CHEMISTRY LETTERS, pp. 1649 - 1650, 1991.

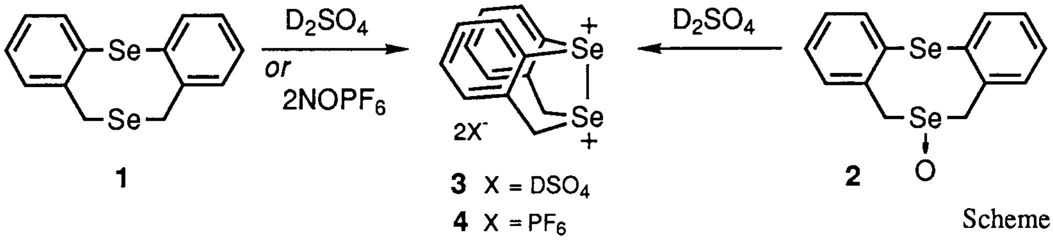
Transannular Se-Se Interaction in Electrochemical Oxidation of *5H,7H*-Dibenzo[*b*,*g*][1,5]diselenocin and Formation of Its Diselena Dication in Concentrated Sulfuric Acid

Hisashi FUJIHARA,* Yoko UENO, Jer-Jye CHIU, and Naomichi FURUKAWA*
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

5H,7H-Dibenzo[*b*,*g*][1,5]diselenocin (**1**) undergoes the reversible electrochemical oxidation with low oxidation potential which is attributed to the transannular Se-Se interaction. The formation of diselena dication of **1** was observed in the reaction of **1** and its *Se*-oxide with concd H_2SO_4 by ^1H, ^{13}C, and ^{77}Se NMR spectroscopy.

Transannular interaction and bond formation (*e.g.*, dication formation) between sulfur atoms in medium-sized cyclic bis-sulfides and related compounds have been extensively studied.[1,2] However, such interactions in medium-sized selenium heterocycles have received less attention. Very recently, we have reported that the reaction of the *Se*-oxide of a new selenium heterocycle, *5H,7H*-dibenzo[*b*,*g*][1,5]diselenocin (**1**), with 2 equiv of trimethylsilyl trifluoromethanesulfonate gave the diselena dication salt containing aromatic ring.[3] We have now studied the formation of the diselena dication from the reaction of **1** and its *Se*-oxide (**2**) with concd H_2SO_4, because the chemical behavior of cyclic bis-selenides in concd H_2SO_4 are not well known.[4] This paper reports the reversible electrochemical oxidation of **1** and the formation of its dication.

In order to confirm the existence of Se-Se interaction in **1**, the electrochemical oxidation of **1** was studied by cyclic voltammetry. Interestingly, when the cyclic voltammogram (CV) of **1** was measured in CH_3CN containing 0.1 M $NaClO_4$ as supporting electrolyte with a glassy carbon working electrode and Ag/0.01 M $AgNO_3$ in CH_3CN as a reference electrode (scan rate; 20 mV/s), one reversible oxidation peak appeared at +0.56 V. The CV of diphenyl selenide (**5**) and dibenzyl selenide (**6**) showed the irreversible oxidation wave at +0.98 V and +1.05 V, respectively. Thus the facile oxidation of **1** and the unusual stability of the cationic species of **1** can be rationally explained in terms of the destabilization of **1** by transannular lone-pair-lone-pair repulsion and the stabilization of the oxidized species by neighboring-group participation, *i.e.*, bond formation between the two selenium atoms. In contrast, its analogous compounds containing sulfur atom, *5H,7H*-dibenzo[*b*,*g*][1,5]-dithiocin (**7**), -thiaselenocin, and -selenathiocin, exhibited irreversible redox behavior. Normally the electrochemical oxidations of the selenides having alkyl and/or aryl groups are irreversible.



Scheme 1.

In conformational properties of **1** and **2** concerning eight-membered rings, two typical different conformers such as chair and boat-forms can exist.5) The conformers can be assigned by the ^{1}H NMR spectral data for benzylic methylene protons of the eight-membered ring.5,6) The ^{1}H NMR (500 MHz) spectra of **1** and **2** in $CDCl_3$ at 25 °C show the existence of two conformers in the ratio of 28 (boat) : 72 (chair) for **1** and of 64 (boat) : 36 (chair) for **2**, [**1**: ^{1}H δ 3.70 (br s, CH_2), 3.91, 5.20 (ABq, *J*=13 Hz, CH_2), 7.02-7.93 (m, ArH);6) **2**: ^{1}H δ 3.79, 4.14 (ABq, *J*=11.5 Hz, CH_2), 4.18, 5.81 (ABq, *J*=11.5 Hz, CH_2), 7.13-7.98 (m, ArH)6,7)]. These conformers can also be characterized by ^{77}Se NMR spectroscopy;8) **1** ($CHCl_3$ at 25 °C): δ 352.5 (chair) and 381.9 (boat) for -SeAr, and δ 380.4 (chair) and 398.7 (boat) for -$SeCH_2Ar$; **2**: δ 368.2 (chair) and 387.6 (boat) for -SeAr, and δ 915.8 (boat) and 940.5 (chair) for -Se(O)CH_2Ar.

