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Communications to the Editor

Synthesis and Properties of Monocyclic Selenophene 1-Oxides

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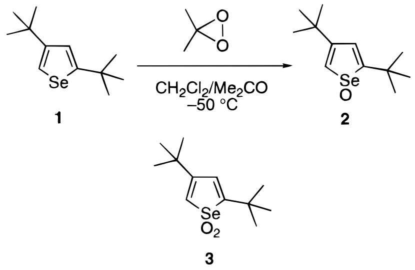
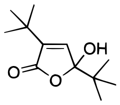
We report here the first synthesis, isolation, and properties of monocyclic selenophene 1-oxides. Thiophene 1,1-dioxides are highly reactive and, hence, both synthetically and theoretically important compounds whose chemistry has been investigated in all of its details.[1] The much more reactive thiophene 1-oxides have eluded isolation until recently,[2,3] with one exception.[4] These successful preparations of isolably stable thiophene 1-oxides have subsequently set the stage for the development of their chemistry. Meanwhile, dibenzoselenophene 5-oxide had been the only known oxide of selenophenes[5] when we started the study on this class of compounds several years ago. After numerous attempts, we have succeeded in the preparation of a series of monocyclic selenophene 1,1-dioxides, which are stabilized electronically or sterically, by oxidation of the corresponding selenophenes with dimethyldioxirane (DMD).[6,7] However, despite our many efforts, selenophene 1-oxides, the intermediates leading to the former dioxides, have never been isolated in pure form.

2,4-Di-*tert*-butylselenophene 1,1-dioxide (**3**) is the most thermally stable of the synthetically available 1,1-dioxides because of steric protection.[7,8] Since this should also be true for selenophene 1-oxides, 2,4-di-*tert*-butylselenophene (**1**)[9] was chosen as the substrate for our oxidation study. Thus, a solution of DMD[10] (1 equiv) in Me_2CO was added to a solution of **1** in CH_2Cl_2 at −50 °C. The addition resulted in rapid oxidation of **1**. The mixture was evaporated under vacuum below −40 °C.[11] The resulting colorless crystals were washed with a small amount of pentane at the same temperature to leave pure 2,4-di-*tert*-butylselenophene 1-oxide (**2**)[12] nearly quantitatively. No formation of the 1,1-dioxide **3** was observed. The 1-oxide **2** is highly hygroscopic and deliquesced on exposure to moist air. It decomposed on warming to liquefy at about 54−55 °C. NMR data of **2** are summarized in Table 1 together with those of **1**, **3**, and a range of compounds derived from **2**. The ^{1}H NMR chemical shift values of **2** fall between those of **1** and **3**. The same trend is also observed with a thiophene series.[3f] The ^{77}Se NMR spectrum showed only one signal at δ 986 which is lower than the chemical shift values of the common selenoxides.[13] The IR spectrum showed the Se−O stretching vibration at 798 cm^{-1}.[14] This assignment was supported by the Raman spectrum in which a strong absorption appeared at 788 cm^{-1}.



The 1-oxide **2** is far less stable than the corresponding thiophene 1-oxide[3f] and selenophene 1,1-dioxide[7,8] and decomposed at 20 °C with half-lives of 42 and 34 min in 0.018 and 0.036 M $CDCl_3$ solutions, respectively.[15] A 0.05 M solution of **2** in CH_2Cl_2 standing at 30 °C for 0.5 h gave **1** (73%), the furanone **4**[16] (25%), and SeO_2 by an unknown process. As is expected from the formation of **1**, **2** functions as an oxidizing agent. Thus, letting a 1:1 mixture of **2** and PhSMe stand in CH_2Cl_2 gave PhS(O)Me in 30% yield along with **1** (67%) and **4** (8%). Ph_3P was also oxidized with **2** (1 equiv) to give Ph_3PO in 80% yield. To our surprise, **2** is readily soluble in water, despite the presence of two hydrophobic *tert*-butyl groups, to give an acidic solution (pH 6.6 for 5.7×10^{-2} M solution) (also easily soluble in MeOH). In addition, it is stabilized by water and persisted in D_2O without marked decomposition at least for 24 h at room temperature. These observations indicate that the Se−O bond is higly polarized, as supported by the foregoing deshielded ^{77}Se chemical shift value, and is solvated in water. The acidity of **2** indicates that an equilibrium involving a selenurane **5**, which lies to the selenoxide side, exists in water.[17,18]



