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 ethanol[15] or water[16] 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 arylselenotrimethylsilane[19] (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 temperature for 3 h. A dilute solution of HCl and diethyl ether was added. The organic layer was washed with water (20 ml × 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.

Scheme 1

1.[20] mp 34–35 °C, δ_H (CCl_4) 3.93 (2 H, s), 7.00–7.40 (10 H, m); $\tilde{\nu}_{max}/cm^{-1}$ 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); $\tilde{\nu}_{max}/cm^{-1}$ 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); $\tilde{\nu}_{max}/cm^{-1}$ 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); $\tilde{\nu}_{max}/cm^{-1}$ 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); $\tilde{\nu}_{max}/cm^{-1}$ 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); $\tilde{\nu}_{max}/cm^{-1}$ 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); $\tilde{\nu}_{max}/cm^{-1}$ 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); $\tilde{\nu}_{max}/cm^{-1}$ 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); $\tilde{\nu}_{max}/cm^{-1}$ 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	$CH_3(CH_2)_7Br$	**2** $PhSe(CH_2)_7CH_3$	80
d	Ph	$CH_3(CH_2)_9Br$	**3** $PhSe(CH_2)_9CH_3$	77
e	Ph	$CH_3(CH_2)_{11}Br$	**4** $PhSe(CH_2)_{11}CH_3$	79
f	Ph	$CH_3(CH_2)_{15}Br$	**5** $PhSe(CH_2)_{15}CH_3$	75
g	*o*-$CH_3C_6H_4$	$PhCH_2Cl$[b]	**6** *o*-$CH_3C_6H_4SeCH_2Ph$	82
h	*o*-$CH_3C_6H_4$	$PhCH_2Br$[b]	**6** *o*-$CH_3C_6H_4SeCH_2Ph$	82
i	*o*-$CH_3C_6H_4$	CH_3I	**7** *o*-$CH_3C_6H_4SeCH_3$	80
j	*o*-$CH_3C_6H_4$	CH_3CH_2I	**8** *o*-$CH_3C_6H_4SeCH_2CH_3$	76
k	*o*-$CH_3C_6H_4$	$CH_3CH(Br)CH_3$	**9** *o*-$CH_3C_6H_4SeCH(CH_3)_2$	68

[a]Of 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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References

1 P. Girard, J. L. Namy and H. B. Kagan, *J. Am. Chem. Soc.*, 1980, **102**, 2693.
2 G. A. Molander, *Chem. Rev.*, 1992, **92**, 29.
3 G. A. Molander and C. R. Harris, *Chem. Rev.*, 1996, **96**, 307.
4 S. X. Jia and Y. M. Zhang, *Synth. Commun.*, 1994, **24**, 787.
5 Y. M. Zhang, Y. P. Yu and R. H. Lin, *Synth. Commun.*, 1993, **23**, 189.
6 M. Sevrin, D. Van Ende and A. Krief, *Tetrahedron Lett.*, 1976, **30**, 2643.
7 W. Dumont, P. Bayet and A. Krief, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 804.
8 D. Seebath and A. K. Beck, *Angew. Chem. Int. Ed. Engl.*, 1974, **13**, 804.
9 D. N. Jones, D. Mundy and R. D. Whitehouse, *Chem. Commun.*, 1970, 86.
10 K. B. Sharpless and M. W. Young, *J. Org. Chem.*, 1975, **40**, 947.
11 S. Halazy and A. Krief, *Tetrahedron Lett.*, 1979, **49**, 4233.
12 M. Sevrin and A. Krief, *Tetrahedron Lett.*, 1976, **30**, 2647.
13 M. Sevrin and A. Krief, *J. Chem. Soc., Chem. Commun.*, 1980, **2**, 656.
14 D. Linotta, W. Markiewicz and H. Santiesteben, *Tetrahedron Lett.*, 1977, **50**, 4365.
15 D. L. Klayman and T. S. Griffin, *J. Am. Chem. Soc.*, 1973, **95**, 197.
16 J. Bergman and L. Engman, *Org. Prep. Proced. Int.*, 1978, **10**, 289.
17 J. Bergman and L. Engman, *Synthesis*, 1980, **7**, 569.
18 M. Clarembeau and A. Krief, *Tetrahedron Lett.*, 1984, **25**, 3625.
19 M. R. Detty, *J. Org. Chem.*, 1979, **44**, 4528.
20 S. I. Fukuzawa, Y. Niimoto, T. Fujinami and S. Sakai, *Heteroat. Chem.*, 1990, **1**, 491.
21 G. Pandey, B. B. V. Soma Sekhar and U. T. Bhalerao, *J. Am. Chem. Soc.*, 1990, **112**, 5650.
22 A. Krief, W. Dumont, J. Noel, G. Everard and B. Norbery, *J. Chem. Soc., Chem. Commun.*, 1985, 569.
23 A. Toshimitsu, H. Owada, S. Uemura and M. Okano, *Tetrahedron Lett.*, 1980, **21**, 5037.
24 G. Paul and T. M. Aellen, *J. Chem. Soc. Chem. Commun.*, 1980, 558.
25 A. D. Baker, G. H. Armen and G. D. Yang, *J. Org. Chem.*, 1981, **46**, 4127.