

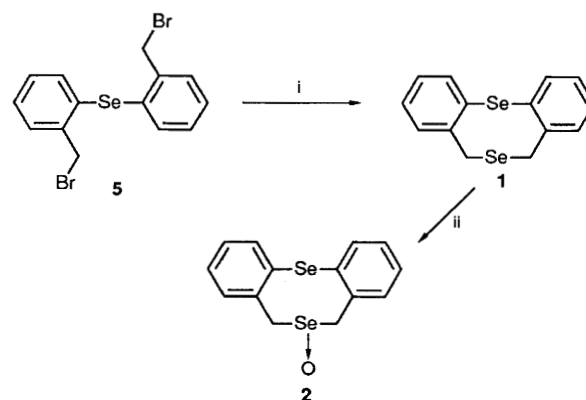
A New Preparative Method and Reactivity of Diselenide Dication Salt from 5*H*,7*H*-Dibenzo[*b,g*][1,5]diselenocine

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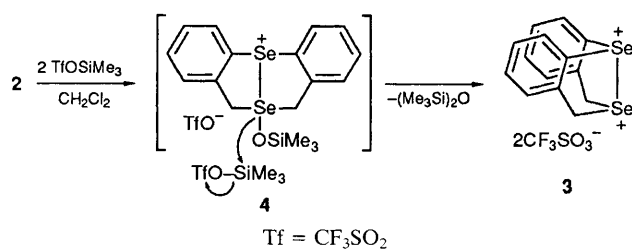
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A new medium-sized heterocycle, 5*H*,7*H*-dibenzo[*b,g*][1,5]diselenocine **1**, has been synthesized; the reaction of the selenoxide of **1** with two equivalents of CF₃SO₃SiMe₃ gave the stable diselenide dication salt, this is a new method for the preparation of the diselenide dication.

Transannular bond formation (*e.g.* dication) between heteroatoms in medium-sized heterocyclic compounds containing nitrogen and/or sulphur atoms has been extensively studied.¹⁻³ However, the properties of medium-sized selenium heterocycles have received less attention. Recently, we reported the first crystal structure and reactivity of a tetraalkyl substituted diselenide dication salt, 1,5-diselenoniabicyclo[3.3.0]octane bis(tetrafluoroborate), obtained by a two-electron oxidation of 1,5-diselenacyclooctane (1,5-DSeCO) with NOBF₄.⁴ We have now found that the reaction of the selenoxide **2** of 5*H*,7*H*-dibenzo[*b,g*][1,5]diselenocine **1** with 2 equiv. of CF₃SO₃SiMe₃ afforded the corresponding diselenide dication salt **3** containing aromatic rings. This paper reports the conformational properties of **1** and **2**, and a new preparative method of the diselenide dication **3**, together with its reactivity.



Scheme 1 Reagents: i, Na₂Se in EtOH; ii, *m*-CPBA in CHCl₃



Scheme 2

Compound **1** was synthesized as follows (Scheme 1). Bis(2-bromomethylphenyl)selenide **5**[†] (500 mg, 1.2 mmol) was treated with Na₂Se (150 mg, 1.2 mmol) in ethanol (400 cm³) using a high dilution technique at room temperature under an Ar atmosphere. The whole mixture was stirred at room temperature for 10 h. After usual work-up, the residue was recrystallized from benzene to give **1** in 71% yield.^{†‡} The oxidation of **1** with *m*-chloroperbenzoic acid (*m*-CPBA) gave exclusively **5H,7H**-dibenzo[*b,g*][1,5]diselenocine 6-oxide **2** in 80% yield.^{†‡}

