A NEW MODE FOR THE FORMATION OF ENDOCYCLIC DOUBLE BOND FROM THE SELENONIUM SALT OF 1,11-METHANOSELENOMETHANO-*5H,7H*-DIBENZO[*b,g*][1,5]DISELENOCIN: SYNTHESIS OF METHANOSELENOMETHANO-BRIDGED DIBENZO[*b,f*]SELENEPIN

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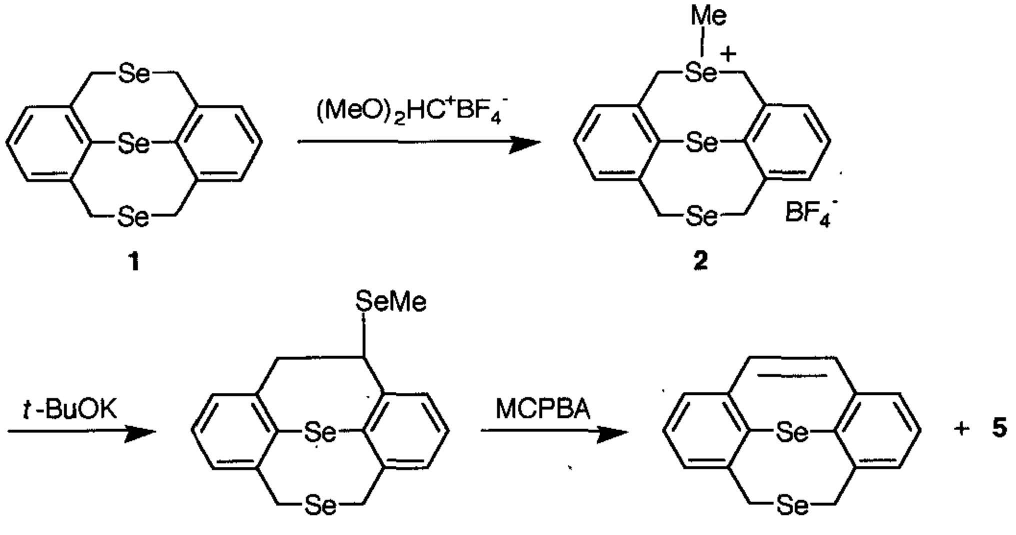
Abstract — Benzylic selenonium salt of 1,11-methanoselenomethano-*5H,7H*-dibenzo[*b,g*][1,5]diselenocin was treated with *tert*-BuOK to give the corresponding Stevens-type rearrangement product which was converted into a new heterocyclic compound, 1,11-ethano-*5H,7H*-dibenzo[*b,g*][1,5]diselenocin (**4**), upon treatment with *m*-chloroperbenzoic acid. The conformational property of **4** is described.

Although we recently reported that the oxidation of a cyclic trisselenide, 1,11-methanoselenomethano-*5H,7H*-dibenzo[*b,g*][1,5]diselenocin (**1**), with 2 equiv of $NOPF_6$ gave a novel selenurane dication salt containing a transannular Se-Se-Se bond,[1] the reactivities of the trisselenide have remained less explored. We now report a new type formation of the endocyclic double bond via the Stevens-type rearrangement of the selenonium salt of **1**, together with some conformational properties.

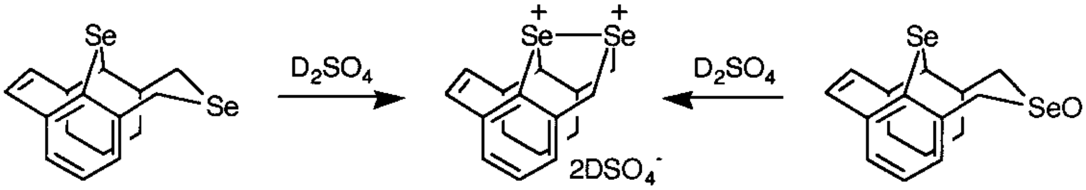
It has been known that the transformation of sulfide linkages in dithia[3.3]metacyclophane to carbon-carbon double bonds can be performed by a reaction sequence of a Stevens rearrangement followed by a Hofmann elimination.[2] However, such reactions of cyclic selenides were not explored, a little information of the reactivity of alkyl substituted selenonium salts are available.[3] A new strategy for the synthesis of selenepin involving endocyclic double bond was performed as follows (Scheme 1). Treatment of the trisselenide (**1**) with $(MeO)_2HC^+BF_4^-$ at room temperature gave the monoselenonium salt (**2**).[4] When the benzylic selenonium salt (**2**) was allowed to react with *tert*-BuOK at -20 °C, the Stevens-type rearrangement product (**3**) was obtained in 67% yield.[5,6] Reaction of **3** with *m*-chloroperbenzoic acid (MCPBA) led to the olefinic products, the selenepin (**4**) (16%) and its selenoxide (**5**) (43%).[7] This is a new method for the preparation of the endocyclic olefin from diselena[3.3]metacyclophane,[3] and may be applied to a synthesis of olefinic [2.2]metacyclophane from diselena[3.3]metacyclophane.



