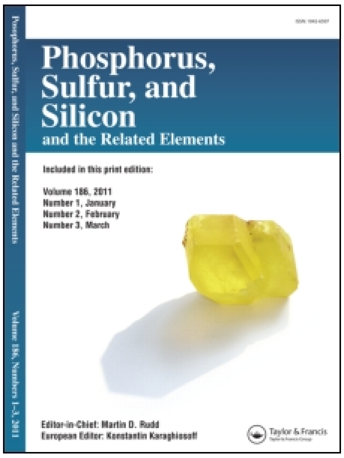

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Reduction of Sulfonium and Selenonium Salts with Samarium Diiodide

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REDUCTION OF SULFONIUM AND SELENONIUM SALTS WITH SAMARIUM DIIODIDE

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Abstract Treatment of sulfonium and selenonium salts with 2 equiv of a THF solution of samarium diiodide caused the reductive cleavage of the C-S or C-Se bonds in high yields. The bond cleavage took place regioselectively between the positive sulfur or selenium atom and the carbon atom with an electron-withdrawing group or a vinyl group. Some medium-sized cyclic sulfides or selenides were synthesized by this method.

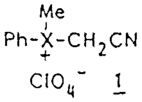
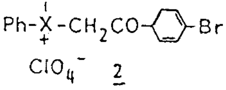
INTRODUCTION

We recently found that sulfonium or selenonium salts were reduced by the single electron transfer (SET) process and the C-S or C-Se bonds were homolytically cleaved.[1] The reaction intermediates would be hypervalent species, sulfuranyl or selenuranyl radicals. Selenonium salts were reduced with magnesium more readily than the corresponding sulfonium salts.[1,2] On the other hand, samarium diiodide, a good reagent for the SET reduction, is widely used for organic synthesis.[3] However, reduction of onium salts with samarium diiodide has not been reported. In order to reduce both sulfonium and selenonium salts effectively, we selected a homogeneous solution of samarium diiodide in THF as a reducing agent. This report describes the reduction of sulfonium and selenonium salts with samarium diiodide.

RESULTS AND DISCUSSION

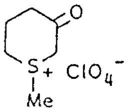
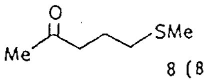
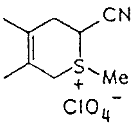
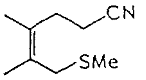
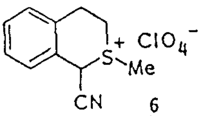
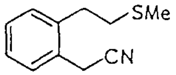
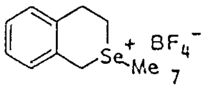
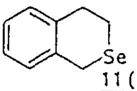
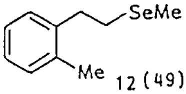
Reduction of acyclic 1, 2 and cyclic onium salts 4 - 7 were examined. A suspension of an onium salt in THF containing 2 equiv of methanol was treated with 2 equiv of 0.1M solution of samarium diiodide under nitrogen at room temperature. The results are summarized in Tables 1 and 2.

Table 1. Reduction of Acyclic Onium Salts

Onium Salt	Product (%yield)
 $Ph-\overset{Me}{\underset{+}{X}}-CH_2CN \; ClO_4^-$ **1** a: X=S b: X=Se	PhXMe 3a (85), 3b (87)
 **2**	PhXMe[a] 3a (90), 3b (92)

a) 4'-Bromoacetophenone was also produced as a counterpart in yields of 73% and 72% from 2a and 2b, respectively.

