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Three-center Selenium Interaction in Electrochemical Oxidation of a Linear Trisselenide, 2,6-Bis(phenylselenomethyl)phenyl Phenyl Selenide, and *Se*-Monooxygenation from Hydrolysis of Its Sulfuric Acid Solution

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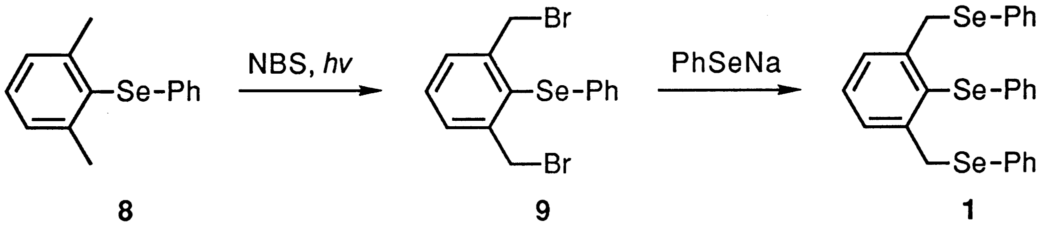
The cyclic voltammogram of a new trisselenide, 2,6-bis(phenylselenomethyl)-phenyl phenyl selenide (**1**), showed the reversible electrochemical oxidation with low oxidation potential which is attributed to the three-center selenium participation. The monoselenoxide of **1** was formed in the hydrolysis of concd H_2SO_4 solution of **1**, while the MCPBA oxidation of **1** gave a mixture of the corresponding mono- and bis-selenoxides.

The transannular interaction between two heteroatoms of medium-sized cyclic compounds containing two nitrogen or two sulfur atoms has been found in the chemical and electrochemical oxidations.[1,2] As a typical example, Wilson and co-workers reported the facilitation of the electrochemical oxidation of sulfide in cyclic bis-sulfides.[2] However, the electrochemical oxidation of compounds containing multiheteroatoms has received less attention. Recently, we reported that the reaction of a cyclic trisselenide, 1,11-(methanoselenomethano)-5*H*,7*H*-dibenzo[*b*,*g*][1,5]diselenocin, with 2 equiv of $NOPF_6$ gave a new hypervalent selenurane dication involving a transannular bond between the three selenium atoms.[3] This paper presents the first example of electrochemically reversible oxidation with low oxidation potential of a new linear trisselenide, 2,6-bis(phenylselenomethyl)phenyl phenyl selenide (**1**), and the *Se*-monooxygenation from the hydrolysis of the concd H_2SO_4 solution of **1**.

A new trisselenide **1** was synthesized from 2,6-dimethylphenyl phenyl selenide (**8**) which was obtained by general methods (Scheme 1). Selenide **8** was irradiated using a high-pressure mercury lamp after addition of *N*-bromosuccinimide (NBS) in CCl_4 to afford the bisbromide **9**. To a solution of **9** (4.0 g, 9.55 mmol) in $CHCl_3$-EtOH (50 mL) was added a solution of PhSeNa (1.9 g, 10.5 mmol) in EtOH (120 mL) at room



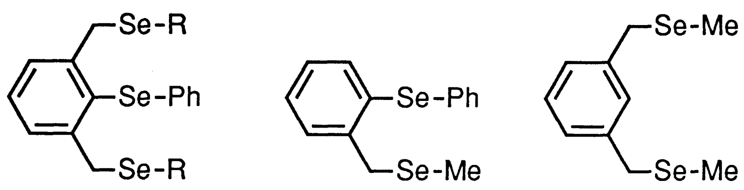
8 **9** **1**

Scheme 1.

temperature under an Ar atmosphere. The mixture was stirred for 3 h. After the usual work-up, the crude product was purified by silica-gel column chromatography (eluent, hexane-$CHCl_3$) to give **1** in 32% yield.[4)]