Scheme 1

In conformational properties of **4** concerning eight-membered rings, two typical different conformers such as chair and boat-forms can exist.[8] The conformers can be assigned by the ^{1}H-nmr spectral data for benzylic methylene protons of the eight-membered ring. The ^{1}H-nmr spectrum of **4** in $CDCl_3$ at 25 °C shows the benzylic protons as an AB quartet peak at δ 3.72 and 5.88 (J = 13 Hz), which is assigned to the chair form. When the selenide (**4**) was dissolved in concentrated D_2SO_4 (98%) at room temperature,[9] the conformation of **4** in $CDCl_3$ was changed completely to the boat form (**6**) in D_2SO_4 as shown by ^{1}H-nmr spectroscopy, i.e., the benzylic methylene protons appear at δ 5.23 and 5.74 (ABq, J = 15 Hz) (Scheme 2).[10] More significant spectroscopic evidence for the formation of **6** was obtained in the ^{77}Se-nmr spectrum. The proton-noise-decoupled ^{77}Se-nmr spectrum of the D_2SO_4 solution of **4** exhibits two resonances at δ 737.2 ($SeCH_2Ar$) and δ

776.6 (SeAr), indicating the formation of diselena dication.[11] Similarly, the dication (**6**) was formed on treatment of the selenoxide (**5**) with concd D_2SO_4, since the ^1H, ^{13}C, and ^{77}Se-nmr chemical shifts of **5** in concd D_2SO_4 observed agreed well with those for **6** obtained from **4**. Further studies on the reactivities of the selenepin and related compounds are in progress.



4 Scheme 2 **6** **5**

ACKNOWLEDGMENT

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3. (a) *The Chemistry of Organic Selenium and Tellurium Compounds*; S. Patai and Z. Rappoport, Eds.; Wiley: New York, 1986; Vol. 1, Chapters 3, 6 and 14, and 1987; Vol. 2. (b) *Selenium Reagents and Intermediates in Organic Synthesis;* C. Paulmier, Pergamon Press; New York, 1986.
4. **2**: mp 265-267 °C (decomp.); ^1H-nmr (CD_3CN) δ 3.01 (s, 3H), 4.01, 5.27 (ABq, J = 13 Hz, 4H, CH_2). 4.56, 5.96 (ABq, J = 12 Hz, 4H, CH_2), 7.28-7.46 (m, 6H, ArH); ^{13}C-nmr (CD_3CN) δ 23.6, 32.7, 49.0, 130.6, 131.1, 132.2, 138.3, 151.7. Anal. Calcd for $C_{17}H_{17}BF_4Se_3$: C, 37.47; H, 3.14. Found: C, 37.50; H, 3.16.
5. To a solution of potassium *tert*-butoxide (61 mg, 0.54 mmol) in tetrahydrofuran (250 ml) was added the monoselenonium salt (**2**) (300 mg, 0.49 mmol). After the mixture was stirred at -20 °C under an Ar atmosphere for 2 h, it was washed successively with diluted aqueous 15% HCl. The organic layer was separated, washed with water, and dried over $MgSO_4$. Removal of the solvent afforded a solid, which was purified by silica gel column chromatography (eluent, $CHCl_3$: n-hexane = 1 : 1) to give **3** in 67% yield. **3**:

