

Reductive Cleavage of the S–Si Bond in Arylsulfanyltrimethylsilanes: a Novel Method for the Synthesis of Unsymmetrical Sulfides†

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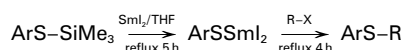
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Arylsulfanyltrimethylsilanes are reduced by samarium diiodide to yield samarium arylthiolates which react with alkyl halides to give unsymmetrical sulfides.

The application of samarium diiodide in organic synthesis has received increasing attention in the last decade.^{1–3} It is a powerful one-electron transfer reductant. We have reported the reductive cleavage of S–S bonds with SmI₂.⁴ Recently, we have considered that the S–Si bond might be also reduced with samarium diiodide.

Since organic sulfur compounds have become increasingly useful and important in organic synthesis,^{5,6} convenient preparations of appropriate sulfides have been developed continuously.^{7–11} For example, sulfoxides are reduced to sulfides with the Cp₂TiCl₂/Sm or TiCl₄/Sm^{7,8} system, while the reaction between benzyl chloride and thiols in the presence of a modified montmorillonite clay containing 3-aminopropyltriethoxysilane has also been reported.¹⁰

Here we report that SmI₂ reduces arylsulfanyltrimethylsilanes to samarium arylthiolates under a nitrogen atmosphere. This new thiolate anion species reacts with alkyl halides to give unsymmetrical sulfides in good yield under neutral conditions (Scheme 1).



Scheme 1

Experimental

General Procedure.—A solution of arylsulfanyltrimethylsilane (1 mmol) in THF (1 ml) was added by syringe to a deep blue solution of SmI₂ (2.2 mmol) in THF (10 ml) at reflux temperature under an inert atmosphere of nitrogen. The deep blue colour of the solution gradually became brown within 5 h, which showed that the S–Si bond had been reductively cleaved by SmI₂ and that the samarium arylthiolate (ArSmI₂) had been generated. An alkyl halide (1 mmol) in THF (1 ml) was then added by syringe to the mixture and stirred under reflux for 4 h; a dilute solution of HCl and diethyl ether were added. The organic layer was washed with water (20 ml × 2) and dried over anhydrous Na₂SO₄. The solvent was removed *in vacuo*. The crude product was purified by preparative

TLC on silica gel (light petroleum:ethyl acetate = 100:1 as eluent). Some results are summarized in Table 1.