The electrochemical oxidation of selenides was studied by cyclic voltammetry. The cyclic voltammogram (CV) of all selenides 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; 50 mV/s). The peak potentials (Ep) of first oxidation peak for **1** and other selenides showed the following values: **1**, +0.57 V; 2-(methylselenomethyl)phenyl phenyl selenide (**2**), +0.65 V; 1,3-bis(methylselenomethyl)benzene (**3**), +1.03 V; diphenyl selenide (**4**), +0.94 V; and dibenzyl selenide (**5**), +1.05 V (Table 1). The oxidations of selenides **2-5** are irreversible. In general, since the cation radicals of heteroatoms having alkyl and aryl groups would be expected to deprotonate or react with nucleophiles very rapidly, the lifetime of these species is short, resulting in the irreversible oxidation wave. In contrast to **2-5**, the oxidation of **1** is reversible. Comparison of the tris-selenide **1** with a monoselenide such as diphenyl selenide shows a peak potential 370 mV more cathodic for the former, so that **1** should be oxidized more readily. This facile oxidation of **1** and the unusual stability of the cationic species of **1** are ascribed to the destabilization of **1** by intramolecular lone pair-lone pair repulsion and the stabilization of the oxidized species by neighboring group participation of selenium atoms. This is the first observation for the reversible electrochemical oxidation of a linear selenide by the three-center selenium participation.

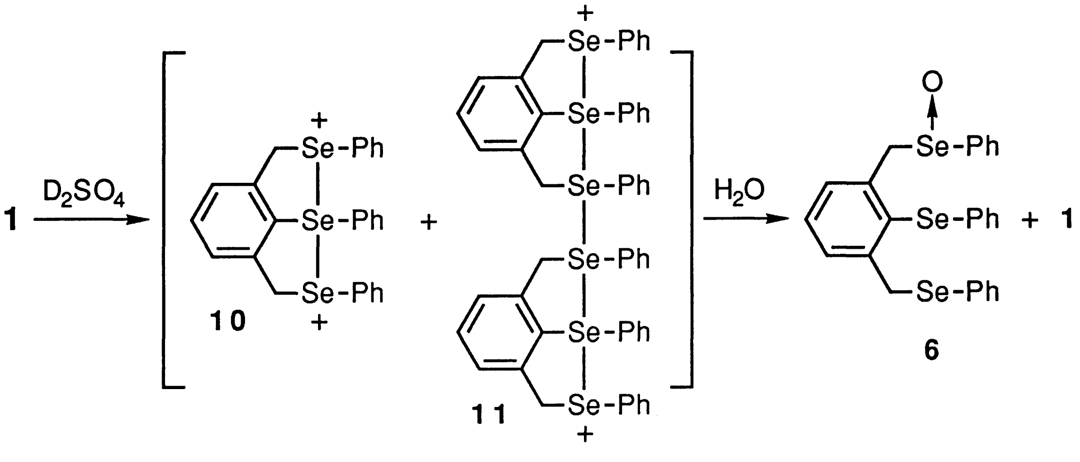
Table 1. Electrochemical Oxidation of Selenides [a)]



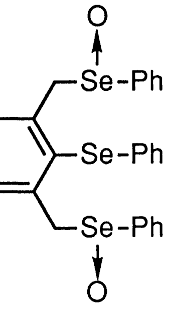
	1 R = Ph	**12** R = Tol	**2**	**3**	**4**	**5**
					Ph_2Se	$(PhCH_2)_2Se$
Ep	+0.57[b)]	+0.56[b)]	+0.65[c)]	+1.03[c)]	+0.94[c)]	+1.05[c)]

a) Ep/V *vs.* Ag/0.01 M $AgNO_3$. b) Reversible. c) Irreversible.

