Synthesis, Properties, Oxidation, and Electrochemistry of 1,2-Dichalcogenins

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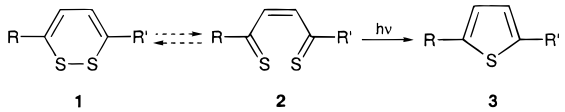
Abstract: Syntheses are presented of the 1,2-dichalcogenins: 1,2-dithiin, 1,2-diselenin, and 2-selenathiin, both substituted and unsubstituted. 1,2-Dithiin and 1,2-diselenin are prepared by reaction of $PhCH_2XNa$ (X = S or Se) with 1,4-bis(trimethylsilyl)-1,3-butadiyne followed by reductive cleavage and oxidation. 2-Selenathiin is similarly prepared using a mixture of $PhCH_2SeNa$ and $PhCH_2SNa$. Reaction of titanacyclopentadienes with $(SCN)_2$ or $(SeCN)_2$ followed by bis(thiocyanate) or bis(selenocyanate) cyclization affords substituted 1,2-dithiins or 1,2-diselenins, respectively. With S_2Cl_2, 1,2-dithiins are directly formed from titanacyclopentadienes. Oxidation of 1,2-dithiins and 1,2-diselenins gives the corresponding 1-oxide and, with 1,2-dithiins and excess oxidant, 1,1-dioxides; oxidation of 2-selenathiin gives the 2-oxide. Electrochemical oxidation of 1,2-dichalcogenins, which have a twisted geometry, affords planar radical cations by an EC mechanism. One-electron $AlCl_3$ oxidation of 3,6-diphenyl-1,2-dithiin gives the corresponding radical cation, characterized by EPR spectroscopy. Theoretical calculations result in a flattened structure for the 1,2-dithiin radical cation and a fully planar structure for the 1,2-diselenin radical cation. The ^{77}Se NMR chemical shifts of 1,2-diselenin are characteristically high-field-shifted with respect to open chain diselenides in good agreement with results of GIAO-DFT calculations based on MP2 and DFT optimum geometries.

Introduction

Since the discovery[1] that plants of the sunflower (*Asteraceae*) family contain thiarubrines A and B (**1a**,**b**, Scheme 1) and related antibiotic pigments,[2] natural and synthetic 1,2-dithiins (**1**, 1,2-dithiacyclohexadienes) have attracted considerable attention.[3] Of particular interest is the potential antiaromaticity of **1** with its 8π electrons,[4] valence tautomerism involving the ring-opened form **2**,[1b] the basis for the red color (λ_{max} 452 and ∼480 nm in **1c** and **1a**,**b**, respectively) in the absence of a conventional chromophore, and the facile light-induced extrusion of sulfur to form thiophenes **3**.[2,3d,5a] Thiarubrines **1a**,**b** display antibiotic activity both in the light and dark; thiophene **3a** from the extrusion of sulfur from **1a** is biologically active only in the light.[2c] The above features have been explored through theoretical and spectroscopic studies of the parent compound and certain of its derivatives, including **1a**,**b**.[4] Because of the difficulty of synthesis of the parent 1,2-dithiin (**1c**) from 1,3-

Scheme 1



a: R = CH_2=CHC≡CC≡C-, R' = MeC≡C- (thiarubrine A)
b: R = CH_2=CHC≡C-, R' = MeC≡CC≡C- (thiarubrine B)
c: R = R' = H; **d**: R = R' = Ph; **e**: R = R' = CH_2OH
f: R = R' = Me; **g**: R = R' = *t*-Bu; **h**: R = R' = *i*-Pr; **i**: R = R' = TMS

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† State University of New York at Albany.
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‖ Technische Universität Dresden.

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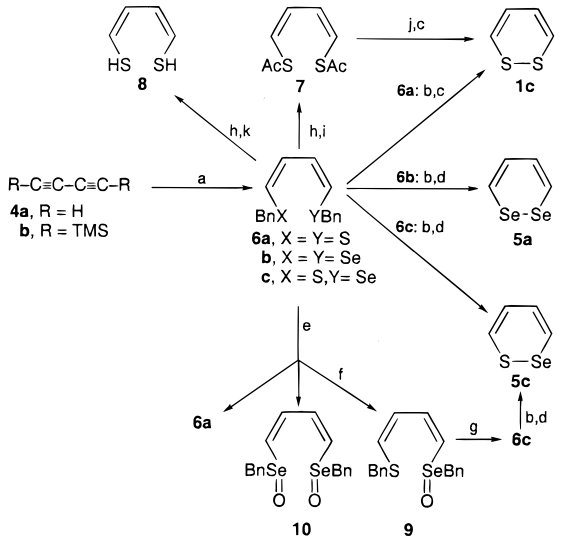
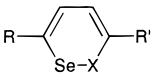
Scheme 2[a]



[a] (a) BnXNa/BnYNa (X, Y = S or Se). (b) Li or Na/NH_3. (c) I_2. (d) O_2, hexane-hexadecane. (e) H_2O_2, THF. (f) Chromatography. (g) $Na_2S_2O_3$, MeOH. (h) LDMAN. (i) AcCl. (j) KOH, MeOH. (k) H^+.

butadiyne (**4a**),[5] its characterization has been limited. In connection with total syntheses of thiarubrines B (**1b**),[6] and A (**1a**),[7a] simple syntheses of **1c** from commercially available 1,4-bis(trimethylsilyl)-1,3-butadiyne (**4b**) were independently discovered by us[6] and by Koreeda and Yang (Scheme 2).[7b] Recently, we reported the synthesis of two previously unknown parent 1,2-dichalcogenins, 1,2-diselenin (**5a**; 1,2-diselenacyclohexadiene) and 2-selenathiin (**5c**; 2-selena-1-thiacyclohexadiene), from **4b** as well as synthesis of 3,6-disubstituted 1,2-



