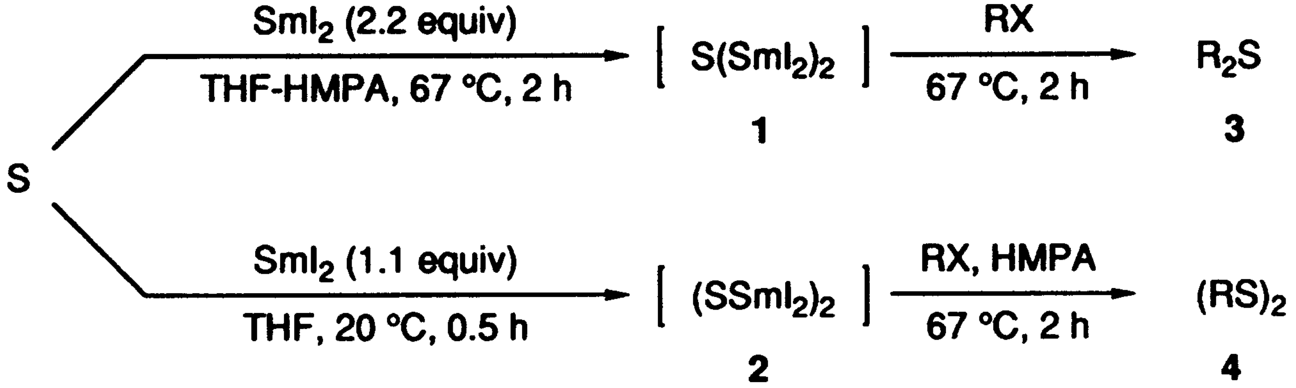


SCHEME 1

the absence of HMPA. The subsequent alkylation with butyl iodide proceeded successfully by the addition of HMPA to the resulting samarium disulfide solution, providing dibutyl disulfide in 80% yield (entry 2). In this reaction, small amounts of dibutyl sulfide (5%) was also formed as a by-product, but the sulfide could be removed easily upon the purification by MPLC or flash chromatography.

Both conditions A and B (see the footnote in Table 1) can be employed with benzyl bromide, giving dibenzyl sulfide and disulfide selectively (entries 3–4). α,α'-Dibromo-*o*-xylene provided the corresponding cyclic sulfide in good yield (entry 6). The procedure (condition B) can be applied to the synthesis of a bis(acyl) disulfide, as exemplified in entry 8. Functionalities such as carbonyl and olefinic groups are tolerant toward the reaction conditions (entries 5, 7, and 8). These results are highly suggestive of the wide range of organic halides that participate in this selective formation of organic sulfides and disulfides.

Recently, Hou and Wakatsuki reported the X-ray structure of the HMPA-coordinated SmI_2 complex, that is, $[SmI_2(hmpa)_4]$ where the Sm(II) ion is bonded by two apical I^- anions and four equatorial HMPA ligands in a distorted octahedron [9]. The result is consistent with the fact that the first bimolecular rate constant for the reduction of primary alkyl radicals with SmI_2 becomes the largest when 5 equiv of HMPA per SmI_2 is used in THF [10]. Accordingly, the strong coordination of HMPA to Sm(II) contributes to the pronounced enhancement of the reducing ability of SmI_2, effecting the reduction of elemental sulfur to $(I_2Sm)_2S$. On the other hand, SmI_2 itself (in the absence of HMPA) could not reduce elemental sulfur to $(I_2Sm)_2S$ but could reduce it to $(I_2Sm)_2S_2$. The formed $(I_2Sm)_2S_2$ probably associates, and therefore, the alkylation of it is very sluggish. The addition of HMPA to $(I_2Sm)_2S_2$ in THF dramatically accelerates the alkylation to R_2S_2.

In summary, a selective method for generating samarium sulfide and disulfide has been revealed. The alkylation of thus formed samarium sulfides offers a useful alternative method for the selective synthesis of organic sulfides and disulfides.

EXPERIMENTAL

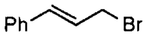
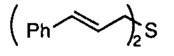
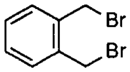
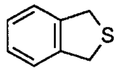
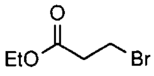
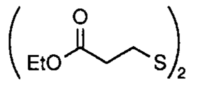
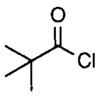
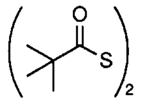
Materials

Unless otherwise noted, materials were obtained from commercial supplies 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 hours under reduced pressure.

A Representative Procedure for the Synthesis of Organic Sulfides

Samarium diiodide (SmI_2) was prepared by the reaction of samarium powder with 1,2-diiodoethane in freshly distilled (sodium/benzophenone ketyl) THF [11], 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). SmI_2 (2.2 mmol) in THF (22 mL) was added to the mixture of sulfur (1.0 mmol) and HMPA (4 mL) in a 30 mL glass vessel filled with argon, and the mixture was stirred for 2 hours under reflux. Each organic halide (3.0 mmol) was added to the resulting mixture, and the reaction was continued for an additional 2 hours. 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

TABLE 1 Selective Synthesis of Organic Sulfides and Disulfides

Entry	*Halide*	*Condition*[a]	*Product*	*Yield, %*
1	^nBuI	A[b]	$^nBu_2S$	79
2		B	$(^nBuS)_2$	80
3	$PhCH_2Br$	A	$(PhCH_2)_2S$	81
4		B	$(PhCH_2S)_2$	84
5		A		96
6		A[c]		64
7		B		88
8		B		87

[a] Condition A: S (1 mmol), SmI_2 (2.2 mmol), HMPA (4 mL), THF (22 mL), 67°C, 2 hours; then halide (3 mmol), 67°C, 2 hours. Condition B: S (2 mmol), SmI_2 (2.2 mmol), THF (22 mL), 20°C, 0.5 hour; then halide (3 mmol), HMPA (4 mL), 67°C, 2 hours.

[b] 24 hours.

[c] Halide (1.5 mmol).

(silica gel, 25–40 mm, length 310 mm, i.d. 25 mm, eluent hexane) or flash chromatography (silica gel, 63–180 nm, length 300 mm, i.d. 25 mm) provided the diorganyl sulfide: di(*n*-butyl) sulfide (Reg. No. 544-40-1) [12], dibenzyl sulfide (Reg. No. 538-74-9) [13], dicinnamyl sulfide (Reg. No. 169886-96-8) [14], and 1,3-dihydro-benzo[c]thiophene (Reg. No. 2471-92-3) [15].

A Representative Procedure for the Synthesis of Organic Disulfides

The blue solution of SmI_2 (2.2 mmol) in THF (22 mL) was added with a syringe to sulfur (2.0 mmol) in a 30 mL glass vessel filled with argon. The solution gradually turned to brown within 0.5 hour along with deposition of pale yellow precipitates. To the mixture was added successively HMPA (1 mL) and each organic halide (3.0 mmol). The solution was stirred under reflux for 2 hours. 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 hexane) or flash chromatography (silica gel, 63–180 nm, length 300 mm, i.d. 25 mm) provided the diorganyl disulfide: di(*n*-butyl) disulfide (Reg. No. 629-45-8) [16], dibenzyl disulfide (Reg. No. 150-60-7) [17], bis[2-(ethoxycarbonyl)ethyl] disulfide (Reg. No. 1609-40-1) [3], and dipivaloyl disulfide (Reg. No. 74491-70-6) [18].

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