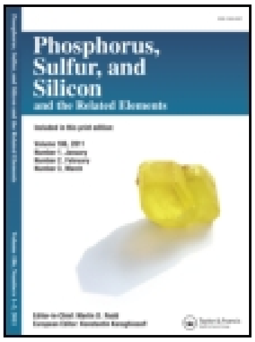

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Synthesis and Thermolysis of the Novel Ring Systems Containing Nitrogen and Tetracoordinate Selenium

NAOKAZU KANO, YUYA DAICHO, NOBUHITO NAKANISHI
and TAKAYUKI KAWASHIMA

*Department of Chemistry, Graduate School of Science, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

Oxidation of β-aminoalkyl selenides bearing the Martin ligand with *m*CPBA gave tetracoordinate 1,2-selenazetidines or a tetracoordinate 1,2,5-oxaselenazolidine as stable colorless crystals. The thermolysis of 1,2-selenazetidines afforded the corresponding aziridine and cyclic selenenate.

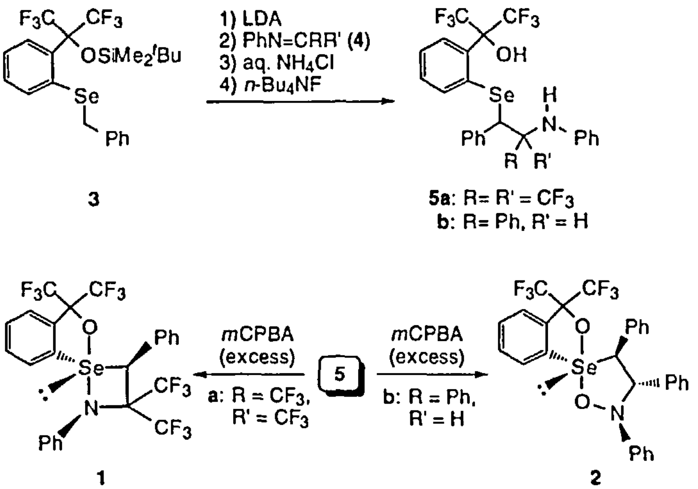
Keywords: 1,2-selenazetidine; selenurane; the Martin ligand; pseudo-TBP structure; 1,2,5-oxaselenazolidine

INTRODUCTION

We have reported the synthesis and thermolysis of several oxetanes bearing highly coordinate main group elements at the position adjacent to oxygen.[1] Although thermolyses of oxetanes with highly coordinate group 13, 14, and 15 elements afforded the corresponding olefins, oxachalcogenetanes which bear phenyl groups at 3-positions extruded not the corresponding olefins but the oxiranes. The thermolysis of other heterachalcogenetanes with highly coordinate chalcogen atoms, such as 1,2-thiazetidines and 1,2-selenazetidines, are expected to undergo the extrusion of the corresponding three membered ring compounds. Here, we present the synthesis and thermolysis of tetracoordinate 1,2-selenazetidine **1**, a novel four-membered heterocycle, together with the synthesis of a tetracoordinate 1,2,5-oxaselenazolidine **2**.

RESULTS AND DISCUSSION

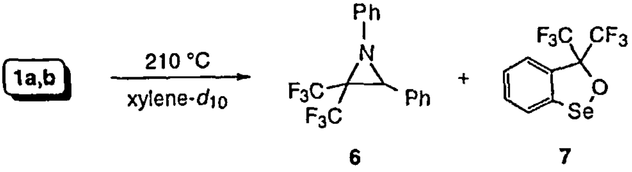
Sequential treatment of benzyl selenide **3** with lithium diisopropylamide (LDA), imine **4**, aqueous solution of NH_4Cl, and *n*-Bu_4NF gave the β-aminoalkyl selenide **5** (Scheme 1). To synthesize a 1,2-selenazetidine, excess amount of *m*CPBA was applied as an oxidant instead of Br_2 used for the synthesis of 1,2-oxaselenetanes.[2] However, a novel five-membered heterocyclic compound, 1,2,5-oxaselenazolidine **2**, was obtained as colorless crystals, and no selenazetidine was yielded at all. Oxidation of both selenium and nitrogen atoms in **5b** with excess amount of *m*CPBA and the successive dehydration would result in the formation of 1,2,5-oxaselenazolidine. On the other hand, treatment of the same reagents with **5a** afforded a



SCHEME I

mixture of two diastereomers of tetracoordinate 1,2-selenazetidines **1a** and **1b**, respectively, which were separated by silica gel chromatography. (Scheme 1). The structures of **1a**, **1b**, and **2** were established by ^{1}H, ^{13}C, ^{19}F and ^{77}Se NMR spectroscopy, elemental analysis, and X-ray analysis. These are the first examples of both ring systems, respectively. Moreover, **2** is the first example of a structurally characterized organic compound with Se–O–N linkage.

Thermolysis of **1a** and **1b** at 210 °C in xylene-d_{10} finally gave the corresponding aziridine **6** and cyclic selenenate **2** as predominant products (Scheme 2). No formation of the corresponding olefin was observed in marked contrast to its phosphorus analogue,



SCHEME 2

pentacoordinate 1,2-azaposphetidine.[3]

In summary, we have revealed that tetracoordinate 1,2-selenazetidines have reactivity similar to that of 1,2-oxaselenetanes in the point of giving the corresponding three-membered ring compound on the thermolysis. This is the first finding for aziridine formation pathways from heterocyclobutanes with highly coordinate main group elements.

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