5a, X = Se, R = R' = H
b, X = Se, R = R' = *t*-Bu
c, X = S, R = R' = H
d, X = Se, R = Me, R' = CH_2OH
e, X = Se, R = R' = Me

dithiins **1g**−**i** and 1,2-diselenin **5b** from titanacyclopentadienes.[8a] We have also determined the structure of **1c** by microwave spectroscopy,[9] and have elucidated the photochemistry of simple 1,2-dithiins as well as the thiarubrines.[10] Here we provide full details on our synthesis and characterization of simple 1,2-dichalcogenins prepared by the above and other routes, and our studies of the chemical and electrochemical oxidation of these compounds, using ab initio theoretical calculations to assist in interpretation of results.[11] A companion paper examines the photoelectron spectroscopy of many of these same compounds.[12]

Results and Discussion

Synthesis. The original synthesis of **1c** reported by Schroth[5a] entails addition of sodium α-toluenethiolate to the volatile and unstable 1,3-butadiyne (**4a**) followed by Na/NH_3 debenzylation of the resulting adduct (*Z*,*Z*)-1,4-bis(benzylthio)-1,3-butadiene (**6a**), and air oxidation (Scheme 2). We find that **1c** is more easily synthesized from commercially available 1,4-bis(trimethylsilyl)-1,3-butadiyne (**4b**) in a reaction conducted in refluxing methanol, to afford **6a** in 71−78% isolated yield.[5a] Compound **6a** can be conveniently cleaved with lithium 1-(*N*,*N*-dimethylamino)naphthalenide (LDMAN) in THF and the resulting dithiolate trapped with acetyl chloride to afford (*Z*,*Z*)-1,3-butadiene-1,4-dithiol *S*,*S*-diacetate (**7**) in good yield. Compound **7** represents a conveniently stored precursor to **1c**, which can be generated in 73% yield by exposure of **7** to KOH in methanol at 0 °C followed by oxidation with iodine. Compound **1c** is an orange, moderately volatile, light-sensitive liquid which is stable if stored in the dark at −78 °C. Acidification of the dithiolate from LDMAN cleavage of **7** affords surprisingly stable (*Z*,*Z*)-1,3-butadiene-1,4-dithiol (**8**), as originally reported by Schroth.[5a]

1,2-Diselenin (**5a**) is readily prepared by reaction of **4b** with BnSeNa, debenzylation (Li/NH_3) of (*Z*,*Z*)-1,4-bis(benzylseleno)-1,3-butadiene (**6b**), removal of hydrocarbons from an aqueous solution of the dilithium salt by hexane extraction, and air oxidation in the presence of hexane−hexadecane. The volatile but easily polymerized wine-red **5a** is purified, after removal of hexane, by vacuum distillation from hexadecane into a liquid N_2-chilled trap.[8b] Solutions for NMR analysis are prepared by addition of $CDCl_3$ prior to vacuum transfer of **5a**. Preparation of **5c** is accomplished by reacting **4b** with a mixture of BnSNa and BnSeNa, oxidizing the mixed product with excess H_2O_2, separating the *Se*-oxide (**9**) of (*Z*,*Z*)-1-benzylseleno-4-benzylthio-1,3-butadiene (**6c**) from bis-(*Se*-oxide) (**10**) and unoxidized **6a**, reducing *Se*-oxide **9** with thiosulfate to **6c**, and treating the latter with Na/NH_3 followed by workup as above. Hexadecane solutions of **5a**,**c** can be used as sources of these compounds for gas-phase or matrix studies.

For our electrochemical, photochemical, and photoelectron spectroscopic studies, we required nonannulated 1,2-dithiins and 1,2-diselenins with simple 3,6-substituents. Schroth's synthesis[5a,13a] of the former class of compounds, involving regio- and stereoselective anti 1,4-addition of α-toluenethiolate to 1,3-butadiynes **4**, followed by debenzylation is useful for preparing 1,2-dithiins such as **1d** (from **4d** via **11a**; Scheme 3)[13a] and **1e** (from **4e** via **11b**) and, using α-tolueneselenolate, 1,2-diselenins **5d**,**e** (from **4e** via **11c**).[7b] Other thio-protecting groups, such as 2-(trimethylsilyl)ethyl[7a] and 2-cyanoethyl,[13b] are also of value in the 1,4-addition sequence. While synthesis of 3,6-dimethyl-1,2-dithiin (**1f**) had been previously reported by Schroth by double addition of α-toluenethiolate to 2,4-hexadiyne (**4f**),[4a] efforts to duplicate this reaction led exclusively to the monoadduct **12a**, which proved resistant to further addition.[11f] Similarly,

