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is predominantly formed when the reaction is carried out in aqueous methanol (1:1) or when the reaction is conducted at a low temperature and for a short duration.[22] Further studies on the scope and the mechanism of these reactions will be reported in due course.

Acknowledgment. We thank NSERCC and FCAR for generous financial assistance and fellowships to R.L. We also thank Sacha Ninkovic for his skillful assistance in optimizing entry j (Table I).

Supplementary Material Available: Experimental procedures, physical constants, and spectroscopic data (9 pages). Ordering information is given on any current masthead page.

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(22) Oxidative destannylation in the presence of a 2,4,6-trimethoxybenzyl or 3,4-(methylenedioxy)benzyl group leads to the aldehyde directly (CAN 2 equiv, MeOH, slow addition, 2 h, 0 °C, 58 and 68%, respectively), a sequence which was used in the total synthesis of lignans: Hanessian, S.; Lêger, R. *Synlett*, in press.

Hypervalent Selenurane with the Chalcogenium Cation (Se^+, S^+) from 1,11-(Methanoselenomethano)-5*H*,7*H*-dibenzo[*b*,*g*]-[1,5]diselenocin and Its Sulfur Derivative: Interconvertible Redox Structures by Multicenter Chalcogenide Participation

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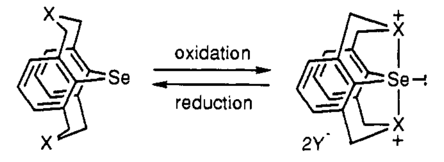
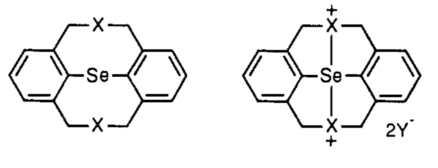
Received December 4, 1991

Although it was recently shown that the transannular interaction between two heteroatoms (Se–Se, Se–N) of selenium heterocycles can produce the diselenide dication and the hypervalent σ-ammonioselenuranes, such behavior by fourth-row elements and multichalcogenides has received less attention.[1,2] We have now found that transannular bond formation occurs between the three chalcogen atoms (Se, S) of the new cyclic chalcogenides 1,11-(methanoselenomethano)-5*H*,7*H*-dibenzo[*b*,*g*][1,5]diselenocin (**1**) and 1,11-(methanothiomethano)-5*H*,7*H*-dibenzo[*b*,*g*][1,5]selenathiocin (**3**) in the oxidation of **1** and **3** with concentrated H_2SO_4 or 2 equiv of $NOPF_6$. This multicenter chalcogenide participation provides a new type of hypervalent σ-selenurane with two apical selenonio or sulfonio ligands. Its selenurane dication undergoes a reversible two-electron reduction, which is an unprecedented reaction mode for selenuranes. Thus, two-electron redox reactions of **1** or **3** are accompanied by conformational changes of the chair and boat forms. Generally, selenuranes bear two electronegative groups such as oxygen atoms or halogen atoms at the apical positions, though the preparation and properties of selenuranes[3] are little known as compared with those of hypervalent organosulfur compounds.[4]

Scheme I



1, **3** (*chair*) **2**, **4** (*boat*)



1 X = Se
3 X = S

2 X = Se, Y = HSO_4
2a X = Se, Y = PF_6
4 X = S, Y = HSO_4
4a X = S, Y = PF_6

With regard to the conformational properties of tris-selenide **1**,[5] the chair and the boat forms can exist.[6] The conformers can be assigned by the ^1H NMR spectral data for the benzylic protons of the eight-membered ring.[6] The ^1H NMR spectrum of **1** in $CDCl_3$ at 25 °C shows the benzylic methylene protons as an AB quartet peak at δ 3.88 and 5.33 (J = 12.8 Hz), which is assigned to the twin chair form (Scheme I). The ^1H NMR spectra of **1** do not change over the temperature range from −50 (in $CDCl_3$) to +180 °C [in $(CD_3)_2SO$], indicating that **1** is conformationally rigid. The proton-coupled ^{77}Se NMR spectrum of **1** in $CHCl_3$ shows the two peaks at δ 208.6 (s, SeAr) and at δ 365.7 (t, $^2J_{Se-H}$ = 31 Hz, $SeCH_2Ar$).[7,8]

