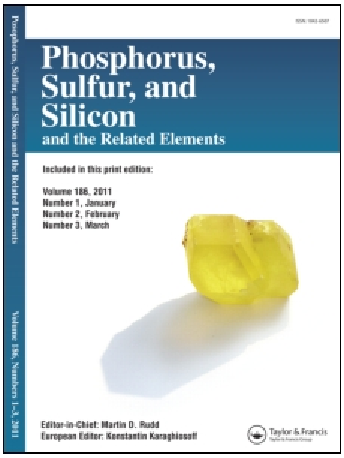

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SYNTHESIS OF TETRACOORDINATE 1,2-OXASELENETANES AND THEIR OXIRANE FORMATION REACTION

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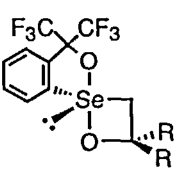
Tetracoordinate *trans*- and *cis*-3,4-diphenyl-4-trifluoromethyl-1,2-oxaselenetanes bearing the Martin ligand were synthesized by the oxidative cyclization of the corresponding β-hydroxyalkyl selenides with Br_2 in the presence of Et_3N. Their thermolysis afforded the corresponding oxiranes stereospecifically in a high yield with retention of configuration, though a small amount (2%) of an inverted product was obtained from the *trans*-isomer.

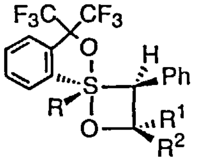
Keywords: tetracoordinate 1,2-oxaselenetanes, oxirane formation reaction, thermolysis, retention of configuration

INTRODUCTION

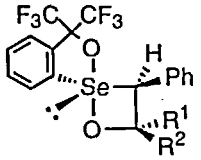
In the course of our study on heteracyclobutanes bearing a highly coordinate main group element at the position adjacent to the heteroatom,[1] we have succeeded in the syntheses and isolations of tetracoordinate 1,2-oxaselenetane **1**,[2] tetra- and pentacoordinate 1,2-oxathietanes **2** and **3**[3,4] by taking advantage of the stabilizing effect of the Martin ligand,[5] and reported the oxirane formation reaction with retention of configuration in the thermolysis of **3**.[4b] The thermolysis of **1** did not give the corresponding oxirane at all.[2] In this paper we wish to report the first example of oxirane formation from tetracoordinate 3-phenyl-1,2λ^4-oxaselenetanes **4** and the stereochemistry of the reaction in connection with the Corey-Chaykovsky reaction.[6]



1



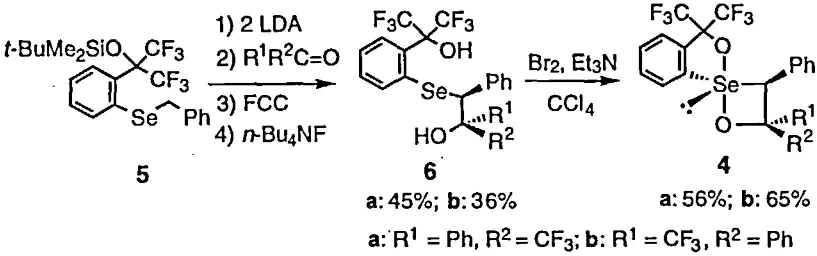
2: R = lone pair
3: R = O



4

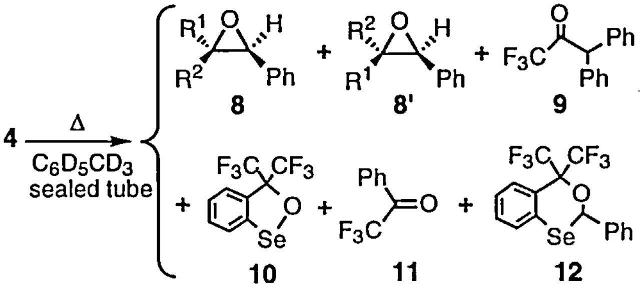
RESULTS AND DISCUSSION

Tetracoordinate 3,4-diphenyl-4-trifluoromethyl-1,2-oxaselenetanes **4a** and **4b** were synthesized by the same method as that for the synthesis of sulfur analogs **2**,[4b] from *o*-$LiC_6H_4C(CF_3)_2OLi$[5c] via benzyl selenide **5** bearing *t*-butyldimethylsilylated Martin ligand and **6a,b**, as shown in the following scheme.



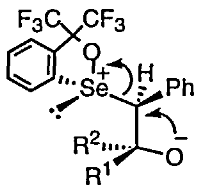
Compounds **4a** and **4b** were colorless plates stable at room temperature in the air, which were determined to be *trans*- and *cis*-isomers, respectively, by differential NOE experiments.

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.

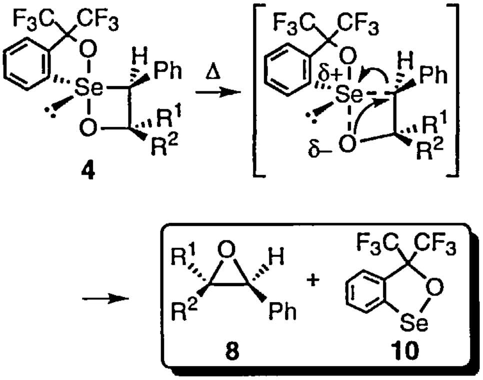


4	R^1	R^2	conditions	products (yield[a]/%)					
				8	8'	9	10	11	12
a	Ph	CF_3	200 °C, 30 h	88	2	8	97	2	2
b	CF_3	Ph	200 °C, 5 h	quant	–	–	quant	–	–

[a] Estimated by ^{19}F and ^{1}H NMR.



anti-betaine



retention

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 λ^4-selenanes.[8]

The present results and the stereochemistry of the thermolysis of **3**[4b] 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.

Acknowledgments

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