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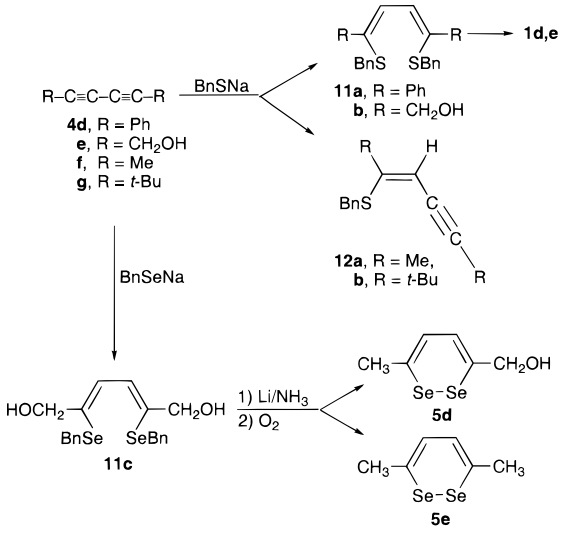
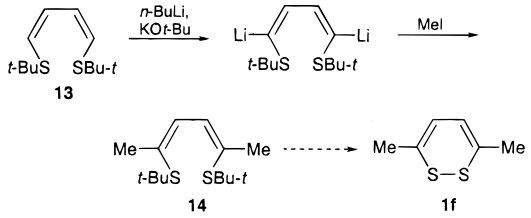
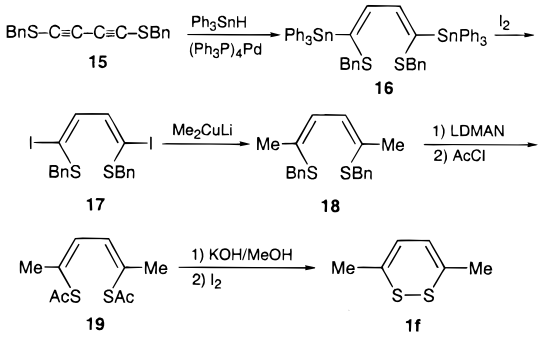
Scheme 3



Scheme 4



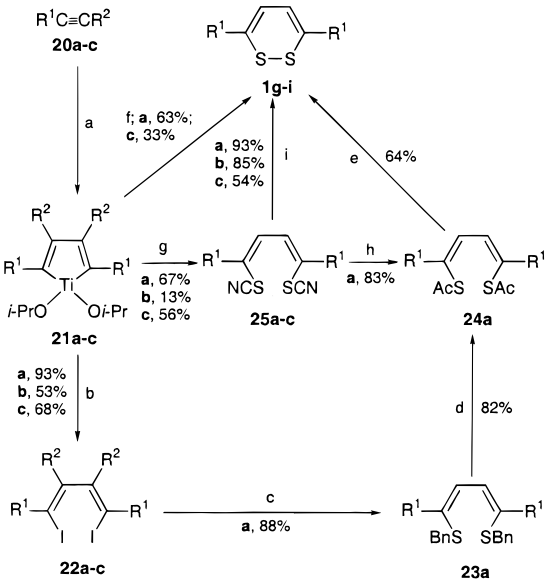
Scheme 5



only monoaddition occurs with excess α-toluenethiolate and 2,2,7,7-tetramethyl-3,5-octadiyne (**4g**).[13a] With **4b**, thiolates presumably cause desilylation to **4a** rather than addition as the first step, leading to **6a**. Nucleophilic 1,4-dithiolation of 1,3-diynes is favored by electron-withdrawing substituents and disfavored by electron-donating substituents such as simple alkyl groups.[13a]

Efforts to prepare **1f** from *Z*,*Z*-1,4-bis(*tert*-butylthio)-1,3-butadiene (**13**)[13c] via the Koreeda route of sequential dilithiation, dialkylation, and oxidation deprotection−cyclization succeeded only through the second step (Scheme 4). Attempts to deprotect (*E*,*E*)-2,4-bis(*tert*-butylthio)-2,4-hexadiene (**14**) using *N*-bromosuccinimide failed. Compound **1f** was ultimately prepared via the sequence **15** → **16** → **17** → **18** → **19** → **1f** (Scheme 5), exploiting our discovery of regio- and stereospecific syn 1,4-hydrostannylation of 1,4-dithio-substituted 1,3-butadiynes.[6] Oxidation of the Na/NH_3-debenzylation products of (*E*,*E*)-2,4-bis(benzylthio)-2,4-hexadiene-1,6-diol (**11b**) is reported to give trace quantities of **1f**.[14] Compound **1f** prepared by this latter route (23% yield based on recovered starting material) was identical to that synthesized via Scheme 5; **5d**,**e** were similarly prepared (Scheme 3).

Scheme 6[a]



[a] **a**, R^1 = *t*-Bu, R^2 = H; **b**, R^1 = *i*-Pr, R^2 = H; **c**, R^1 = TMS, R^2 = H. Reagents a−i: (a) $Ti(Oi\text{-}Pr)_4$, *i*-PrMgCl. (b) I_2. (c) *n*-BuLi; $(BnS)_2$. (d) LDMAN; AcCl. (e)KOH, MeOH; O_2 or I_2. (f) S_2Cl_2. (g) $(SCN)_2$, CH_2Cl_2. (h) $LiAlH_4$; AcCl. (i) Bu_4NF or SmI_2.

In view of the lengthy procedure needed to prepare **1e**, we sought a simpler approach to substituted 1,2-dichalcogenins. The ready availability of *Z*,*Z*-1,4-diiodo-1,3-butadienes **22** from titanacyclopentadienes **21** (Scheme 6), in turn available from alkynes **20** and (η^2-propene)$Ti(OiPr)_2$,[15] suggested a useful approach to 1,2-dithiins **1** via lithiation followed by treatment with dibenzyl disulfide (BnSSBn) or other sulfur electrophiles. Terminal alkynes 3,3-dimethylbutyne, 3-methylbutyne, and trimethylsilylethyne (**20a**−**c**: R^2 = H; R^1 = *t*-Bu, *i*-Pr, and TMS, respectively) afford **21a**−**c**, which give diiodo compounds **22a**−**c** with I_2. Sequential treatment of **22a** with *n*-BuLi, BnSSBn, lithium dimethylaminonaphthalene (LDMAN), acetyl chloride, and KOH/MeOH affords 3,6-bis(*t*-butyl)-1,2-dithiin (e.g., **22a** → **23a** → **24a** → **1g**; 46%). Using thiocyanogen ($(SCN)_2$) instead of I_2 and cyclizing with Bu_4NF[16a] or SmI_2,[16b] **1g** is obtained from **21a** via **25a** (62%), **1h** from **21b** via **25b** (13%), and **1i** from **21c** via **25c** (30%). With sulfur monochloride, S_2Cl_2, **21a** gives **1g** (63%) and thiophene **3g** (16%)[17a] while **21c** gives **1i** (33%) and **3i** (33%).[17b] On exposure to light, dithiins **1g**−**i** give thiophenes **3g**−**i**.[10]

