Formation, Characterization and Reactivity of a Selenaza Dication [R$_2$Se$^+$–N$^+$R$_3$] from *N*-Methyl-5*H*,7*H*-Dibenzo[*b*,*g*][1,5]selenazocine

Hisashi Fujihara,*[a] **Hisatomo Mima,**[a] **Tomoki Erata**[b] **and Naomichi Furukawa***[a]

[a] *Department of Chemistry, and* [b] *Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305, Japan*

A new heterocycle containing selenium and nitrogen atoms, *N*-methyl-5*H*,7*H*-dibenzo[*b*,*g*][1,5]selenazocine **1**, has been synthesized; the reaction of the selenoxide of **1** with $(CF_3SO_2)_2O$ gave a novel selenaza dication salt which was characterized by ^{77}Se NMR spectroscopy, and the dication acts as an oxidizing agent.

Currently, there is considerable interest in the transannular interaction or bond formation (*e.g.*, dication formation) between heteroatoms in medium-sized heterocyclic compounds containing nitrogen and/or sulphur atoms.[1–3] We have recently reported the first isolation and reactivity of the diselenide dication salt, 1,5-diselenoniabicyclo[3.3.0]octane bis(hexafluorophosphate).[4] However, dications consisting of two different positively charged heteroatoms are quite rare.[5] We now report the synthesis of a new eight-membered ring selenium heterocycle, *N*-methyl-5*H*,7*H*-dibenzo[*b*,*g*][1,5]selenazocine **1**, the first example of a dication containing a transannular Se–N bond in **1**, and the reactivity of its dication salt.

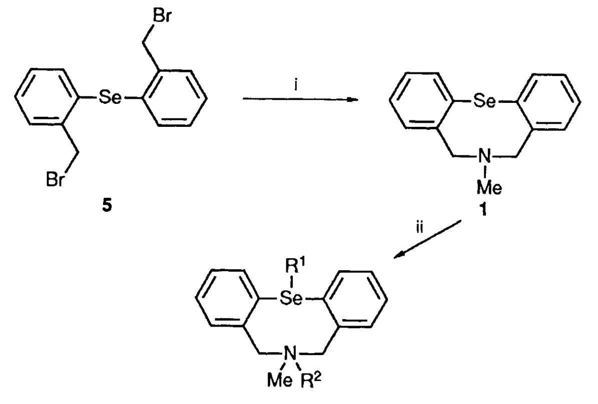
The new compound **1** was synthesized as follows (Scheme 1). Bis(2-bromomethylphenyl)selenide **5**[6] (4 g, 9.55 mmol) was treated with methylamine (143 mmol) in chloroform (400 ml) using a high dilution technique at room temperature under an Ar atmosphere. The whole mixture was stirred at room temperature for 2 h. After the usual work-up, the crude products were purified by silica gel column chromatography (eluent, $CHCl_3$–EtOH) to give **1** in 72% yield.[†] The oxidation

---

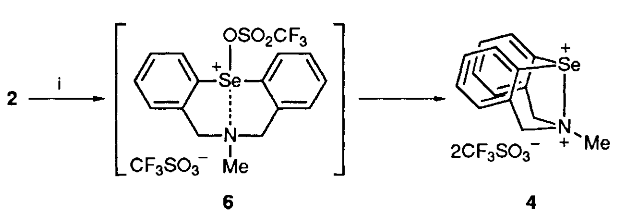
[†] Compound **1**: m.p. 46–48 °C; MS, *m/z* 289 (M$^+$); ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 3H, CH_3), 4.04 (br s, 4H, CH_2), 7.04–7.26 (m, 6H, ArH) and 7.53–7.70 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 40.5, 58.6, 127.6, 128.0, 132.6, 135.2 and 139.0.

Compound **2**: m.p. 165–167 °C; FT-IR (KBr) ν_{max} 810 cm^{-1} (Se=O); MS, *m/z* 305 (M$^+$); ^{1}H NMR ($CDCl_3$) δ 2.62 (s, 3H, CH_3), 3.94 (br s, 4H, CH_2), 7.09–7.56 (m, 6H, ArH) and 8.24–8.33 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 41.7, 58.8, 126.0, 126.6, 129.2, 130.0, 138.5 and 140.1.

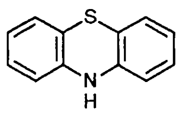
Satisfactory elemental analyses were obtained for **1**, **2** and **4**.



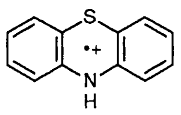
Scheme 1 *Reagents*: i, $MeNH_2$ in $CHCl_3$; ii, MCPBA in $CHCl_3$



Scheme 2 *Reagents*: i, $(CF_3SO_2)_2O$, CH_2Cl_2, −20 °C



7

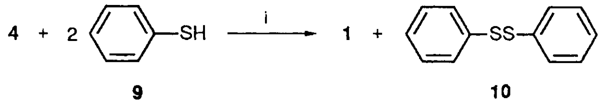


8

of **1** with *m*-chloroperbenzoic acid (MCPBA) afforded the selenoxide **2**, together with the *N*-oxide **3**.†

