

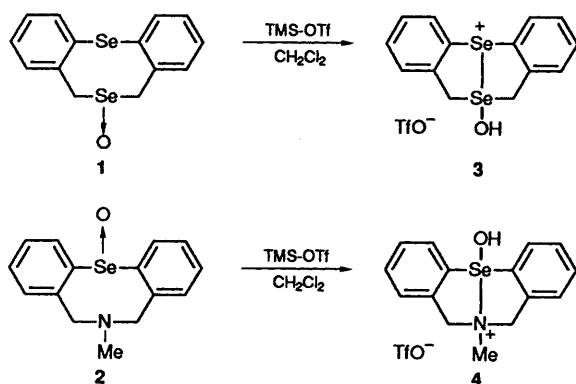
Formation of New Hydroxyselenonio and Hydroxyammonio-selenuranes from Reaction of Se-Oxides of 5*H*,7*H*-Dibenzo[*b,g*][1,5]diselenocine and *N*-Methyl-5*H*,7*H*-dibenzo[*b,g*][1,5]selenazocine with Silyl Triflates

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The transannular reaction of 5*H*,7*H*-dibenzo[*b,g*][1,5]diselenocine Se-oxide **1** or *N*-methyl-5*H*,7*H*-dibenzo[*b,g*][1,5]selenazocine Se-oxide **2** with 1 equiv. of silyl triflates, CF₃SO₃SiMe₃ and CF₃SO₃SiMe₂Bu^t, produced a new hypervalent selenurane which consists of two unsymmetrical apical ligands such as the hydroxy group and the selenonio or ammonio group.

Transannular interaction and bond formation in medium-sized cyclic compounds containing main group elements have been extensively studied.¹ However, the property and reactivity of medium-sized selenium heterocycles have received less attention. Most recently, we reported that *N*-methyl-5*H*,7*H*-dibenzo[*b,g*][1,5]selenazocine reacts with Bu^tOCl to give the first hypervalent chloro(ammonio)selenurane.² We have now found that the reaction of 5*H*,7*H*-dibenzo[*b,g*][1,5]diselenocine Se-oxide **1** or *N*-methyl-5*H*,7*H*-dibenzo[*b,g*][1,5]selenazocine Se-oxide **2** with 1 equiv. of trimethylsilyl trifluoromethanesulfonate (CF₃SO₃SiMe₃) gave the corresponding hydroxyselenurane **3** or **4** containing a transannular Se–Se or Se–N bond. This is a new isolable hydroxyselenurane with a selenonio or ammonio ligand at the apical position. Although a number of hypervalent organosulfur compounds, sulfuranes, have been reported,³ much less is known about the chemistry of selenuranes.⁴

Treatment of the selenoxide **1**⁵ or **2**² with 1 equiv. of trimethylsilyl triflate (TMS-OTf) or *tert*-butyldimethylsilyl triflate (TBS-OTf) resulted in the formation of the hydroxyselenonio or hydroxyammonio selenurane, **3** or **4** (Scheme 1). In



Scheme 1 Reaction conditions not anhydrous

these cases, none of the *O*-silylated compounds of **1** and **2** were obtained after work-up. It is thought likely that these reactions proceed through the initial formation of the *O*-silylated selenonium cations which are stabilized by transannular interaction of the selenium or the nitrogen atom to generate the *O*-silylated selenuranes. Since the experimental procedures were not being carried out under anhydrous conditions, the hydroxy derivatives could be formed as a result of the instability (especially to water) of the group of Se–O–SiR₃.

The structures of compounds **3** and **4** were established on the basis of multinuclear NMR (¹H, ¹³C, ⁷⁷Se and ¹⁹F) and IR spectroscopy and elemental analysis. With regard to the conformational properties of heterocyclic analogues of dibenzo-

cyclooctane, for eight-membered rings typically two different conformers, the boat-chair (*BC*) and the twist-boat (*TB*) and/or the boat-boat (*BB*) forms can exist.^{1,6} The conformers can be assigned from the ¹H NMR spectral data for the benzylic protons of the eight-membered ring.⁶ The ¹H NMR spectrum of **3** in CD₃CN shows signals at δ 4.58, 5.10 (ABq, *J* 15 Hz, 4 H, CH₂), 7.42 (t, *J* 7.5 Hz, 2 H, ArH), 7.50 (t, *J* 7.5 Hz, 2 H, ArH), 7.57 (d, *J* 7.5 Hz, 2 H, ArH) and 7.79 (d, *J* 7.5 Hz, 2 H, ArH); while the ¹³C NMR (CD₃CN) spectrum has signals at δ 56.6, 129.4, 131.7, 136.0, 136.2 and 140.1. The ⁷⁷Se NMR spectrum of **3** in CH₃CN shows two resonances at δ 361.3 (SeAr: relative to Me₂Se) and at δ 858.8 (SeCH₂Ar; the benzylic selenide signal was determined by the off-resonance method). The former resonance is assigned to the selenonium cation and the latter to the selenurane structure.⁷ This spectroscopic evidence indicates that **3** is a single conformer, *i.e.*, *TB* or *BB* form in solution, though the selenoxide **1** shows the existence of two conformers.⁵ The ¹⁹F NMR spectrum of the CF₃SO₃[−] anion of **3** in CH₃CN shows a single fluorine signal at δ 85.1 (relative to C₆F₆). The IR spectrum of KBr pellets of **3** exhibits absorption at 667 cm^{−1} assigned to the Se–OH stretch.

The NMR spectra of **4** are as follows: δ_H(CDCl₃) 2.74 (s, 3 H, Me), 4.14 (s, 4 H, CH₂), 7.26–7.31 (m, 2 H, ArH), 7.47–7.53 (m, 4 H, ArH) and 8.19–8.22 (m, 2 H, ArH); δ_C(CDCl₃) 41.7, 58.5, 127.2, 127.7, 130.3, 131.9, 133.1 and 137.8; δ_{Se}(CHCl₃) 769.6 (relative to Me₂Se); δ_F(CHCl₃) 84.3 (relative to C₆F₆). The spectral data of **4** are very similar to those of the previous reported ammonioselenuranes.²

The selenuranes, **3** and **4**, are new types of tetracoordinate selenium compounds having two unsymmetrical apical ligands, since generally selenuranes bear two symmetrical electro-negative groups such as halogen or oxygen atoms at the apical positions.⁴

Experimental

Typical Procedure.—A solution of CF₃SO₃SiMe₃ (74 mg, 0.33 mmol) in dichloromethane (5 cm³) was added to a stirred solution of compound **2** (100 mg, 0.33 mmol) in dichloromethane (25 cm³) under an Ar atmosphere at −78 °C, and after 1 h the solution was allowed to reach −20 °C and stirred for an additional 8 h. Upon filtration and recrystallization from dichloromethane–diethyl ether, the selenurane **4** was obtained as a crystalline salt (53%), m.p. 179 °C (decomp.); ν_{max}(KBr)/cm^{−1} 663 (Found: C, 42.0; H, 3.5; N, 3.0. C₁₆H₁₆F₃NO₄SSe requires C, 42.30; H, 3.55; N, 3.08). Those procedures were not performed under anhydrous conditions.

Compound **3** was prepared by the same method as **4**: m.p. 240 °C (decomp.) (Found: C, 35.7; H, 2.5. C₁₅H₁₃F₃O₄SSe₂ requires C, 35.73; H, 2.60).

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