Using 3-methyl-1,2-butadiene (**26**), or **26**/**20a**, Ti-mediated cyclizations via **27** and **28**[18] followed by trapping with $(SCN)_2$ and ring-closure (**27** → **29a** → **30a**, Scheme 7, or **28** → **31a** → **32a**, Scheme 8) give **30a**[17c] or **32a**. With two or one exocyclic double bonds, **30a** and **32a** are potential precursors to the corresponding symmetrically and unsymmetrically substituted 1,2-dithiins, as well as useful model compounds for spectro-

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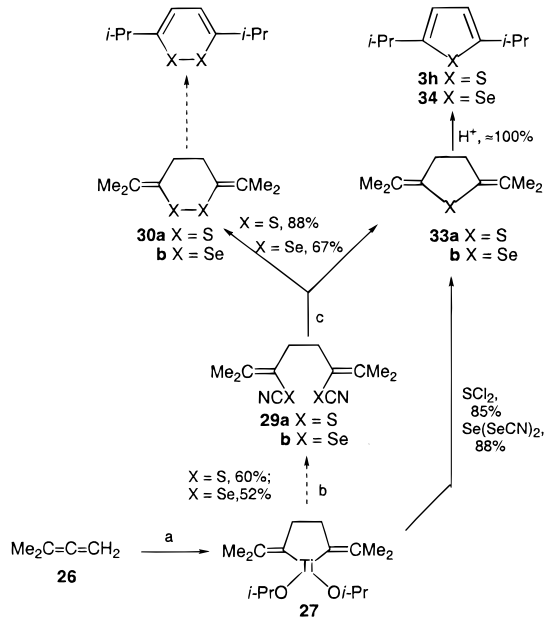
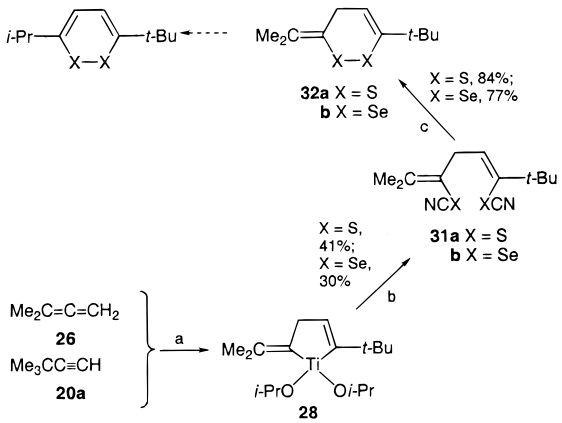
(18) Hideura, D.; Urabe, H.; Sato, F. *J. Chem. Soc., Chem. Commun.* **1998**, 271−272.

Scheme 7[a]



[a] (a) Ti(Oi-Pr)$_4$, *i*-PrMgCl. (b) (SCN)$_2$ or (SeCN)$_2$ [(XCN)$_2$], CH_2Cl_2. (c) Bu_4NF or SmI_2.

Scheme 8[a]

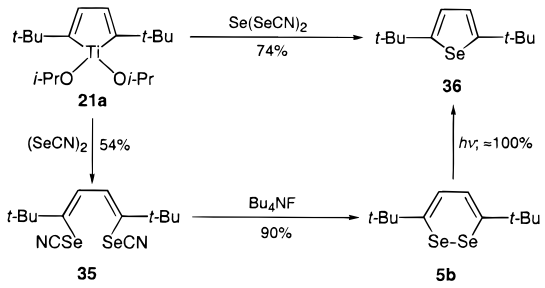


[a] (a) Ti(Oi-Pr)$_4$, *i*-PrMgCl. (b) (SCN)$_2$ or (SeCN)$_2$ [(XCN)$_2$], CH_2Cl_2. (c) Bu_4NF or SmI_2.

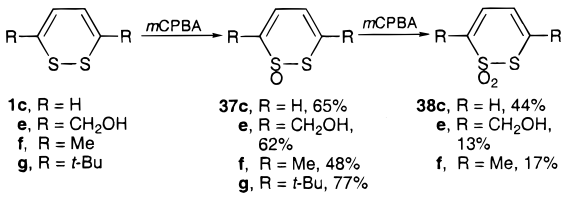
scopic comparison with 1,2-dithiins (see below). Schemes 6−8 work equally well with **21a**, **27**, and **28** using selenocyanogen ((SeCN)$_2$),[19a] giving 3,6-bis(*tert*-butyl)-1,2-diselenin (**5b**; 49%) from **20a** (**20a** → **21a** → **35** → **5b**; Scheme 9), **30b** from **26**, and **32b** from **20a**/**26**. An additional five-membered ring product, 2,5-bis(isopropylidene)selenolane (**33b**), formed along with **30b** from **29b**, can be prepared in 88% yield via reaction of **27** with selenium diselenocyanate (Se(SeCN)$_2$).[19b] Although it is not formed as a side product from **29a**, 2,5-bis(isopropylidene)thiolane **33a**[19c] can be prepared in 85% yield via reaction of **27** with sulfur dichloride. Both **33a** and **33b** are quantitatively isomerized to heterophenes **3h**[19d] and **34** with a trace of acid.[19c] Visible light converts **5b** into 2,5-di-*tert*-butylselenophene (**36**), which can also be prepared from **21a** and Se(SeCN)$_2$.

