

Reductive Cleavage of the Se–Si Bond in Arylselenotrimethylsilanes: Novel Method for the Synthesis of Unsymmetrical Selenides†

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Arylselenotrimethylsilanes are reduced by samarium diiodide to yield samarium areneselenolates, which react with alkyl halides to give unsymmetrical selenides.

As a powerful and versatile one-electron transfer reducing and coupling reagent, SmI_2 has been applied widely in organic synthesis.^{1–3} Our previous work on the reductive cleavage of S–S, Se–Se and Te–Te bonds with SmI_2 ^{4,5} led us to investigate the reductive cleavage of Se–Si bonds by SmI_2 .

Selenides are involved in important transformations such as the synthesis of alkanes,^{6–8} alkenes,^{9–11} and alkyl halides,^{12,13} but relatively few syntheses of selenides have been described. A useful approach to the synthesis of selenides is based on the alkylation of selenide ion, which can easily be prepared from elemental selenium by reduction with sodium in liquid ammonia,¹⁴ sodium tetrahydroborate in ethanol¹⁵ or water¹⁶ or with tetraalkylammonium tetrahydroborates.¹⁷ In another approach, alcohols and selenols were treated with acid to give selenides.¹⁸ Most of these methods have been applied successfully to the synthesis of selenides.

Here we report that SmI_2 reduces arylselenotrimethylsilanes to samarium areneselenolates under a nitrogen atmosphere. This new selenolate anion species reacts with alkyl halides to give unsymmetrical selenides in good yield under neutral conditions (Scheme 1).

In summary, a novel method for the preparation of unsymmetrical selenides has been elucidated, the advantages of which are simple manipulation, mild and neutral conditions.

Experimental

General Procedure.—A solution of arylselenotrimethylsilane¹⁹ (1 mmol) in THF (1 ml) was added by syringe to a deep blue solution of SmI_2 (2.2 mmol) in THF (10 ml) at reflux temperature under a nitrogen atmosphere. The deep blue solution gradually became brown within 3 h, which showed that the Se–Si bond had been reductively cleaved by SmI_2 and that the samarium areneselenolate (ArSeSmI_2)²⁰ had been generated. Alkyl halides (1 mmol) in THF (1 ml) were then added by syringe and stirred at refluxing



Scheme 1

temperature for 3 h. A dilute solution of HCl and diethyl ether was added. The organic layer was washed with water (20 ml $\times$ 2) and dried over anhydrous Na_2SO_4 . The solvent was removed *in vacuo*. The crude product was purified by preparative TLC on silica gel (cyclohexane as eluent). Some results are summarized in Table 1.

1.²⁰ mp 34–35 °C, δ_{H} (CCl_4) 3.93 (2 H, s), 7.00–7.40 (10 H, m); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 3100, 3080, 3040, 2950, 1610, 1590, 1500, 1485, 1460, 1440, 1180, 1080, 1020, 1000, 910, 760, 740, 660, 600.

2.²¹ Oil, δ_{H} (CCl_4) 0.80 (3 H, t), 1.07–1.60 (12 H, m), 2.75 (2 H, t), 7.00–7.50 (5 H, m); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 3100, 3080, 2980, 2980–2940, 2870, 1590, 1485, 1460, 1440, 1380, 1075, 1020, 1000, 730, 690, 660.

3.²² Oil, δ_{H} (CCl_4) 0.80 (3 H, t), 1.07–1.57 (16 H, m), 2.77 (2 H, t), 7.00–7.60 (5 H, m); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 3100, 3080, 2980, 2960–2940, 2870, 1590, 1486, 1440, 1380, 1080, 1020, 1000, 730, 690, 665.

4.¹⁰ Oil, δ_{H} (CCl_4) 0.82 (3 H, t), 1.07–1.60 (20 H, m), 2.77 (2 H, t), 7.00–7.60 (5 H, m); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 3100, 3080, 2980, 2960–2940, 2870, 1590, 1485, 1470, 1440, 1380, 1080, 1020, 1000, 730, 690, 660.

5.²³ mp 33–34 °C, δ_{H} (CCl_4) 0.80 (3 H, t), 1.07–1.60 (28 H, m), 2.77 (2 H, t), 7.00–7.60 (5 H, m); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 3100, 3080, 2980, 2960–2940, 2870, 1590, 1485, 1470, 1440, 1075, 1020, 1000, 730, 690, 665.

6.²⁴ Oil, δ_{H} (CCl_4) 2.20 (3 H, s), 3.87 (2 H, s), 6.83–7.40 (9 H, m); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 3100, 3080, 3040, 2990, 2950, 2870, 1600, 1500, 1470, 1460, 1385, 1270, 1200, 1180, 1040, 820, 760, 690, 650, 600.

7.²⁵ Oil, δ_{H} (CCl_4) 2.30 (3 H, s), 2.54 (3 H, s), 6.90–7.40 (4 H, m); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 3100, 3080, 2980, 2950, 2870, 1595, 1485, 1470, 1440, 1380, 1040, 735, 650.

8.²⁵ Oil, δ_{H} (CCl_4) 1.30 (3 H, t), 2.30 (3 H, s), 2.73 (2 H, q), 6.91–7.45 (4 H, m); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 3100, 3080, 2980, 2960, 2870, 1590, 1485, 1470, 1440, 1380, 1040, 730, 690, 660.

9.²⁵ Oil, δ_{H} (CCl_4) 1.36 (6 H, d), 2.30 (3 H, s), 3.01–3.08 (1 H, m), 6.90–7.40 (4 H, m); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 3100, 3080, 2980–2960, 2870, 1590, 1485, 1470, 1440, 1380, 1040, 730, 690, 665.

¹H NMR spectra were recorded on a PMX-60 MHz instrument (TMS as internal reference), IR spectra on a PE-683 spectrometer.

Table 1 Yields of the products ArSeR

Entry	Ar	R–X	Product	Yield ^a (%)
a	Ph	PhCH_2Cl^b	1 PhSeCH_2Ph	84
b	Ph	PhCH_2Br^b	1 PhSeCH_2Ph	84
c	Ph	$\text{CH}_3(\text{CH}_2)_7\text{Br}$	2 $\text{PhSe}(\text{CH}_2)_7\text{CH}_3$	80
d	Ph	$\text{CH}_3(\text{CH}_2)_9\text{Br}$	3 $\text{PhSe}(\text{CH}_2)_9\text{CH}_3$	77
e	Ph	$\text{CH}_3(\text{CH}_2)_{11}\text{Br}$	4 $\text{PhSe}(\text{CH}_2)_{11}\text{CH}_3$	79
f	Ph	$\text{CH}_3(\text{CH}_2)_{15}\text{Br}$	5 $\text{PhSe}(\text{CH}_2)_{15}\text{CH}_3$	75
g	<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4$	PhCH_2Cl^b	6 <i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{SeCH}_2\text{Ph}$	82
h	<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4$	PhCH_2Br^b	6 <i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{SeCH}_2\text{Ph}$	82
i	<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4$	CH_3I	7 <i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{SeCH}_3$	80
j	<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4$	$\text{CH}_3\text{CH}_2\text{I}$	8 <i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{SeCH}_2\text{CH}_3$	76
k	<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4$	$\text{CH}_3\text{CH}(\text{Br})\text{CH}_3$	9 <i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{SeCH}(\text{CH}_3)_2$	68

^aOf isolated product. ^b Alkylation at room temperature for 4 h.

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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)*.

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