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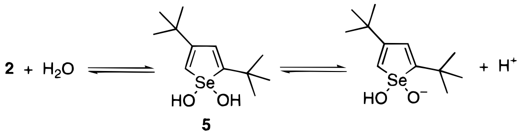

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The 1-oxide **2** quantitatively forms a 1:1 adduct (**6**)[12] with BF_3 when treated with $BF_3{\cdot}Et_2O$ (1 equiv) at −40 °C (Table 1).[19] The 1-oxide **2** also quantitatively formed a 1:1 adduct (**7**)[12] with *p*-toluenesulfonic acid (1 equiv) at −40 °C, similar in structure to that of the adduct reportedly formed with dibenzyl selenoxide.[20]

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[1] (a) For a review, see Nakayama, J.; Sugihara, Y. In *Topics in Current Chemistry (Organosulfur Chemistry)*, Page, P., Ed.; Springer-Verlag: Heidelberg, to appear in 1999. (b) For the parent thiophene 1,1-dioxide, see Nakayama, J.; Nagasawa, H.; Sugihara, Y.; Ishii, A. *J. Am. Chem. Soc.* **1997**, *119*, 9077.

[2] For a review, see Nakayama, J.; Sugihara Y. *Sulfur Reports* **1997**, *19*, 349.

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[11] Removal of the solvents and volatile materials below −40 °C is crucial to isolate **2** in pure form.

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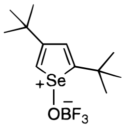
Table 1. ^{1}H NMR,[a] ^{13}C NMR,[b] and ^{77}Se NMR[c] Data (δ) of **2** and Related Compounds

compd	**1**	**2**	**2**[d]	**2**[g]	**3**[h]	**6**	**7**	**8**	**9**
C3-H	6.99	6.67	6.93[e]	6.92	6.57	6.81	6.72	6.75, 6.77	6.72
C5-H	7.31	6.83	6.94	6.97	6.75	6.98	7.07	7.21, 7.32	6.79
C-2	164.5	170.1	171.2[e]	170.8	157.6	169.7	168.7	164.0, 164.3	163.8
C-3	123.1	128.1	133.8	130.8	121.2	132.4	128.8	132.4, 132.5	130.9
C-4	153.9	163.1	169.8	166.1	155.6	164.6	164.4	168.55, 168.57	165.7
C-5	118.2	127.3	128.5	128.2	119.0	121.5	125.6	124.8, 124.9	118.0
^{77}Se	552	986	965[f]		1054[i]	953−955	959[j]	957, 959	610

[a] In $CDCl_3$ with TMS as the internal standard at 233 K, unless otherwise stated (400 MHz). [b] In $CDCl_3$ with $CDCl_3$ (δ 77.0) as the internal standard at 233 K, unless otherwise stated (100 MHz). [c] In $CDCl_3$ with the parent selenophene (δ 608.6) as the external standard at 233 K, unless otherwise stated (76 MHz). [d] In D_2O. [e] DSS as the internal standard at 297 K. [f] At 278 K. [g] In CD_3OD with TMS as the internal standard at 297 K. [h] At 297 K. [i] In $CDCl_3$ with D_2SeO_3 (δ 1282) as the external standard. [j] In CD_3CN at 248 K.

