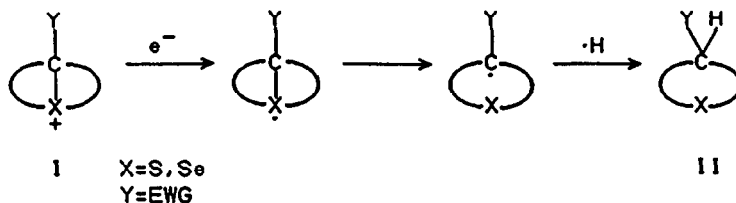


NOVEL SYNTHESIS OF MEDIUM-SIZED HETEROCYCLES  
 CONTAINING A SULFUR OR SELENIUM ATOM

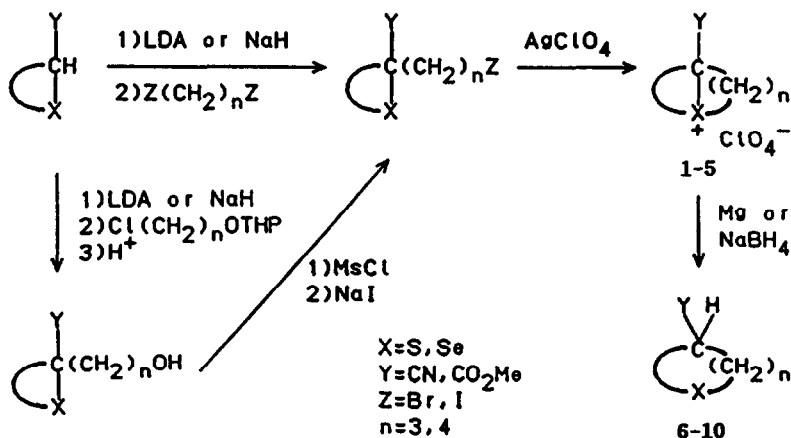
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**Abstract:** Medium-sized sulfur- or selenium-containing heterocyclic compounds were synthesized by the reductive cross-piece bond cleavage of bicyclic sulfonium and selenonium salts bearing a bridgehead sulfur or selenium atom with magnesium metal or sodium borohydride.

Recently, we have found that organometallic reagents or magnesium metal caused the single electron transfer (SET) reduction of sulfonium and selenonium salts.<sup>1)</sup> We intended to develop novel synthesis of sulfur- or selenium-containing medium-sized heterocycles (II) by applying this new reaction to selective cleavage of the cross-piece bonds of bicyclic onium salts (I) with a bridgehead sulfur or selenium atom.



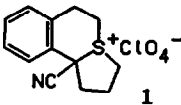
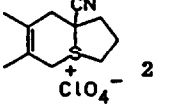
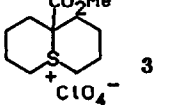
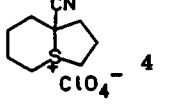
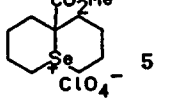
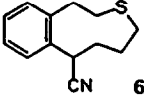
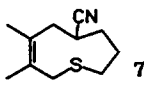
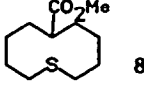
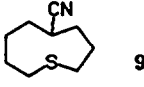
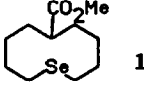
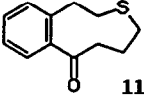
There have been only a few synthetic reports for the medium-sized sulfur-containing heterocyclic compounds from sulfonium compounds: [2,3]-sigmatropic rearrangement of sulfonium ylides,<sup>2)</sup> and reductive C-S bond cleavage<sup>3)</sup> or nucleophilic substitution<sup>4)</sup> of cyclic sulfonium salts. In this communication, we describe the synthesis of sulfur- or selenium-containing medium-sized heterocycles. Cyclic onium salts (1-5),<sup>5)</sup> the substrates, having an electron-withdrawing group (Y=CN, CO<sub>2</sub>Me) were synthesized as shown below.



Reactions of 1-5 with magnesium metal provided the expected heterocycles 6-10 (Method A), respectively. The results are listed in Table 1. When reaction of 1 was carried out in *N,N*-dimethylformamide (DMF), ketone derivative 11 was formed as a by-product. The yield of 11 was not increased by treatment of 1 in DMF containing water, but increased on bubbling air into the reaction mixture. These experiments indicate that the radical formed by SET reduction of the sulfonium salt reacts with oxygen to give a cyanohydrin intermediate, which is hydrolyzed to the ketone. Selenonium salt 5 gave the product of ring-enlargement 10 in better yield, than the reactions of sulfonium salts (e.g. 3) probably because of poor solubilities of the latter in tetrahydrofuran (THF). Yields of 6-9 were improved by  $\text{NaBH}_4$  reduction of 1-5 in ethanol (Method B).

Further application of the new methods to the synthesis of heterocycles having various functional groups other than  $-\text{CN}$  and  $-\text{CO}_2\text{R}$  is currently under investigation.

Table 1 Syntheses of Medium-sized Thia- and Selenacyclic Compounds

Onium Salts	Methods	Solvents	Products (% Yields)
	A	THF Benzene DMF DMF <sup>a</sup> )	6(38) 6(47) 6(27), 11(6) 6(trace), 11(15)
	B	EtOH	6(66)
	A	Benzene	7(58)
	B	EtOH	7(87)
	A	THF	8(28)
	B	EtOH	8(48)
	A	THF	9(57)
	B	EtOH	9(67)
	A	THF	10(74)
			
			
			
			
			
			

a) Air was bubbled into the reaction mixture.

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3. D. M. Roush, E. M. Price, L. K. Templeton, D. H. Templeton, and C. H. Heathcock, *J. Am. Chem. Soc.*, **1979**, 101, 2971.
4. H. Matsuyama, T. Nakamura, and N. Kamigata, *J. Org. Chem.*, **1989**, 54, 5218.
5. All compounds exhibited spectral data in full accord with assigned structures and gave satisfactory elemental analyses.