Two-Electron Atom-Transfer Oxidation of 1,2-Dichalcogenins. Oxidation of 1,2-dithiins is relatively straightforward

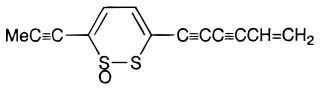
Scheme 9



Scheme 10



using *m*CPBA or other oxidants. The resulting 1,2-dithiin *S*-oxides are pale yellow compounds which can be reduced back to the 1,2-dithiins.[20,21] A 1,2-dithiin *S*-oxide, thiarubrine J (**37a**),



37a

occurs naturally.[2c] Because of the instability of 1,2-dithiins toward sulfur extrusion under both thermal and photochemical conditions, oxidation of **1c**,**e**−**g** was examined using *m*CPBA at 0 °C in the dark, giving thermally unstable *S*-oxides **37c**,**e**−**g** in 48−86% yields (Scheme 10). *S*-Oxide formation is accompanied by a hypsochromic shift in the UV−vis spectra (e.g., from λ_{max} 406 to 314 nm for **1g** → **37g**). Moreover, the patterns of absorptions in the ^{1}H and ^{13}C NMR spectra of **37** reflect the loss of symmetry compared to **1**. All peaks in the ^{1}H NMR spectra of **37** are deshielded relative to those in **1**. The IR spectra of **37c**,**f** show the characteristic thiosulfinate S═O peak at 1072−4 cm^{-1}. Further *m*CPBA oxidation of *S*-oxides **37c**,**e**,**f** gave cyclic thiosulfonates **38c**,**e**,**f**, in yields up to 66%,[22] with expected spectra (IR (**38c**,**f**): SO_2 peaks, 1127−9 and 1306−1326 cm^{-1}; UV−vis (**38c**): λ_{max} 316 nm; ^{1}H and ^{13}C NMR spectra of **38** are shielded and deshielded, respectively, compared to those of **37**). Photolysis (300 nm) of **38c** in CD_3OD at −30 to 25 °C gave thiophene.[23]

1,2-Diselenins **5a** and **5b** were oxidized by *m*CPBA to give 1,2-diselenin 1-oxides (selenoseleninates)[24] **39a** and **39b**; analogous oxidation of 2-selenathiin **5c** gave 2-selenathiin 2-oxide **39c** (eq 1). Due to the instability of **39a**−**c** at room temperature,

(1)

the oxidations were performed in NMR tubes at −40 °C in

(19) (a) Meinke, P. T.; Krafft, G. A.; Guram, A. *J. Org. Chem.* **1988**, *53*, 3632−3634. (b) Barton, D. H. R.; Bridon, D.; Herve, Y.; Potier, P.; Thierry, J.; Zard, S. Z. A. *Tetrahedron* **1986**, *42*, 4983−4990. (c) Kates, M. J.; Schauble, J. H. *J. Org. Chem.* **1994**, *59*, 494−496. (d) Miki, Y.; Sugimoto, Y.; Yamadaya, S. *Nippon Kagaku Kaishi* **1993**, 79.

(20) Schroth, W.; Hintzsche, E.; Spitzner, R.; Ströhl, D.; Sieler, J. *Tetrahedron* **1995**, *51*, 13247−13260.

(21) Wang, Y.; Koreeda, M. *Synlett* **1996**, 885−886.

(22) A stable 1,2-dithiin 1,1-dioxide has been prepared by a Diels−Alder route: Bard, M.; Meslin, J. C.; Quiniou, H. *J. Chem. Soc., Chem. Commun.* **1973**, 672.

Table 1. Selected Spectroscopic Data for 1,2-Dithiins, 1,2-Diselenins, and Related Compounds

compound	NMR[i] Hα, Hα′ (Cα, Cα′)	NMR[i] Hβ, Hβ′(Cβ, Cβ′)	NMR ^{77}Se	UV−vis (ϵ)[h]
1,2-dithiin (**1c**)	6.07 (119.43)[a]	6.29 (129.74)[a]		452 (90)
thiophene (**3c**)	7.18 (125.6)[j]	6.99 (127.3)[j]		231 (7410)
1,2-diselenin (**5a**)	6.10 (112.78)[b]	6.27 (132.22)[b]	119	504 (107)
selenophene	7.88 (131.0)	7.23 (129.8)	565	249 (5620)
2-selenathiin (**5c**)	(113.76, 119.25)	(131.97, 129.67)	228	488
3,6-di-*tert*-butyl-1,2-dithiin (**1g**)	(146.52)	6.16 (122.02)		406 (175)
2,5-di-*tert*-butylthiophene (**3g**)	(154.21)	6.58 (120.18)		296 (850)
3,6-di-*tert*-butyl-1,2-diselenin (**5b**)	(144.18)	6.22 (124.69)	165	448 (235)
2,5-di-*tert*-butylselenophene (**36**)	(162.40)	6.75 (122.37)	565	262 (1400)
3,6-dimethyl-1,2-dithiin (**1f**)	(128.47)	6.05 (125.93)		422 (47)
3,6-dimethyl-1,2-diselenin (**5f**)	(123.71)	6.06 (128.67)	206	478 (155)
3,6-diisopropyl-1,2-dithiin (**1h**)	(142.06)	6.08 (122.78)		420
2,5-diisopropylthiophene (**3h**)	(150.22)	6.57 (120.97)		
3,6-bis(trimethylsilyl)-1,2-dithiin (**1i**)	(139.08)	6.43 (135.47)		478 (520)
2,5-bis(trimethylsilyl)thiophene (**3i**)	(140.3)	6.98 (134.6)		235 (9951)
3-*tert*-butyl-6-isopropylidene-1,2-dithiacyclohex-3-ene (**32a**)		6.12		316 (1460)
3-*tert*-butyl-6-isopropylidene-1,2-diselenacyclohex-3-ene (**32b**)		6.08	287, 415	414 (190)
1,2-dithiin 1-oxide (**37c**)	7.18, 7.03−7.08[c]	6.98, 7.03−7.08[c]		
1,2-dithiin 1,1-dioxide (**38c**)	7.14, 6.83[d]	6.76, 6.94[d]		316
thiophene 1,1-dioxide	6.59 (131.1)[j]	6.79 (129.3)[j]		289 (1230)
1,2-diselenin 1-oxide (**39a**)	7.24, 6.87[e]	7.11, 6.95[e]		
2-selenathiin 2-oxide (**39c**)	7.22, 6.81	7.36, 7.01		
3,6-di-*tert*-butyl-1,2-dithiin 1-oxide (**37g**)	(145.70, 138.42)	6.69, 6.64[f] (120.01, 116.21)		314
3,6-di-*tert*-butyl-1,2-diselenin 1-oxide (**39b**)	(144.70, 139.43)	6.79, 6.56[g] (123.75, 119.56)		266