With regard to the conformational properties of **1**, for eight-membered rings typically two different conformers, the chair and boat-forms can exist.^{6‡§} The ¹H NMR (500 MHz) spectrum of **1** in CDCl₃ at 25 °C shows the benzylic methylene protons as a broad singlet at δ 3.70 and an AB type absorption at δ 3.91 and 5.20 (*J* 13 Hz); the former resonance is assigned to the boat form (28%), and the latter pair to the chair form (72%). These conformers can also be characterized by ⁷⁷Se NMR spectroscopy;¶ the ⁷⁷Se NMR spectrum of **1** in CHCl₃ at 25 °C shows four peaks at δ 352.5 (chair) and 381.9 (boat) for –SeAr, and δ 380.4 (chair) and 398.7 (boat) for –SeCH₂Ar, respectively, the ratio of the conformers being consistent with that obtained from the ¹H NMR spectrum. The methylene protons in the ¹H NMR (500 MHz) spectrum of selenoxide **2** in CDCl₃ at 25 °C showing one AB system at δ 3.79 and 4.14 (*J* 11.5 Hz), and another AB system at δ 4.18 and 5.81 (*J* 11.5 Hz), are assigned to the boat-form (64%) for the former and the chair-form (36%) for the latter. An analogous result was found from the ⁷⁷Se NMR (CHCl₃) spectrum of **2** which shows four peaks at δ 368.2 (chair) and 387.6 (boat) for –SeAr, and δ 915.8 (boat) and 940.5 (chair) for –Se(O)CH₂Ar.¶¶

The stable diselenide dication salt **3** was prepared by the reaction of selenoxide **2** with 2 equiv. of silylating reagent, trimethylsilyl trifluoromethanesulphonate (CF₃SO₃SiMe₃) as follows. A solution of CF₃SO₃SiMe₃ (125 mg, 0.56 mmol) in anhydrous CH₂Cl₂ (5 cm³) was added to a stirred solution of **2** (100 mg, 0.28 mmol) in anhydrous CH₂Cl₂ (30 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 12 h, and

[†] Compound **1**: m.p. 140 °C; MS, *m/z* 340 (M⁺); ¹H NMR (500 MHz, CDCl₃) δ 3.70 (br s, CH₂), 3.91, 5.20 (ABq, *J* 13 Hz, CH₂) and 7.02–7.93 (m, ArH).

Compound **2**: m.p. 119–120 °C; MS, *m/z* 356 (M⁺); FTIR (KBr) 829 cm^{–1} (Se=O); ¹H NMR (500 MHz, CDCl₃) δ 3.79, 4.14 (ABq, *J* 11.5 Hz, CH₂), 4.18, 5.81 (ABq, *J* 11.5 Hz, CH₂) and 7.13–7.98 (m, ArH).

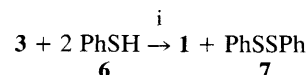
Satisfactory elemental analyses were obtained for compounds **1** and **2**.

[‡] The protons and carbons of the aromatic rings in the NMR spectra (500 MHz, ¹H and 125 MHz, ¹³C) of **1** and **2**, except for dication **3**, show two sets of signals due to the existence of two conformers; the detailed analysis will be reported in elsewhere.

[§] In each ¹³C NMR (CDCl₃) spectrum of **1** and **2**, two signals of the benzylic carbon atoms due to the two conformers appear at δ 25.5 and 32.1 for **1**, and δ 52.2 and 60.6 for **2**, respectively.

¶ The chemical shifts are relative to Me₂Se. The conformers were assigned by the integration of the selenium peaks. The peak of benzylic selenide of **1** was determined by off-resonance method.

¶¶ ⁷⁷Se chemical shifts for Ph₂Se(O) and (PhCH₂)₂Se(O) in CHCl₃ (relative to Me₂Se) are: δ 860.1 and 928.0, respectively.