With regard to the conformational properties of **1**, for eight-membered rings typically two different conformers, the chair and boat forms can exist.[7,8] The ^1H NMR spectrum of **1** in $CDCl_3$ at 25 °C shows the benzylic methylene protons as a broad singlet at δ 4.04. At −50 °C, this resonance is split into two, at δ 3.75 (br s) and at δ 4.09 and 5.08 (ABq, *J* 14 Hz); the former resonance is assigned to the boat form (74%), and the latter pair to the chair form (26%). Interestingly, these conformers can be characterized by ^{77}Se NMR spectroscopy: the ^{77}Se NMR spectrum of **1** in $CHCl_3$ at 25 °C shows a very broad peak at δ 379, which becomes two singlet peaks at δ 383 and 356 at −50 °C, the ratio of the conformers being consistent with that obtained from the ^1H NMR spectrum.‡ In contrast, the selenoxide **2** exists as a single conformer, the boat form, as shown by variable temperature ^1H and ^{77}Se NMR spectroscopy.[8]

Addition of a solution of trifluoromethanesulphonic anhydride (1.58 mmol) in anhydrous dichloromethane (20 ml) to a stirred solution of **2** (1.58 mmol) in anhydrous dichloromethane (100 ml) under an Ar atmosphere at −20 °C resulted in a colourless crystalline precipitate. Upon filtration under anhydrous conditions and recrystallization from anhydrous acetonitrile–dichloromethane, the dication **4** was obtained as a stable crystalline salt, m.p. 198 °C (decomp.).† This reaction may proceed *via* the initial formation of the trifluoromethylsulphonyloxy selenonium salt **6** which subsequently would be converted into the dication **4** by nucleophilic displacement of the $CF_3SO_3^-$ ion by the remote nitrogen atom, *i.e.*, by a transannular reaction (Scheme 2).



Scheme 3 *Reagents*: i, MeCN, Ar, 0 °C, 4 h

The dication **4** was characterized by spectroscopic and chemical means. The ^1H NMR spectrum of **4** in CD_3CN exhibits absorptions at δ 3.31 (br s, 3H), 4.82 (br s, 4H) and 7.46–8.54 (m, 8H).[8] The ^{77}Se NMR spectrum of **2** in $CHCl_3$ shows a singlet peak at δ 847 (relative to Me_2Se),‡ while the dication **4** in MeCN shows a singlet peak at δ 1005. These are marked downfield shifts, consistent with a dicationic structure for **4**. The ^{19}F NMR spectrum of the $CF_3SO_2^-$ anion of **4** in MeCN shows a single absorption at δ 85.4 (relative to C_6F_6), in the region of ionic $CF_3SO_3^-$. Treatment of an acetonitrile solution of **4** with aqueous sodium hydrogencarbonate gave the selenoxide **2** in quantitative yield, and none of the *N*-oxide **3** was obtained, contrasting with the oxidation of **1** using MCPBA which afforded a mixture of **2** and **3**.

When a solution of phenothiazine **7** (2 equiv.) in anhydrous MeCN was added to a solution of the dication **4** (1 equiv.) in anhydrous MeCN under an Ar atmosphere at room temperature, the solution became orange. Its UV–VIS spectrum showed absorptions at λ_{max} 438 and 515 nm (lit.,[10] 437 and 515 nm) for the cation radical of **7**. This phenomenon indicates that **7** was oxidized to its cation radical **8** by the dication **4**, since the oxidation potential of **7** is lower than that of the dication precursor.

The redox reaction was found to proceed in the treatment of benzenethiol **9** (2 equiv.) with the dication **4** (1 equiv.) in MeCN under argon which gave diphenyl disulphide **10** as the oxidation product in 98% yield and selenazocine **1** as the reduction product in 82% yield (Scheme 3). Thus, the new dication **4** acts 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.

Received, 21st August 1990; Com. 0/03827J

References

1 R. W. Alder, *Acc. Chem. Res.*, 1983, **16**, 321; R. W. Alder, R. B. Sessions, J. O. Gmünder and C. A. Grob, *J. Chem. Soc., Perkin Trans. 2*, 1984, 411; R. W. Alder, A. G. Orpen and J. M. White, *J. Chem. Soc., Chem. Commun.*, 1985, 949.
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 H. Fujihara, R. Akaishi, T. Erata and N. Furukawa, *J. Chem. Soc., Chem. Commun.*, 1989, 1789.
5 W. K. Musker, A. S. Hirschon and J. T. Doi, *J. Am. Chem. Soc.*, 1978, **100**, 7754.
6 H. Fujihara, H. Mima, J.-J. Chiu and N. Furukawa, *Tetrahedron Lett.*, 1990, **31**, 2307.
7 R. P. Gellatly, W. D. Ollis and I. O. Sutherland, *J. Chem. Soc., Perkin Trans. 1*, 1976, 913; L. E. Brieaddy, B. S. Hurlbert and N. B. Mehta, *J. Org. Chem.*, 1981, **46**, 1630.
8 The detailed analysis will be reported elsewhere.
9 N. P. Luthra and J. D. Odom in *The Chemistry of Organic Selenium and Tellurium Compounds*, vol. 1, eds. S. Patai and Z. Rappoport, Wiley, New York, 1986, ch. 6.
10 C. Bodea and I. Silberg, *Adv. Heterocycl. Chem.*, 1968, **9**, 321.

---

‡ ^{77}Se chemical shifts for Ph_2Se and $Ph_2Se{=}O$ in $CHCl_3$ (relative to Me_2Se) are: δ 402 and 863, respectively.[9]