[a] $J_{\alpha\beta} = 9.3$, $J_{\beta\beta'} = 5.8$, $J_{\alpha\alpha'} = 1.6$, $J_{\alpha\beta'} = -0.1$. [b] $J_{\alpha\beta} = 9.1$, $J_{\beta\beta'} = 5.1$, $J_{\alpha\alpha'} = 1.9$. [c] $J_{\alpha\beta} = 9.5$, $J_{\beta\beta'} = 4.7$, $J_{\alpha\alpha'} = 1.1$. [d] $J_{\alpha\beta} = 10$, $J_{\beta\beta'} = 6.5$, $J_{\alpha\alpha'} = 1.0$. [e] $J_{\alpha\beta} = 10.2$, $J_{\beta\beta'} = 7.2$, $J_{\alpha\alpha'} = 0.9$. [f] $J_{\beta\beta'} = 7.7$. [g] $J_{\beta\beta'} = 8$. [h] Long wavelength maxima only. [i] Ring positions only. [j] From refs 28e, f.

CD_2Cl_2, and the ^{1}H and ^{13}C NMR spectra were obtained immediately. In the case of **5b**, formation of the thermally very unstable *Se*-oxide was accompanied by a hypsochromic shift in the UV spectrum from λ_{max} 448 to 266 nm. The patterns of absorptions in the ^{1}H NMR spectra (and ^{13}C spectra, in the case of **39b**) reflect the loss of symmetry in **39a**,**b** compared to that in **5a**,**b**. All peaks in the ^{1}H NMR spectra of **39a**,**b** are shifted downfield relative to the respective peaks in **5a**,**b**.

Spectroscopic Data for 1,2-Dichalogenins and Related Compounds. Spectroscopic data for 1,2-dichalogenins **1c**,**f**−**i**, **5a**−**e** their oxides **37c**,**g**, **38c**, **39a**−**c**, and related compounds are summarized in Table 1. Comparison of NMR spectroscopic data for 1,2-dithiins **1** with those for identically substituted thiophenes **3** shows that both the α- and β-protons are significantly shielded in **1** compared to **3**, reflecting the thiophene aromatic ring current. The α-carbons in **3** are slightly shielded, while the β-carbons are deshielded compared to those in **1**. There is a striking bathochromic shift in the UV spectra of **1** compared to those of **3**.[25a] When ^{1}H NMR and UV spectroscopic data for 1,2-diselenins **5** are compared with those for analogous selenophenes, the differences are even greater than those seen comparing **1** and **3**. The differences between pairs of 1,2-dichalcogenins (e.g., **1** and **5**) are much less pronounced than between pairs of heterophenes (e.g., **3g** and **36**). The H−H coupling constants for **1c** and **5a** are quite similar.

The UV−vis spectra of oxides **37c**, **39a** show loss of long wavelength absorption compared to the UV spectra of parent 1,2-chalcogenins **1c**, **5c**, respectively. The NMR spectra of **37c**, **39a** show significant deshielding of the ring protons compared with those of **1c, 5c**.[25d,e] Oxidation of thiophenes and selenophenes to their respective 1-oxides and 1,1-dioxides results in 0.2−0.8 ppm shielding of the ring protons in the ^{1}H NMR spectra (see Table 1). The NMR shielding effects seen on oxidation of the chalcogenophenes are opposite to expectations based on the relative electronegativities of Se/SeO and S/SO/SO_2 and are attributed to loss of aromaticity on oxidation.[25b−e] Of particular interest on going from 1,2-dichalcogenins **1** to **5** is replacement of the "spectroscopically silent" sulfur with selenium. The ^{77}Se NMR peaks in **5a**−**e** (δ = 119, 165, 228, 177/185, 206, respectively) are shielded compared to those in model compounds (PhSeSePh (δ = 464), MeSeSeMe (δ = 275), PhSeSPh (δ = 526),[26] **30b** (δ = 326), **32b** (δ = 287/415), 2,4-di-*tert*-butylselenophene[25g] (δ = 552), **36** and selenophene (both δ = 565)).

