Novel Ring System with an Se–O–N Linkage: Synthesis and Crystal Structure of the First 1,2λ^4,5-Oxaselenazolidine

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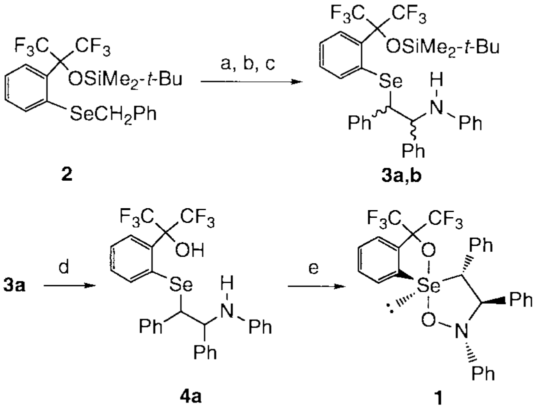
Oxidation of β–aminoalkyl selenide **4a** with an excess amount of *m*CPBA gave 1,2λ^4,5-oxaselenazolidine **1**, a novel heterocyclic compound with an Se–O–N linkage. Its X-ray crystallographic analysis revealed that the oxaselenazolidine ring has an envelope conformation.

Heterocycles containing plural heteroatoms in their rings have attracted the current interest from the standpoint of the structures and properties, which are considerably governed by the variety of the elements contained in each ring as well as their order of connection.[1] Although several kinds of heterocycles containing both selenium and other heteroatoms have been synthesized,[1] there has been no report on heterocyclic compounds bearing an Se–O–N moiety in this order except for pentalene type compounds with a tricoordinate selenium atom.[2] Moreover, only one compound has been reported for the organoselenium compound with acyclic Se–O–NR$_2$ moiety, i.e., Se[ON(CF$_3$)$_2$]$_4$, whose formula was only supported by the selenium analysis and by its hydrolysis reaction giving bis(trifluoromethyl)hydroxylamine.[3] Thus, the basic structural characters and reactivity of the compounds with an Se–O–N unit have been scarcely understood. On the other hand, we have previously reported the synthesis of the heteracyclobutanes bearing a tetracoordinate selenium atom at the neighboring position of oxygen or nitrogen by the oxidation of the corresponding β–hydroxyalkyl or β–aminoalkyl selenide, respectively,[4,5] as the part of our study on the hypervalent compounds.[6] These oxidative cyclization methods are expected to give the compounds with higher oxidation state when substrates have a functionality that is readily oxidized. Here, we present the first synthesis and crystal structure of a novel five-membered heterocyclic compound, a tetracoordinate 1,2λ^4,5-oxaselenazolidine **1**.

Sequential treatment of **2**[4b] (5.88 g, 11.0 mmol) with lithium diisopropylamide (LDA) (2.3 molar equiv) in THF at –78 °C, *N*-benzylideneaniline (2.0 molar equiv), and aqueous solution of NH$_4$Cl gave a mixture of two diastereomers of the β-aminoalkyl selenide, **3a** and **3b** (98% from **2**, **3a**: **3b** = 88: 12) (Scheme 1). Recrystallization from carbon tetrachloride and benzene enabled the isolation of the major diastereomer **3a**. Only **3a** was used for the further reaction because the other diastereomer **3b** was separated from **3a** neither by silica gel chromatography nor by recrystallization. Desilylation of **3a** (405 mg, 0.570 mmol) with (n-Bu)$_4$NF in THF at 0 ˚C gave β-aminoalkyl selenide **4a** (312 mg, 92%). Treatment of **4a** (100 mg, 0.168 mmol) with *m*CPBA (4.0 molar equiv) at 0 °C gave tetracoordinate 1,2λ^4,5-oxaselenazolidine **1** (79.5 mg, 78%) as colorless solids, while use of 1.0 molar equiv of *m*CPBA afforded **1** in 28% yield with the recovery of **4a** (29%). 1,2,5-Oxaselenazolidine **1** is stable in the air at the ambient temperature, although it decomposed at 60 °C in benzene solution.