Dissolution of the selenide **1** in concd D_2SO_4 led to the formation of the diselena dication **3** as evidenced by the ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy; the benzyl proton signals for **1** in $CDCl_3$ disappeared and new AB quartet peaks appeared at δ 5.15 and 5.36 (*J*=15 Hz) in concd D_2SO_4, and the signal of the methylene carbon atoms was shifted to downfield from δ 25.5 and 32.1 (**1** in $CDCl_3$) to δ 57.5, while the ^{77}Se NMR spectrum showed only *two* peaks at δ 812.0 (SeAr) and 815.7 ($SeCH_2Ar$).9) These spectral data indicate that **3** is a single conformer, *i.e.*, boat-form in concd D_2SO_4 solution [**3**: ^{1}H δ 5.15, 5.36 (ABq, *J*=15 Hz, 4H), 7.17-7.28 (m, 6H), 7.45-7.47 (m, 2H); ^{13}C δ 57.5, 131.6, 133.6, 134.4, 135.9, 137.4, 141.0] (Scheme 1). This reaction may proceed *via* an electron transfer pathway because, two-electron oxidation of **1** with 2 equiv of $NOPF_6$ as a one-electron-oxidizing agent afforded the diselena dication PF_6 salt **4**: mp 100 °C (decomp); ^{1}H (CD_3CN) δ 5.38, 5.66 (ABq, *J*=15 Hz, 4H), 7.50-7.60 (m, 6H), 7.79-7.83 (m, 2H); ^{13}C δ 60.1, 130.6, 131.1, 132.0, 132.7, 133.9, 139.2]. In contrast to **1** in D_2SO_4, the ^{1}H and ^{13}C NMR spectra of D_2SO_4 solutions of the selenide **6** and the dithiocin **7** showed complex signals due to the instability of **6** and **7** in D_2SO_4. This result suggests that the cationic species of **1** is more stabilized by transannular bond between two selenium atoms as compared with that of **7**.

The dication **3** was also formed on treatment of the selenoxide **2** with concd D_2SO_4, since the ^{1}H, ^{13}C, and ^{77}Se NMR chemical shifts of **2** in concd D_2SO_4 observed agreed well with those for **3** obtained from **1**. Hydrolysis of the D_2SO_4 solution of **2** resulted in the formation of the selenoxide **2** (84%).

This work was supported by the Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency No. 03233101 from the Ministry of Education, Science and Culture, Japan. One of us (H.F.) thanks a Scientific Research Grant (No. 03640435) from the Ministry of Education, Science and Culture, Japan.

References

1) W. K. Musker, T. L. Wolford, and P. B. Roush, *J. Am. Chem. Soc.*, **100**, 6416 (1978).
2) H. Fujihara, A. Kawada, and N. Furukawa, *J. Org. Chem.*, **52**, 4254 (1987); H. Fujihara, J.-J. Chiu, and N. Furukawa, *J. Am. Chem. Soc.*, **110**, 1280 (1988).
3) H. Fujihara, Y. Ueno, J.-J. Chiu, and N. Furukawa, *J. Chem. Soc., Chem. Commun.*, in press.
4) Concd H_2SO_4 acts both as an oxidizing agent and a strong acid: A. J. Bard, A. Ledwith, and H. J. Shine, *Adv. Phys. Org. Chem.*, **12**, 155 (1976).
5) R. P. Gellatly, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc., Perkin Trans.1*, **1976**, 913.
6) The protons and carbons of the aromatic rings in the NMR spectra (500 MHz-^{1}H and 125 MHz-^{13}C) of **1** and **2**, *except for dications* **3** and **4**, showed two sets of signals due to the existence of two conformers; the details are described in Ref. 3.
7) The benzylic carbon atoms of **2** ($CDCl_3$) appear at δ 52.2 and 60.6.
8) The chemical shifts are relative to Me_2Se. The conformers were assigned by the intergration of the selenium peaks. The peak of benzylic selenide of **1** was determined by off resonance method.
9) The ^{77}Se chemical shift of the aliphatic diselena dication salt of 1,5-diselenacyclooctane is 806.5 ppm: H. Fujihara, R. Akaishi, T. Erata, and N. Furukawa, *J. Chem. Soc., Chem. Commun.*, **1989**, 1789.

(Received June 24, 1991)