To understand the basis for the unusual ^{77}Se NMR chemical shifts of compounds **5a**−**e**, the shifts were calculated by the gauge-independent atomic orbital (GIAO) method[27a] with the basis set 6-311+G(2d,p), which proved to be useful in chemical shift calculations[27b,c] by means of density functional theory (DFT). The B3LYP exchange-correlation hybrid functional was used in all (either GIAO or DFT) calculations. Calculations of Se-chemical shifts of various compounds performed by GIAO-DFT,[27d] GIAO-SCF and GIAO-MP2[27e] resulted in errors of about 70−100 ppm in general, that is, a small percentage of the ∼3000 ppm selenium chemical shift range, as shown in Table 2. However, the coincidence of the theoretical and experimental shifts for the parent compounds is accidental

(23) In contrast, unsaturated six-membered ring sultones undergo electrocyclic ring opening on photolysis: King, J. F.; Mayo, P. D.; Morkved, E.; Sattar, A. B. M.; Stoessl, A. *Can. J. Chem.* **1963**, *41*, 100−107.

(24) A limited number of selenoseleninates are known: (a) Reich, H. J.; Hoeger, C. A.; Willis, W. W., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 2936−2937. (b) Reich, H. J.; Hoeger, C. A.; Willis, W. W., Jr. *Tetrahedron* **1985**, *41*, 4771−4779. (c) Ishii, A.; Matsubayashi, S.; Takahashi, T.; Nakayama, J. *J. Org. Chem.* **1999**, *64*, 1084−1085.

(25) (a) While the long wavelength maxima of **1c** compared to saturated cyclic disulfides is unusual, it is noteworthy that a bicyclic dithiirane also has an absorption at 452 nm (ϵ 104): Ishii, A.; Akasawa, T.; Maruta, T.; Nakayama, J.; Hoshino, M.; Shiro, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 777−779. (b) Umezawa, T.; Sugihara, Y.; Ishii, A.; Nakayama, J. *J. Am. Chem. Soc.* **1998**, *120*, 12351−12352. (c) Nakayama, J.; Yu, T.; Sugihara, Y.; Ishii, A. *Chem. Lett.* **1997**, 499−500. (d) Nakayama, J.; Nagasawa, H.; Sugihara, Y.; Ishii, A. *J. Am. Chem. Soc.* **1997**, *119*, 9077−9078. (e) Nagasawa, H.; Sugihara, Y.; Ishii, A.; Nakayama, J. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1919−1926. (f) Oxidation of thiophene to its 1,1-dioxide results in a *bathochromic* shift in the UV λ_{max} from 231 to 288 nm.[25d] (g) The spectroscopic properties of **36** are very similar to those reported for the isomeric 2,4-di-*tert*-butylselenophene.[25b]

Table 2. GIAO-DFT B3LYP/6-311+G(2d,p) Calculated and Experimental ^{77}Se NMR Chemical Shifts Relative to Dimethyl Selenide (ppm; in $CDCl_3$)

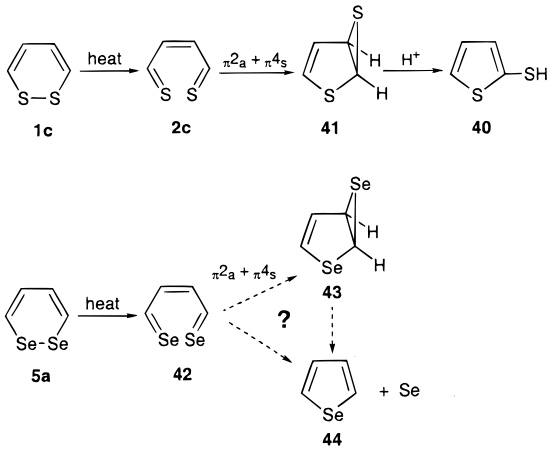
compound	symmetry	calcd chemical shifts a[a]	calcd chemical shifts b[b]	experimental chem. shifts
1,2-diselenin (**5a**)	C_2	56	119	119
2-selenathiin (**5c**)	C_1	192	228	228
3,6-di-*tert*-butyl-1,2-diselenin (**5b**)	C_2	156	- -	165
3-hydroxymethyl-6-methyl-1,2-diselenin (**5d**)	C_1	87, 193 145, 190	138, 250[c] 179, 232[d]	178, 185[e]
3,6-dimethyl-1,2-diselenin(**5f**)	C_2	178	222	206
MeSeSeMe	C_2	334	367	275

[a] Using the B3LYP/6-31+G(d) calculated geometry. [b] Using the MP2/6-311+G(2d,p) calculated geometry. [c] Rotation about the C−O bond dramatically alters the difference in ^{77}Se chemical shift values from 112 ppm, as shown, to 8 ppm. [d] These chemical shifts are for another conformer, 1.7 kcal/mol higher in energy than the conformer of minimum energy whose chemical shifts are reported first. [e] 3,6-Bis(hydroxymethyl)-1,2-diselenin, whose preparation will be described elsewhere, shows a ^{77}Se NMR peak in MeOD at 140 ppm (E. Block and F. Tries, unpublished results).

because of the approximations inherent in the theoretical model and the marked gas-to-liquid shift not considered in the calculations. The calculations, in agreement with experiment, show that the ^{77}Se shifts of selenium-containing 1,2-dichalcogenins are high-field-shifted relative to those of acyclic diselenides. The ^{77}Se shifts calculated with MP2-optimized geometries are closer to the experimental values than those calculated with DFT geometries. The DFT geometries differ from the MP2 geometries mainly by longer bonds to selenium and less puckering of the ring. However, there are no other experimental studies, as yet, independently establishing the geometries of the 1,2-diselenins and 2-selenathiins.[27f]