When tris-selenide **1** was dissolved in concentrated D_2SO_4 (98%) at room temperature,[9] the conformation of **1** in $CDCl_3$ was changed completely to the twin boat form **2** in D_2SO_4, as shown by ^1H NMR spectroscopy, i.e., the benzylic methylene protons appear at δ 4.07 and 4.59 (AB q, J = 16.0 Hz) (Scheme I). This D_2SO_4 solution of **2** was stable for several weeks, and no deuterium exchange was observed at all. More significant spectroscopic evidence for the formation of **2** was obtained in the ^{77}Se NMR spectrum. The proton-noise-decoupled ^{77}Se NMR spectrum of the H_2SO_4 solution of **2** exhibits two resonances at δ 543.8 ($SeCH_2Ar$)[10] and at δ 816.6 (SeAr) (ratio 2:1), indicating remarkable

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[†] Institute of Applied Physics.

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(4) For a review, see: Hayes, R. A.; Martin, J. C. Sulfurane Chemistry. In *Organic Sulfur Chemistry, Theoretical and Experimental Advances*; Bernardi, F., Csizmadia, I. G., Mangini, A., Eds.; Elsevier: Amsterdam, 1985; Chapter 8.

(5) NMR data. **1** ($CDCl_3$): ^1H δ 3.88, 5.33 (AB q, J = 12.8 Hz, 8 H), 6.97–7.01 (m, 4 H), 7.07–7.13 (m, 2 H); ^{13}C δ 32.9, 127.1, 130.3, 133.7, 149.3. **2** (D_2SO_4): ^1H δ 4.07, 4.59 (AB q, J = 16.0 Hz, 8 H), 7.04 (d, J = 7.6 Hz, 4 H), 7.33 (t, J = 7.6 Hz, 2 H); ^{13}C δ 41.3, 131.9, 134.8, 138.6, 142.3. **2a** (CD_3CN): ^1H δ 4.56, 5.06 (AB q, J = 15.8 Hz, 8 H), 7.53 (d, J = 7.6 Hz, 4 H), 7.79 (t, J = 7.6 Hz, 2 H); ^{13}C δ 39.7, 132.2, 135.3, 141.6. The ^{31}P NMR spectrum for **2a** shows a ^{31}P peak at δ −144.9 (sept, J_{PF} = 707 Hz, relative to H_3PO_4) in the region of ionic PF_6^-. **3** ($CDCl_3$): ^1H δ 3.79, 5.27 (AB q, J = 14.4 Hz, 8 H), 6.97–7.03 (m, 4 H), 7.08–7.15 (m, 2 H); ^{13}C δ 42.3, 127.8, 130.3, 134.5, 148.0. **4** (D_2SO_4): ^1H δ 4.05, 4.61 (AB q, J = 17.3 Hz, 8 H), 7.13 (d, J = 7.6 Hz, 4 H), 7.34 (t, J = 7.6 Hz, 2 H); ^{13}C δ 44.9, 130.1, 133.7, 139.1, 141.0; ^{77}Se δ 917.8 (s). **4a** (CD_3CN): ^1H δ 4.60, 5.10 (AB q, J = 16.2 Hz, 8 H), 7.59 (d, J = 7.6 Hz, 4 H), 7.78 (t, J = 7.6 Hz, 2 H); ^{13}C δ 43.4, 131.0, 135.7, 140.5; ^{31}P δ −144.9 (sept, J_{PF} = 707 Hz).

(6) (a) Gellatly, R. P.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1* **1976**, 913–925. (b) Brieaddy, L. E.; Hurlbert, B. S.; Mehta, N. B. *J. Org. Chem.* **1981**, *46*, 1630–1634.

(7) All ^{77}Se chemical shifts (^{77}Se: spin $^1/_2$, natural abundance 7.6%) are relative to Me_2Se.