Thus, the trisselenide **1** was oxidized readily by electrochemical method. Therefore, the trisselenide **1** was treated with concentrated sulfuric acid (concd H_2SO_4) as an oxidant.[5)] Hydrolysis of the H_2SO_4 solution of **1** led to the monoselenoxide (**6**) (59%) and **1** (22%) (Scheme 2).[6)] On the other hand, the H_2SO_4 solutions of selenides **2** and **3** were unstable and none of the selenoxides were obtained after hydrolysis of the corresponding H_2SO_4 solutions. Namely, the H_2SO_4 solution of **1** was stabilized by introduction of the third selenium atom. These observations suggest that the positive charge developed on one selenium atom is delocalized over the three selenium atoms in the trisselenide **1**. The formation of **1** and the selenoxide **6** by the hydrolysis of H_2SO_4 solution of **1** might be explained by observation of the ^{77}Se NMR spectral data for the H_2SO_4 solution of **1**. The ^{77}Se NMR spectrum of **1** in $CDCl_3$ showed the two absorptions at δ 290.3 (SeAr) and at δ 392.3 ($SeCH_2Ar$).[7,8)] Whilst, the H_2SO_4 solution of **1** showed the five peaks at δ 578.8, δ 600.1, δ 631.9, δ 727.2, and δ 767.6, indicating remarkable downfield shifts. These peaks may be attributed to the dication **10** and the dication dimer **11** (Scheme 2).[9] Namely, the peaks of δ 600.1 ($^+SeCH_2Ar$) and δ 727.2 (SeAr) correspond to the dication **10**; the former resonance is assigned to the selenonium cation and the latter peak to the selenurane.[10,11] The other peaks of δ 578.8 ($^+SeCH_2Ar$), δ 631.9 ($SeCH_2Ar$), and δ 767.6 (SeAr) correspond to the dication dimer **11**; the former one peak is assigned to the selenonium cation and the latter two peaks to the selenurane. The dication **10** reacts with H_2O to form the monoselenoxide **6**, while the dication dimer **11** gives a mixture of **6** and **1** upon reaction with H_2O.



Scheme 2.



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Similar treatment of H_2SO_4 solution of 2,6-bis(*p*-tolylselenomethyl)phenyl phenyl selenide (**12**) with H_2O led to the monoselenoxide (**13**) (67%) and the trisselenide **12** (27%), of course, the CV of **12** showed a reversible oxidation potential, +0.56 V (Table 1). In contrast, the oxidation of **1** or **12** with *m*-chloroperbenzoic acid (MCPBA) afforded the mixtures of the following oxidation products: monoselenoxide **6** (27%) and bisselenoxide **7** (34%) from **1**, and monoselenoxide **13** (27%) and bisselenoxide **14** (57%) from **12**.[6,12] Thus, the hydrolysis of the H_2SO_4 solution of **1** and **12** showed the selective *Se*-monooxygenation, in which the results are caused from the nature of the dication species involving three-center selenium bond.

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2) R. W. Alder and R. B. Sessions, "The Chemistry of Amino, Nitroso and Nitro Compounds and their Derivatives," ed by S. Patai, John Wiley & Sons, New York (1982), Vol. 1, Chap. 18; G. S. Wilson, D. D. Swanson, J. T. Klug, R. S. Glass, M. D. Ryan, and W. K. Musker, *J. Am. Chem. Soc.*, **101**, 1040 (1979); M. D. Ryan, D. D. Swanson, R. S. Glass, and G. S. Wilson, *J. Phys. Chem.*, **85** 1069 (1981).

3) H. Fujihara, H. Mima, T. Erata, and N. Furukawa, *J. Am. Chem. Soc.*, **114**, 3117 (1992).

4) **1**: ^{1}H NMR ($CDCl_3$) δ 4.29 (s, 4H, CH_2), 7.01-7.28 (m, 12H, ArH), and 7.38-7.43 (m, 6H, ArH); ^{13}C NMR ($CDCl_3$) δ 34.6, 125.9, 127.4, 128.8, 128.9, 129.1, 129.2, 129.4, 134.2, 134.4, and 144.8; ^{77}Se ($CDCl_3$) δ 290.3 (SeAr) and 392.3 ($SeCH_2Ar$); MS, *m/z* 572 (M^+).

5) 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).