mp 195-195.5 °C (decomp.); ^{1}H-nmr ($CDCl_3$) δ 2.05 (s, 3H), 2.87 (dd, J = 9 Hz, J =16 Hz, 1H), 3.59, 5.66 (ABq, J = 13 Hz, 2H), 3.67, 5.61 (ABq, J = 13 Hz, 2H), 4.12 (dd, J = 11 Hz, J = 16 Hz, 1H), 5.57 (dd, J = 9 Hz, J = 11 Hz, 1H), 6.71-7.55 (m, 6H, ArH); ^{13}C-nmr ($CDCl_3$) δ 5.5, 30.9, 31.1, 44.0, 44.4, 126.0, 126.8, 128.3, 129.6, 130.0, 130.2, 135.7, 139.7, 140.2, 142.3, 143.6, 144.5; ^{77}Se-nmr ($CDCl_3$) δ 160.3 (MeSe), 194.8 (ArSe), 369.8 ($ArCH_2Se$) relative to Me_2Se; ms (m/z) 458 (M^+). Anal. Calcd for $C_{17}H_{16}Se_3$: C, 44.66; H, 3.53. Found: C, 44.69; H, 3.51.

6. Gassman and coworkers reported that the treatment of a benzylic selenonium salt, dibenzylmethylselenonium tetrafluoroborate, with sodium amide afforded the [2,3]sigmatropic rearrangement product: P. G. Gassman, T. Miura, and A. Mossman, *J. Org. Chem.*, 1982, **47**, 954.

7. (a) To a stirred solution of **3** (85 mg, 0.19 mmol) in $CHCl_3$ (9 ml) at 0 °C was added MCPBA (32 mg, 0.19 mmol) in $CHCl_3$ (4 ml). The mixture was stirred at room temperature for 3 h and treated with anhydrous ammonia. The resulting solid was separated by filtration, and the filtrate was evaporated in vacuo to afford the crude products, which were purified by silica gel column chromatography (eluent, $CHCl_3$) to give **4** (16%) and **5** (43%). **4**: mp 195.5-197.5 °C (decomp.); ^{1}H-nmr ($CDCl_3$) δ 3.72, 5.88 (ABq, J = 13 Hz, 4H), 7.02-7.17 (m, 6H, ArH), 7.28 (s, 2H); ^{13}C-nmr ($CDCl_3$) δ 33.1, 125.1, 127.5, 128.0, 128.5, 133.0, 140.9, 144.4; ^{77}Se-nmr ($CDCl_3$) δ 231.9 (ArSe), 399.4 ($ArCH_2Se$) relative to Me_2Se; ms (m/z) 364 (M^+). Anal. Calcd for $C_{16}H_{12}Se_2$: C, 53.06; H, 3.34. Found: C, 53.18; H, 3.27. **5**: ^{1}H-nmr ($CDCl_3$) δ 4.16, 6.40 (ABq, J = 12 Hz, 4H), 7.16-7.46 (m, 8H, ArH, CH=); ^{13}C-nmr ($CDCl_3$) δ 62.6, 126.5, 128.2, 130.9, 131.0, 132.9, 133.3, 141.0; ^{77}Se-nmr ($CDCl_3$) δ 247.1 (ArSe), 979.4 ($ArCH_2Se$) relative to Me_2Se. Exact mass calcd for $C_{16}H_{12}OSe_2$: 379.9219. found: 379.9205. (b) It has been known that selenoxides bearing β-hydrogen atoms decompose into olefins.[3]

8. (a) R. P. Gellatly, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc., Perkin Trans. 1*, 1976, 913. (b) L. E. Brieaddy, B. S. Hurlbert, and N. B. Mehta, *J. Org. Chem.*, 1981, **46**, 1630 and references cited therein.

9. Concd H_2SO_4 acts either as an oxidant or as a strong acid: A. J. Bard, A. Ledwith, and H. J. Shine, *Adv. Phys. Org. Chem.*, 1976, **12**, 155.

10. Dication **6**: ^{1}H-Nmr (D_2SO_4) δ 5.23, 5.74 (ABq, J = 15 Hz, 4H), 7.04-7.34 (m, 8H); ^{13}C-nmr (D_2SO_4) δ 61.3, 132.7, 134.2, 135.5, 136.4, 136.6, 136.7, 138.4.

11. H. Fujihara, Y. Ueno, J.-J. Chiu, and N. Furukawa, *J. Chem. Soc., Chem. Commun.*, 1991, 1052.

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