(8) The proton-decoupled ^{77}Se NMR (76.3 MHz) spectrum of **1** in $CHCl_3$ shows that the Se peak of $SeCH_2Ar$ appears as a singlet at δ 365.7. The value of $^2J(^{77}Se, H_A \text{ or } H_B)$ is most likely related to the Se–C–H dihedral angle; the details will be reported elsewhere.

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

(10) The ^{77}Se peak of $SeCH_2Ar$ for **2** appears as a triplet peak ($^2J_{Se-H}$ = 28 Hz) a δ 543.8 in the proton-coupled ^{77}Se NMR spectrum.

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downfield shift. The former resonance is assigned to the selenonium cation and the latter peak to the selenurane structure;[11] particularly, each peak exhibits two clearly resolved satellite peaks due to the ^{77}Se–^{77}Se coupling (large coupling constant of $^1J_{Se-Se}$ = 210 Hz) about each central peak.[12] This observation of ^{77}Se satellites clearly indicates the occurrence of bond formation between the three selenium atoms.

A new selenurane 2PF$_6^-$ salt **2a** (mp 190 °C, dec) was isolated in the two-electron oxidation of **1** with 2 equiv of NOPF$_6$, a one-electron oxidant, in CH$_3$CN.[13] The selenurane **2a** was stable and easily handled. The structure of **2a** in CH$_3$CN was analyzed by multinuclear NMR spectroscopy.[5] Specifically, the ^{77}Se NMR spectrum of **2a** shows two resonances at δ 535.2 (SeCH$_2$Ar) and δ 830.0 (SeAr), and the ^{77}Se satellites in the proton-decoupled ^{77}Se NMR spectrum of **2a** give a value of 200 Hz for $^1J_{Se-Se}$; i.e., **2a** has the selenurane structure having two apical selenonium cations. The selenurane **2a** exists solely as a single conformer from −40 to +75 °C as evidenced by its ^{1}H NMR spectrum. The conformation of **2a** was fixed as the boat form by transannular bonds between the three selenium atoms, although normally the chair conformer has been shown to be more stable and rigid than the boat conformer.[6]

Analogously, oxidation of **3** with concentrated H$_2$SO$_4$ or 2 equiv of NOPF$_6$ gave the selenurane **4** or its salt **4a** (mp 185 °C, dec).[5] The ^{77}Se NMR spectrum of **3** in CHCl$_3$ shows a singlet peak at δ 207.0, while **4a** in CH$_3$CN shows a singlet at δ 946.7, as is characteristic of a selenurane.[11] This is the first example of multicentered bond formation involving two different chalcogens.

The redox behavior of **2a** was examined since little information on the reactivity of selenuranes was available.[3] Treatment of benzenethiol (PhSH) (2 equiv) with **2a** (1 equiv) in CH$_3$CN under an Ar atmosphere at room temperature for 1 h gave diphenyl disulfide (PhSSPh) (87%) as the oxidation product and neutral **1** (85%) as the reduction product. Similar reaction of **2a** with triphenylphosphine (Ph$_3$P, 2 equiv) afforded **1** (90%) and the phosphine oxide (Ph$_3$P=O) (76%) after treatment with H$_2$O.[14] The selenurane **2a** could also be reduced by phenothiazine (**5**, 2 equiv) in CH$_3$CN to give **1** (91%) by two-electron transfer, accompanied by the formation of the cation radical of **5** as evidenced by the UV-visible spectrum (λ_{max} = 437 and 515 nm).[15] Interestingly, **2a** undergoes two-electron reduction to give **1** in quantitative yield by treatment with samarium(II) iodide, SmI$_2$,[16] at room temperature. From these novel results, an electron-transfer pathway is likely and **2a** is a good oxidant.