Scheme 3 Conditions: i, MeCN, Ar, room temp., 30 min

a white precipitate was formed. Filtration under anhydrous conditions and recrystallization from anhydrous acetonitrile-diethyl ether gave a crystalline salt **3** in 97% yield, m.p. 140 °C (decomp.).** None of the silylated compound was obtained. This reaction may proceed via the initial formation of the *O*-silylated selenurane intermediate **4** which subsequently would be converted into the dication **3** (Scheme 2). This is a new method for the preparation of the diselenide dication, although the preparative methods of heteroatom dications from medium-sized heterocyclic compounds are little known.^{1–3}

The dication salt **3** was identified by NMR spectroscopy and elemental analysis. The ¹H and ¹³C NMR spectra of **3** in CD₃CN are: ¹H δ 5.57, 5.76 (ABq, *J* 14 Hz, 4 H, CH₂), 7.54–7.72 (m, 6 H, ArH) and 7.99–8.11 (m, 2 H, ArH); ¹³C δ 54.4, 129.2, 130.2, 131.1, 132.5, 133.0 and 139.7; while the ⁷⁷Se NMR spectrum of **3** in MeCN shows only two peaks at δ 761.4 and 789.9.^{††} These spectral data indicate that the dication **3** exists as a single conformer, the boat-form. The ¹⁹F NMR spectrum of the CF₃SO₃[–] anion of **3** in MeCN shows a single peak at δ 85.2 (relative to C₆F₆), in the region of ionic CF₃SO₃[–]. These results are consistent with a dicationic structure for **3**.

Hydrolysis of the salt **3** gave the selenoxide **2** in 85% yield. In contrast, a tetraalkyl substituted diselenide dication salt (1,5-DSeCO²⁺, *vide supra*) was stable in H₂O.^{4a} The difference in reactivity between **3** and 1,5-DSeCO²⁺ was also observed, *i.e.* the dication **3** led to the selenide **1** (70%) on treatment with *N,N*-dimethylaniline (DMA, 2 equiv.), contrasting with the reaction of 1,5-DSeCO²⁺ with DMA which gave the *para*-substituted product, selenonium salt.^{4c} Thus, the dication **3** can be reduced by DMA, since the oxidation potential of DMA is lower than that of the dication precursor.

The redox reaction was found to proceed in the treatment of benzenethiol **6** (2 equiv.) with dication **3** (1 equiv.) in MeCN under argon which afforded diphenyl disulphide **7** as the oxidation product (86%) and selenide **1** as the reduction product (78%) (Scheme 3). This new dication **3** reacts as an oxidizing agent.

This work was supported by the Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency No. 02247101 from the Ministry of Education, Science and Culture, Japan. We thank Dr T. Erata of this University for helpful advice for NMR measurements.

Received, 8th May 1991; Com. 1/02182F

References

- 1 R. W. Alder, A. G. Orpen and J. M. White, *J. Chem. Soc., Chem. Commun.*, 1985, 949; R. W. Alder, *Tetrahedron*, 1990, **46**, 683.
- 2 W. K. Musker, *Acc. Chem. Res.*, 1980, **13**, 200.
- 3 H. Fujihara and N. Furukawa, *J. Mol. Struct. (Theochem.)*, 1989, **186**, 261 and references cited therein.
- 4 (a) H. Fujihara, R. Akaishi, T. Erata and N. Furukawa, *J. Chem. Soc., Chem. Commun.*, 1989, 1789; (b) F. Iwasaki, M. Morimoto, M. Yasui, R. Akaishi, H. Fujihara and N. Furukawa, *Acta Crystallogr.*, in the press. (c) H. Fujihara, A. Nakamura, R. Akaishi and N. Furukawa, *Chem. Lett.*, 1990, 393.
- 5 H. Fujihara, H. Mima, J.-J. Chiu and N. Furukawa, *Tetrahedron Lett.*, 1990, **31**, 2307.
- 6 R. P. Gellatly, W. D. Ollis and I. O. Sutherland, *J. Chem. Soc., Perkin Trans. 1*, 1976, 913; L. E. Brieady, B. S. Hurlbert and N. B. Mehta, *J. Org. Chem.*, 1981, **46**, 1630.

** Satisfactory C and H analyses were obtained for dication salt **3**.

†† The ⁷⁷Se chemical shift of 1,5-DSeCO dication salt is δ 806.5.^{4a}