Scheme 1. a) LDA, THF, –78 °C; b) PhCH=NPh, THF, –78 °C; c) aq NH$_4$Cl; d) (n-Bu)$_4$NF, THF, 0 °C; e) *m*CPBA, CHCl$_3$, 0 °C.

In the ^{1}H NMR spectrum of **1**, the ortho proton of the Martin ligand[7] resonated at low field (δ 8.36–8.39),[8] which is a typical feature of compounds with a trigonal-bipyramidal (TBP) and a pseudo TBP structure bearing polar apical bonds.[9] No NOE was observed for two protons located at α- and β-positions of the selenium, respectively, in differential NOE experiment, indicating that they are *trans* to each other. In the ^{77}Se NMR spectrum, **1** showed a broad singlet at δ 819.9 in CDCl$_3$, which is consistent with that of a tetracoordinate selenurane.[10,11]

The molecular structure of **1** was definitively elucidated by X-ray crystallographic analysis (Figure 1).[12] This is the first example of synthesis and structural analysis of a 1,2,5-oxaselenazolidine compound. The selenium atom has a slightly distorted pseudo TBP structure with two oxygen atoms at two apical positions, respectively. Its oxaselenazolidine ring exists in almost envelope form, where the nitrogen atom is located at the tip above the least-square plane defined by the other four atoms, i.e., C1, C2, Se1 and O1. In contrast to the planar rings of previously reported pentalene type compounds,[2] the oxaselenazolidine ring is folded to relieve not only the steric repulsion among the four aryl groups, which situated in all *trans* configuration with one another, but also the electrostatic repulsion of the lone pairs on N1 and O1. The bond angle between two apical bonds deviates by 10.4(3)° from 180° presumably due to its ring strain. The configuration of the N1 atom is pyramidalized judging from the bond angles around the N1 atom (105.2(7)°–112.3(7)°). The O1–N1–C angles and Se1–O1–N1 angle (107.7(5)°) are usual values. The C1–C2, C2–N1 and N1–O1 bond lengths, which are contained in the 1,2,5-oxaselenazolidine ring, are in good agreement with the sum of the corresponding covalent bond radii, respectively, taking into consideration of the standard deviations. Each of these bond lengths as well as Se–C bond lengths are longer than those of the pentalene type compounds, which show the delocalization of double-bonds.[2] On the other hand, the elongation of the Se–O bonds [1.904(7) Å] relative to the sum of the respective covalent bond radii [1.83 Å][13] is consistent with those in the tetracoordinate selenium compounds.[4,5,10] Moreover, the difference between two Se–O bond lengths indicates that the present alkoxy group is more electron-withdrawing than the aminoxy group, because the apical bond length elongates with a decrease in electronegativity of another apical substituent.[14] These results show that the N–O bond of the Se–O–N unit in **1** is a usual covalent bond, while the O–Se bond is a hypervalent bond.

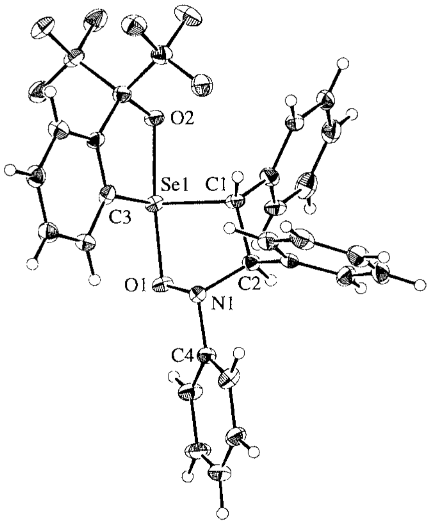
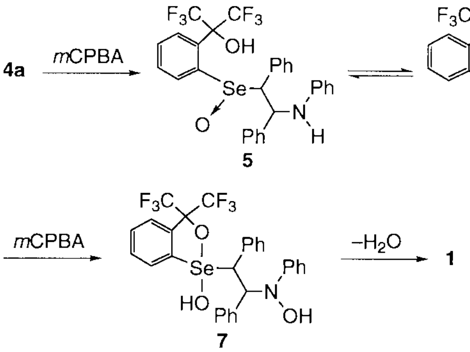