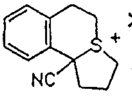
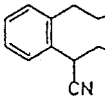
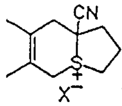
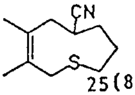
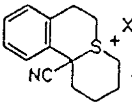
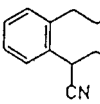
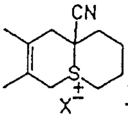
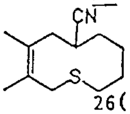
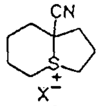
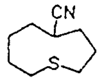
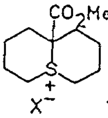
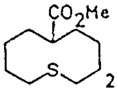
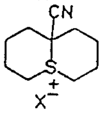
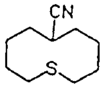
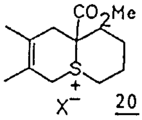
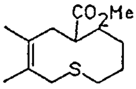
Table 2. Reduction of Cyclic Onium Salts

Onium Salt	Products(%yields)	
 **4**	 8 (82)	
 **5**	 9 (63)	
 **6**	 10 (98)	
 **7**	 11 (32)	+  12 (49)

Reductive cleavage of C-S or C-Se bond occurred chemoselectively and regioselectively. Demethylated products were not obtained from onium salts 1 and 2, but isoselenochroman 11 was produced from selenonium salt 7. This result was different from that of magnesium reduction of 7 giving the ring-opened selenide 12 only.[1] This shows that samarium diiodide was a stronger reducing agent than magnesium and lowered the regioselectivity of the C-Se bond cleavage. Therefore, an electron-withdrawing group is necessary to cleave the C-S or C-Se bond regioselectively using samarium diiodide. Sulfonium salts were smoothly reduced to afford sulfides in high yields.

Next, bicyclic onium salts, 13 - 20 and 29 - 31 were reduced with samarium diiodide in the same manner described above. Medium-sized cyclic sulfides and selenides were afforded in satisfactory yields as shown in Tables 3 and 4.

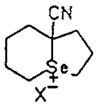
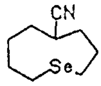
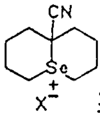
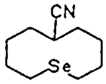
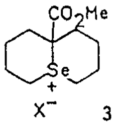
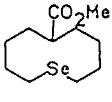
TABLE 3. Synthesis of medium-sized cyclic sulfides

Sulfonium Salt		Product(%yield) a)		Sulfonium Salt		Product(%yield) a)	
	13		21(99)		17		25(84)
	14		22(97)		18		26(91)
	15		23 (83)		19		27(79)
	16		24 (77)		20		28(78)

X=ClO$_4$ a) %yield by magnesium reduction: 23 (57); 24 (0); 25 (58); 26 (39); 27 (28); 28 (56).

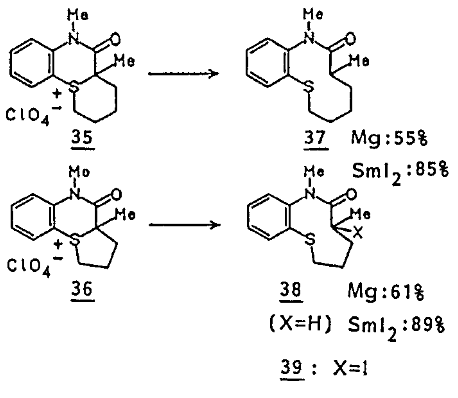
In contrast, cyano-substituted sulfonium salt 16 was not reduced by magnesium and other sulfonium salts, 15 and 17 - 20 were reduced in low to moderate yields. The magnesium reduction was affected by the substituents on an α-carbon to the sulfonio moiety or by the ring strain. Selenonium salts were reduced by magnesium in good yields.

TABLE 4. Synthesis of medium-sized cyclic selenides

Selenonium Salt		Product(%yield)	
	29		32 (88)
	30		33 (88)
	31		34 (86)

X=ClO$_4$

SCHEME



Some medium-sized compounds containing a nitrogen and a sulfur atoms show the interesting pharmacological activities.[4] Therefore, we tried to synthesize lactams containing a sulfur atom. Nine- 37 and ten-membered lactam sulfide 38 were produced by reduction of 35 and 36 with samarium diiodide in higher yields than that with magnesium. When the quantity of samarium diiodide was reduced, the iodide 39 was formed as a by-product.

In conclusion, samarium diiodide is a very useful reagent for reduction of sulfonium and selenonium salts.

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