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### SYNTHESIS OF TETRACOORDINATE 1,2-OXASELENETANES AND THEIR OXIRANE FORMATION REACTION

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Tetracoordinate *trans*- and *cis*-3,4-diphenyl-4-trifluoromethyl-1,2-oxaselenetanes bearing the Martin ligand were synthesized by the oxidative cyclization of the corresponding  $\beta$ -hydroxyalkyl selenides with Br<sub>2</sub> in the presence of Et<sub>3</sub>N. Their thermolysis afforded the corresponding oxiranes stereospecifically in a high yield with retention of configuration, though a small amount (2%) of an inverted product was obtained from the *trans*-isomer.

<u>Keywords</u>: tetracoordinate 1,2-oxaselenetanes, oxirane formation reaction, thermolysis, retention of configuration

### INTRODUCTION

In the course of our study on heteracyclobutanes bearing a highly coordinate main group element at the position adjacent to the heteroatom,<sup>[1]</sup> we have succeeded in the syntheses and isolations of tetracoordinate 1,2-oxaselenetane 1,<sup>[2]</sup> tetra- and pentacoordinate 1,2-oxathietanes 2 and 3<sup>[3,4]</sup> by taking advantage of the stabilizing effect of the Martin ligand,<sup>[5]</sup> and reported the oxirane formation reaction with retention of configuration in the thermolysis of 3.<sup>[4b]</sup> The thermolysis

of 1 did not give the corresponding oxirane at all.<sup>[2]</sup> In this paper we wish to report the first example of oxirane formation from tetracoordinate 3-phenyl-1,2 $\lambda^4$ -oxaselenetanes 4 and the stereochemistry of the reaction in connection with the Corey-Chaykovsky reaction.<sup>[6]</sup>

### RESULTS AND DISCUSSION

Tetracoordinate 3,4-diphenyl-4-trifluoromethyl-1,2-oxaselenetanes  $\bf 4a$  and  $\bf 4b$  were synthesized by the same method as that for the synthesis of sulfur analogs  $\bf 2$ , [4b] from o-LiC<sub>6</sub>H<sub>4</sub>C(CF<sub>3</sub>)<sub>2</sub>OLi<sup>[5c]</sup> via benzyl selenide  $\bf 5$  bearing  $\bf t$ -butyldimethylsilylated Martin ligand and  $\bf 6a$ , $\bf b$ , as shown in the following scheme.

$$\begin{array}{c} \text{t-BuMe}_2\text{SiO} \quad \text{CF}_3 \\ \text{Se} \quad \text{Ph} \\ \text{3)} \quad \text{FCC} \\ \text{4)} \quad \text{n-Bu}_4\text{NF} \\ \text{5} \\ \text{a: } 45\%; \text{ b: } 36\% \\ \text{a: } R^1 = \text{Ph}, \, R^2 = \text{CF}_3; \text{ b: } R^1 = \text{CF}_3, \, R^2 = \text{Ph} \\ \text{a: } 50\text{ CF}_3 \\ \text{OH} \quad \text{Se} \quad \text{Ph} \\ \text{Se} \quad \text{Ph} \\ \text{Se} \quad \text{Ph} \\ \text{CCI}_4 \\ \text{R}_2 \\ \text{CCI}_4 \\ \text{R}_2 \\ \text{CI}_4 \\ \text{R}_2 \\ \text{CCI}_4 \\ \text{R}_3 \\ \text{CCI}_4 \\ \text{R}_4 \\ \text{CCI}_4 \\ \text{R}_4 \\ \text{CCI}_4 \\ \text{R}_5 \\ \text{CCI}_4 \\ \text{R}_5 \\ \text{CCI}_6 \\ \text{R}_7 \\ \text{CCI}_8 \\ \text{R}_8 \\ \text{CCI}_8 \\$$

Compounds 4a and 4b were colorless plates stable at room temperature in the air, which were determined to be *trans*- and *cis*-isomers, respectively, by differential NOE experiments.

Thermolysis of **4a** and **4b** afforded the corresponding oxiranes stereospecifically in a high yield with retention of configuration, though a small amount (2%) of an inverted product was obtained from **4a**. The difference in the reactivity between **1** and **4** is due to the presence of the phenyl group at the 3-carbon.

$$4 \frac{\Delta}{\frac{A}{C_6D_5CD_3}} = \frac{R_1^{1} + \frac{A}{R_1^{2}} + \frac{A}$$

4	R <sup>1</sup>	R <sup>2</sup>	conditions	products (yield <sup>a)</sup> /%)					
				8	8'	9	10	11	12
а	Ph	CF <sub>3</sub>	200 °C, 30 h	88	2	8	97	2	2
b	CF <sub>3</sub>	Ph	200 °C, 5 h	quant	_	_	quant	_	-

<sup>&</sup>lt;sup>a</sup> Estimated by <sup>19</sup>F and <sup>1</sup>H NMR.

These results indicate that the stereochemistry of the oxirane formation from 1,2-oxaselenetanes 4 is reverse to that expected for the back side attack of the oxido anion via an *anti*-betaine, [7] and hence the reaction can be recognized as a carbon-oxygen ligand coupling reaction of  $\lambda^4$ -selenanes. [8]

The present results and the stereochemistry of the thermolysis of 3<sup>[4b]</sup> strongly suggest that such a concerted oxirane formation from highly coordinate oxachalcogenetanes generally proceed regardless of the kind of the central atom or its coordination number.

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