Data of Products.—**1:** mp 38–39 °C; δ_H (CCl₄) 3.97 (2 H, s), 7.00–7.28 (10 H, m); ν_{max}/cm⁻¹ 3080, 3040, 2940, 1595, 1500, 1488, 1460, 1445, 1250, 1090, 1070, 1025, 735, 690. **2:** oil; δ_H 0.83 (3 H, t), 1.0–1.67 (16 H, m), 2.80 (2 H, t), 7.03–7.23 (5 H, m); ν_{max}/cm⁻¹ 3090, 3080, 2960–2920, 2860, 1595, 1495, 1470, 1445, 1022, 730, 682. **3:** oil; δ_H 0.87 (3 H, t), 1.02–1.70 (8 H, m), 2.80 (2 H, t), 7.03–7.22 (5 H, m); ν_{max}/cm⁻¹ 3090, 3080, 2970–2940, 2860, 1600, 1496, 1470, 1446, 1022, 728, 680. **4:** mp 45–46 °C; δ_H 0.86 (3 H, t), 1.03–1.72 (28 H, m), 2.83 (2 H, t), 7.03–7.24 (5 H, m); ν_{max}/cm⁻¹ 3092, 3080, 2960–2920, 2860, 1600, 1469, 1470, 1447, 1021, 729, 678. **5:** mp 47–49 °C; δ_H 3.46 (4 H, s), 7.17 (10 H, s); ν_{max}/cm⁻¹ 3080, 3060, 3019, 1585, 1480, 1450, 1240, 1185, 900, 760, 682. **6:** oil; δ_H 0.84 (3 H, t), 1.07–1.43 (16 H, m), 2.23 (2 H, t), 3.54 (2 H, s), 7.20 (5 H, s); ν_{max}/cm⁻¹ 3100, 3080, 3040, 2970–2930, 2860, 1610, 1500, 1470, 1460, 1380, 1070, 1030, 760, 690. **7:** oil; δ_H 0.84 (3 H, t), 1.07–1.43 (20 H, m), 2.23 (2 H, t), 3.54 (2 H, s), 7.20 (5 H, s); ν_{max}/cm⁻¹ 3100, 2080, 3040, 2980–2940, 2864, 1610, 1500, 1472, 1465, 1460, 1380, 1070, 1029, 760, 690. **8:** oil; δ_H 0.86 (3 H, t), 1.02–1.70 (8 H, m), 2.23 (2 H, t), 3.53 (2 H, s), 7.17 (5 H, s); ν_{max}/cm⁻¹ 3100, 3080, 3040, 2982–2940, 2860, 1610, 1500, 1470, 1460, 1380, 1070, 1030, 760, 690. **9:** oil; δ_H 0.87 (3 H, t), 1.10–1.60 (8 H, m), 2.77 (2 H, t), 7.13–7.23 (4 H, m); ν_{max}/cm⁻¹ 3090, 3085, 2900–2800, 1585, 1490–1480, 1400, 1100–1090, 1010, 810, 740, 720. **10:** oil; δ_H 0.87 (3 H, t), 1.13–1.40 (20 H, m), 2.76 (2 H, t), 7.14–7.23 (4 H, m); ν_{max}/cm⁻¹ 3090, 3085, 2920–2800, 1585, 1490–1480, 1395, 1100–1090, 1010, 810, 740, 720. **11:** oil; δ_H 0.87 (3 H, t), 1.15–1.42 (16 H, m), 2.76 (2 H, t), 7.14–7.23 (4 H, m); ν_{max}/cm⁻¹ 3090, 3085, 2920–2800, 1585, 1490–1480, 1395, 1100–1095, 1010, 810, 740, 720.

¹H NMR spectra were recorded on a PMX-60 MHz instrument, and IR spectra were determined on a PE-683 spectrometer.

We are grateful to the National Natural Science Foundation of China and Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, for financial support.

Table 1 Sulfide products from arylsulfanyltrimethylsilanes (ArSSiMe₃) and alkyl halides (RX)

Entry	Ar	R–X	Product	Yield ^c (%)
1	Ph	PhCH ₂ Cl ^a	PhSCH ₂ Ph (1)	85
2	Ph	PhCH ₂ Cl ^b	PhSCH ₂ Ph (1)	80
3	Ph	Me[CH ₂] ₉ Br	PhS[CH ₂] ₉ Me (2)	89
4	Ph	Me[CH ₂] ₅ Br	PhS[CH ₂] ₅ Me (3)	83
5	Ph	Me[CH ₂] ₁₅ Br	PhS[CH ₂] ₁₅ Me (4)	78
6	PhCH ₂	PhCH ₂ Cl ^a	PhCH ₂ SCH ₂ Ph (5)	84
7	PhCH ₂	Me[CH ₂] ₅ Br	PhCH ₂ S[CH ₂] ₅ Me (6)	78
8	PhCH ₂	Me[CH ₂] ₁₁ Br	PhCH ₂ S[CH ₂] ₁₁ Me (7)	77
9	PhCH ₂	Me[CH ₂] ₅ Br	PhCH ₂ S[CH ₂] ₅ Me (8)	77
10	4-CIC ₆ H ₄	Me[CH ₂] ₅ Br	4-CIC ₆ H ₄ [CH ₂] ₅ Me (9)	78
11	4-CIC ₆ H ₄	Me[CH ₂] ₁₁ Br	4-CIC ₆ H ₄ [CH ₂] ₁₁ Me (10)	80
12	4-CIC ₆ H ₄	Me[CH ₂] ₉ Br	4-CIC ₆ H ₄ [CH ₂] ₉ Me (11)	82

^aAlkylation at room temp. for 4 h; ^breduction at room temp. for 10 h, alkylation at room temp. for 4 h; ^cyields of isolated products.

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Received, 21st July 1997; Accepted, 12th September 1997
Paper E/7/05190E

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