6) **6**: IR ($CHCl_3$) 821 cm^{-1} (Se-O); ^{1}H NMR ($CDCl_3$) δ 4.10-4.44 (m, 4H, CH_2), 6.93-7.28 (m, 12H, ArH), and 7.38-7.55 (m, 6H, ArH); ^{13}C NMR ($CDCl_3$) δ 34.5, 62.7, 125.9, 126.5, 127.6, 128.8, 128.9, 129.3, 129.6, 130.0, 130.5, 131.1, 132.2, 134.2, 137.1, 140.5, and 145.2; ^{77}Se NMR ($CDCl_3$) δ 290.5 (SeAr), 401.0 ($SeCH_2Ar$), and 897.4 ($Se(O)CH_2Ar$); FABMS, *m/z* 589 (M^++1). **7**: IR ($CHCl_3$) 817 cm^{-1} (Se-O); ^{1}H NMR ($CDCl_3$) δ 4.24-4.42 (m, 4H, CH_2), 6.98-7.07 (m, 3H, ArH), 7.10-7.27 (m, 5H, ArH), and 7.48-7.58 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$) δ 61.3, 125.9, 126.7, 128.5, 129.2, 129.3, 129.7, 131.3, 131.6, 131.8, 136.7, 136.9, 140.0, and 140.1; ^{77}Se ($CDCl_3$) δ 291.7, 291.9 (SeAr), and 892.7, 896.1 ($Se(O)CH_2Ar$); FABMS, *m/z* 605 (M^++1).

7) ^{77}Se-chemical shifts are relative to Me_2Se.

8) The ^{77}Se peak of $SeCH_2Ar$ for **1** appears as a triplet peak ($^2J_{Se-H}$ = 11 Hz).

9) The dications **10** and **11** are assigned by the integration of the selenium peaks. Each benzylic selenium resonances in H_2SO_4 appeared as the proton-coupled peaks, but the coupling constants of J_{Se-H} could not be determined clearly due to the somewhat broad peaks.

10) Generally, the ^{77}Se chemical shifts of selenonium cations are δ 300-600, while those of selenuranes (tetracoordinate selenium compounds) are δ 400-1100.[11]

11) "The Chemistry of Organic Selenium and Tellurium Compounds," ed by S. Patai and Z. Rappoport, John Wiley & Sons, New York (1986), Vol. 1, Chap. 14.

12) **12**: mp 66.5-67.5; ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 6H, CH_3), 4.25 (s, 4H, CH_2), 6.98-7.19 (m, 12H, ArH), and 7.24-7.34 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.1, 34.8, 125.8, 126.6, 128.8, 129.1, 129.2, 129.7, 130.0, 133.3, 134.4, 137.4, and 145.0; ^{77}Se NMR ($CDCl_3$) δ 283.3, 379.3; MS, *m/z* 600 (M^+). **13**: IR ($CHCl_3$) 826 cm^{-1} (Se-O); ^{1}H NMR ($CDCl_3$) δ 2.33 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 4.18-4.38 (m, 4H, CH_2), and 6.98-7.40 (m, 16H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.1, 21.4, 34.8, 62.8, 125.9, 126.4, 128.8, 129.5, 129.6, 129.7, 129.9, 130.0, 130.5, 132.3, 134.4, 134.6, 137.2, 137.3, 137.7, 141.5, and 145.5; ^{77}Se NMR ($CDCl_3$) δ 290.7, 395.5, and 897.8; FABMS, *m/z* 617 (M^++1). **14**: mp 117-123 °C (decomp); IR (KBr) 812 cm^{-1} (Se-O); ^{1}H NMR ($CDCl_3$) δ 2.40 (s, CH_3), 2.41 (s, CH_3), 4.24-4.44 (m, 4H, CH_2), and 6.98-7.42 (m, 16H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.4, 61.5, 61.7, 125.9, 126.8, 128.6, 129.8, 129.9, 130.0, 131.6, 131.75, 131.84, 136.8, 137.0, 137.1, 141.76, and 141.8; ^{77}Se NMR ($CDCl_3$) δ 290.4, 290.7, 894.8, and 896.8; FABMS, *m/z* 633 (M^++1). The NMR spectral data indicate the existence of the diastereomers.

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