Reduction of **2a** is also facile electrochemically; cyclic voltammetry of **2a** in CH$_3$CN reveals that the reduction potential is remarkably lower (−0.10 V vs Ag/0.01 M AgNO$_3$) than those of some selenonium salts (ca. −1.5 to −1.8 V vs Ag/0.01 M AgNO$_3$)[17] and ammonioselenuranes[1c] (−0.8 to −2.0 V vs Ag/0.01 M AgNO$_3$),[17] though the electrochemistry of selenuranes and selenonium salts is virtually unknown.

Thus, the facile structural changes (chair $\rightleftharpoons$ boat) in the redox reactions of **1** or **3** are ascribed to the stabilization of the oxidized species by multicenter chalcogenide participation, i.e., the formation of selenurane dications, and the destabilization by transannular lone pair–lone pair repulsion of the neutral boat forms derived from the reduction of the dications. Further studies on the structural changes during electrochemical oxidation and reduction of the tris-chalcogenides are in progress.

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

Registry No. 1, 139526-19-5; **2**, 139526-21-9; **2a**, 139526-25-3; **3**, 139526-22-0; **4**, 139526-24-2; **4a**, 139526-26-4; ^{77}Se, 14681-72-2.

Supplementary Material Available: Proton-noise-decoupled ^{77}Se NMR spectrum of selenurane **2a** (2 pages). Ordering information is given on any current masthead page.

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(11) Generally, the ^{77}Se chemical shifts of selenonium compounds are δ 300–600, while those of selenuranes are δ 400–1100.[12]

(12) Chapter 6 of ref 3a. Reference 3b. Iwamura, H.; Nakanishi, W. *Yuki Gosei Kagaku Kyokaishi (Japan)* **1981**, *39*, 795–804.

(13) **2a**: Anal. Calcd for C$_{16}$H$_{14}$Se$_3$P$_2$F$_{12}$: C, 26.21; H, 1.92. Found: C, 26.39; H, 1.82. Although **2a** has been obtained in solid form, we have as yet been unable to grow crystals suitable for X-ray analysis.

(14) Ph$_3$P is known to transfer an electron to a suitable acceptor, resulting in the formation of its phosphinium cation radical which reacts with H$_2$O to give Ph$_3$P=O; Powell, R. L.; Hall, C. D. *J. Am. Chem. Soc.* **1969**, *91*, 5403–5404.

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On the Nature of Cubyl Cation

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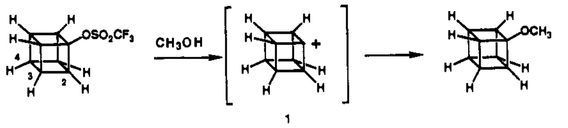
Received January 6, 1992

Cubanes carrying good nucleofugal substituents undergo remarkably rapid solvolysis.[1,2] For example, the half-life of cubyl triflate in methanol is 15 min at 70 °C. The reaction (eq 1) is clean and proceeds without rearrangement; cubyl methyl ether is formed in high yield. Sufficient data has been presented already to establish that such reactions proceed by way of cubyl cation (**1**).[1–3]



1

(1)

Schleyer and co-workers[4] have shown that S$_N$1 solvolysis rates correlate (as log *k*) inversely with the strain energy difference between starting material and intermediate cation. We have constructed Table I by taking published rate data for solvolysis, "correcting" it insofar as possible to a common set of conditions,[5] and comparing the results to the predictions of molecular mechanics.[4] Within 1 or 2 powers of ten, the agreement is excellent except for the cubane system. In this case, theory and experiment differ by more than 15 powers of ten!

What is so different about the cubane system? Borden and Hrovat have applied ab initio 6-31G* calculations (including electron correlation) to cubyl cation and have concluded that delocalization of the positive charge occurs via interaction with the strained, p-rich cubane CC bonds.[6] No comparable interaction is found by calculation in the cation from any other system in Table I. In the cubyl case there is a positive bond order between the p orbital at the cation carbon and the p orbital aligned with it at each of the β carbons (C-3). Population analysis reveals that the γ-CH (C-4) and α-CH (C-2) groups bear considerable positive charge (0.16) and more than the β-CH groups. As such delocalization of charge is not considered in classical molecular mechanics calculations, it is no wonder that the deviation boxed in Table I is so large.

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