Since the selenium atom of **2** is chiral, optical resolution should be possible provided the inversion on the selenium atom and the well-known racemization process through hydration is slow.[17,21] As an approach to this goal, **2** was treated with (1*S*)-(+)-10-camphorsulfonic acid (1 equiv). The ^{1}H NMR of the resulting 1:1 adduct (**8**)[12] showed a pair of signals of equal intensities due to the α- and β-hydrogens, revealing the formation of a pair of diastereomers. This conclusion was also supported by ^{13}C- and ^{77}Se-NMR (observations of two signals at δ 957 and 959) spectra (Table 1), although separation of the diastereomers was impeded by instability of the adduct. Treatment of **2** with malononitrile (1 equiv) at −40 °C in the presence of $MgSO_4$ gave the selenonium ylide **9**[12] quantitatively, thus providing a new route to selenophenium ylides.[22]



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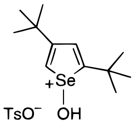

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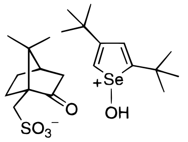

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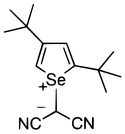

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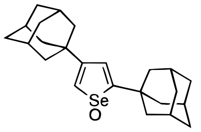
Similar oxidation of 2,4-di(1-adamantyl)-[12,23] and tetraphenylselenophenes[24] also gave the corresponding 1-oxides **10**[12] and **11**[12] nearly quantitatively. The 1-oxide **10**, which deliquesces on exposure to air and is slightly soluble in water, quickly decomposed at 30 °C in CH_2Cl_2 to give 2,4-di(1-adamantyl)-selenophene (85%) and the furanone **12**[12] (12%), whereas **11** gave tetraphenylselenophene (73%) and *cis*-butenedione **13** (25%) under the same conditions.



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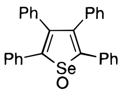

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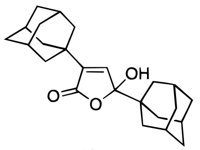

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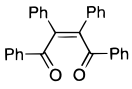

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Oxidation of thiophenes, including the parent thiophene, is difficult to stop at the 1-oxide stage[3] and, therefore, generally affords the corresponding thiophene 1,1-dioxides[1] since the oxidation of thiophene 1-oxides, which are no longer aromatic, to the 1,1-dioxides takes place much faster than that of thiophenes to the 1-oxides. By contrast, the present results lead to the conclusion that the oxidation of selenophenes to the 1-oxides is much faster than that of 1-oxides to the 1,1-dioxides. This might be explained by (1) weaker aromaticity of selenophenes compared to thiophenes[25] and (2) decreased electron density on the selenium atom because of the highly polarized Se−O bond.

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Supporting Information Available: Characterization data for new compounds **2** and **6**−**12** and ^{1}H and ^{13}C NMR spectra of **2** and **6**−**11**, ^{77}Se spectra of **2**, **10**, and **11**, and IR and Raman spectra of **2** (29 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(12) Supporting spectral data were obtained for all new compounds.

(13) Resonance range of selenoxides is δ = 812−941 except δ 1095 for $(CF_3)_2SeO$.; Duddeck, H. *Prog. Nucl. Magn. Reson. Spectrosc.* **1995**, *27*, 1.

(14) The ^{18}O-labeled **2**, which was prepared by treatment of **2** with $H_2{}^{18}O$ showed the absorption due to the Se−^{18}O stretching vibration at 762 cm^{-1}. See Shimizu, T.; Kobayashi, M.; Kamigata, N. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3761.

(15) Kinetics of the decomposition fitted neither first- or second-order in **2**.

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(18) The absorption due to the Se−O stretching vibration persisted even in the wet (deliquesced) **2**.

(19) Thiophene 1-oxides form stable 1:1 complexes with Lewis acids such as BF_3 and $SbCl_5$: (a) Hori, M.; Kataoka, T.; Shimizu, H.; Onogi, K. *Chem. Pharm. Bull.* **1978**, *26*, 2811. (b) Zhang, S.; Horn, E.; Sato, S.; Furukawa, N. private communication.

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