Figure 1. ORTEP drawing of **1** with thermal ellipsoid plot (30% probability). Selected bond lengths [Å] and angles [deg] for **1**: Se1–O1, 1.904(7); Se1–O2, 1.997(6); Se1–C1, 2.003(9); Se1–C3, 1.956(9); C1–C2, 1.55(1); C2–N1, 1.49(1); N1–O1, 1.43(1); O1–Se1–C1, 84.3(3); Se1–C1–C2, 107.3(6); C1–C2–N1, 107.9(7); C2–N1–O1, 105.2(7); N1–O1–Se1, 107.7(5); O1–Se1–O2, 169.6(3); C1–Se1–C3, 105.9(4); C1–Se1–O2, 87.6(3); C1–Se1–C3, 105.9(4); O1–Se1–C3, 94.2(4); O2–Se1–C3, 81.8(4); C4–N1–O1, 107.3(8); C2–N1–C4, 112.3(7).

The reactivity of β-aminoalkyl selenide **4a** giving **1** contrasts sharply with that of a (hexafluoroisopropylidene)aniline derivative giving tetracoordinate $1\lambda^4$,2-selenazetidines.[5] The recovery of **4a** in the reaction with 1 molar equiv of *m*CPBA indicates that the oxidation of the nitrogen of intermediate **5** and/or **6** proceeds faster than the cyclization–dehydration of **5** or the dehydration of **6**. The phenyl group which is much less electron-withdrawing than trifluoromethyl group would less deactivate the lone pair of the nitrogen atom of them in the reaction above. The successive dehydration of **7** finally affords **1** (Scheme 2).



Scheme 2.

In conclusion, we have synthesized $1,2\lambda^4$,5-oxaselenazolidine **1** and elucidated its crystal structure. This is the first example of the crystallographically characterized saturated heterocyclic compound with an Se–O–N linkage as a ring component. Further study on the reactivity of **1** is under current investigation.

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8 Compound **1** gave satisfactory spectroscopic and analytical data. Selected spectroscopic data for **1**: colorless crystals, mp 133.5 °C (dec.); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.49 (d, $^3J_{HH}$ = 9.6 Hz, 1H), 5.07 (d, $^3J_{HH}$ = 9.6 Hz, 1H), 6.84 (d, $^3J_{HH}$ = 7.1 Hz, 2H), 7.04–7.25 (m, 8H), 7.34–7.40 (m, 5H), 7.70–7.75 (m, 2H), 7.83 (br s, 1H), 8.37–8.41 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) δ 80.08 (s), 84.56 (sept, $^2J_{CF}$ = 29.6 Hz, *C*(CF_3)$_2$), 84.78 (s, $^1J_{CSe}$ = 31.6 Hz, Se*C*HPh), 121.76 (s), 123.06 (q, $^1J_{CF}$ = 289.3 Hz, *C*F_3), 123.28 (q, $^1J_{CF}$ = 289.3 Hz, *C*F_3), 125.69 (s), 126.53 (s), 127.54 (s), 128.28 (s), 128.36 (s), 128.65 (s), 128.80 (s), 129.00 (s), 129.13 (s), 129.78 (s), 130.56 (s), 130.89 (s), 132.13 (s), 133.86 (s), 134.41 (s), 134.78 (s), 135.50 (s).

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12 Crystallographic data for **1**: $C_{29}H_{21}F_6NO_2Se$, monoclinic, space group $P2_1$, a = 7.8530(3), b = 11.7020(5), c = 14.2730(5) Å, β = 100.405(3)°, V = 1290.06(8) Å^3, Z = 2, D_{calcd} = 1.566 g cm^{-3}, T = 300 K, μ = 15.27 cm^{-1}, R = 0.086, wR_2 = 0.229, GOF = 1.21.

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