Mass spectra of 1,2-dichalcogenins show strong parent ions, indicating loss of an electron to give particularly stable radical cations. Comparison of the UV−vis maxima of 1,2-dithiins **1c**,**f**−**i** (457, 422, 406, 420, 478 nm, respectively) reveals an interesting hypsochromic shift for **1f**−**h**, most pronounced with **1g**, and a bathochromic shift for **1i**, relative to that for **1c**. The hypsochromic shift in **1g** may be a consequence of steric effects on ring conformation since 3,6-bis(2-hydroxy-2-propyl)-1,2-dithiin shows a UV−vis maxima (412 nm) which is shifted to shorter wavelengths compared to that for **1e** (428 nm).[28] The UV−vis maxima of **5a** (504 nm) and **5c** (488 nm) are bathochromically shifted compared to that of **1c**, as are those of **5b** (448 nm) and **5e** (478 nm) compared to those of **1g** and **1f**.[29] Bathochromic UV shifts are observed as the exocyclic positions of the two double bonds in **30a**,**b** are independently changed to endocyclic, for example, in the series **30a**, **32a** (both 320 nm) → **1g** and **30b** (390 nm) → **32b** (414 nm) → **5b**. There is little change in the positions of the olefinic C−H ^{1}H and ^{13}C chemical shifts in **32a**,**b** compared to those in **1g** and **5b**, consistent with the nonaromatic character of **5b**. In summary, similarities in the spectroscopic data for 1,2-diselenins **5a**/**5b** and 1,2-dithiins **1c**/**1g**, respectively, suggest structural similarities, for example, twist conformations with ϕ(CXXC) ≈ 50° and ϕ(CCCC) ≈ 30°.[9]

Scheme 11



Thermal Decomposition of 1,2-Dichalcogenins. On GC−MS with an injection port at 150 °C, 1,2-dithiin (**1c**) gives a single peak with the molecular ion (*m*/*z* 114) as base peak. When the injection port temperature is increased to 300 °C, the dithiin peak is replaced by another peak with slightly shorter retention time whose *m*/*z* 114 M^+ indicates that it is isomeric with **1c**. At intermediate injection port temperatures mixtures of the two compounds are seen along with traces of a longer retention time compound with *m*/*z* 230 (corresponds to 2 × 114−2). The isomer, generated by flash vacuum pyrolysis at 500 °C, was isolated and identified as 2-thiophenethiol (**40**) by comparison with an authentic sample;[30] the *m*/*z* 230 product is the corresponding disulfide. Presumably, heating causes electrocyclic ring opening of **1c** to (*Z*)-2-butene-1,4-dithial (**2c**) which cyclizes to 2,6-dithiabicyclo[3.1.0]hex-3-ene (**41**), previously isolated upon low-temperature photolysis of **1c** and shown to give **40** with traces of acid[10a] (Scheme 11). Thermolysis may have a different course than photolysis, since photochemical formation of **41** is accompanied by formation of thiophene and elemental sulfur, neither of which is seen during thermolysis of 1,2-dithiin **1c**. The photochemistry of 1,2-dithiins will be discussed in more detail elsewhere. Pyrolysis of 1,2-diselenin (**5a**) in a 200−300 °C GC−MS inlet, as described for **1c**, gave selenophene (**44**) as the only identified organic product. (*Z*)-2-Butene-1,4-diselenal (**42**) may be an intermediate, giving **44** directly or via **43** (Scheme 11).

Electrochemical Oxidation of 1,2-Dichalcogenins. While electrochemical reduction of 1,2-dithiins has been examined (the polarographic half-wave reduction potential of 1,2-dithiin itself, $E_{1/2}$ = −0.67 V in Et_4NI/90% EtOH, is similar to that for diphenyl disulfide),[13a] electrochemical oxidations of 1,2-dithiins have not been previously studied. Electrochemical oxidation of 1,2-dithiin, **1c**, its derivatives **1a**, **d**−**h** and selenium analogues **5** was studied by the technique of cyclic voltammetry in CH_2Cl_2 as well as in CH_3CN. Compounds **1d**−**g** showed a reversible oxidation followed by an irreversible oxidation at higher potential. A typical cyclic voltammogram is shown in Figure 1 for **1d**.

(26) Luthra, N. P.; Odom, J. in *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1986; Vol. 1, pp 189−241.

(27) (a) Cheeseman, J. R.; Trucks G. W.; Keith, T. A.; Frisch J. *J. Chem. Phys.* **1996**, *104*, 5497−5509 and references therein. (b) Chesnut, D. B. *Rev. Comput. Chem.* **1996**, *8*, 245−297. (c) Wiberg, K. B., *J. Comput. Chem.* **1999**, *12*, 1299−1303. (d) Schreckenbach, G.; Ruiz-Morales, Y.; Ziegler, T. *J. Chem. Phys.* **1996**, *104*, 8605−8612. (e) Buhl, M.; Thiel, W.; Fleischer, U.; Kutzelnigg, W. *J. Phys. Chem.* **1995**, *99*, 4000−4007. (f) The microwave spectra of the ^{80}Se and ^{78}Se isotopomers of **5c** have been recently assigned with a pulsed-beam Fourier transform microwave spectrometer: Gillies, C. W., Nathan, C., Gillies, J. Z., Block, E., Birringer, M. Shan, Z., unpublished studies.

(28) (a) Personal communication, W. Schroth. (b) See Note Added in Proof in the accompanying paper (ref 12) for details on the X-ray structure of **1g**.

(29) 1,2-Diselenane UV spectra: Djerassi, C.; Wolf, H.; Bunnenberg, E. *J. Am. Chem. Soc.* **1962**, *84*, 4552−4561.

(30) Jones, E.; Moodie, I. M. In *Organic Syntheses*; Wiley & Sons: New York, 1988; Collect. Vol. VI, pp 979−980.

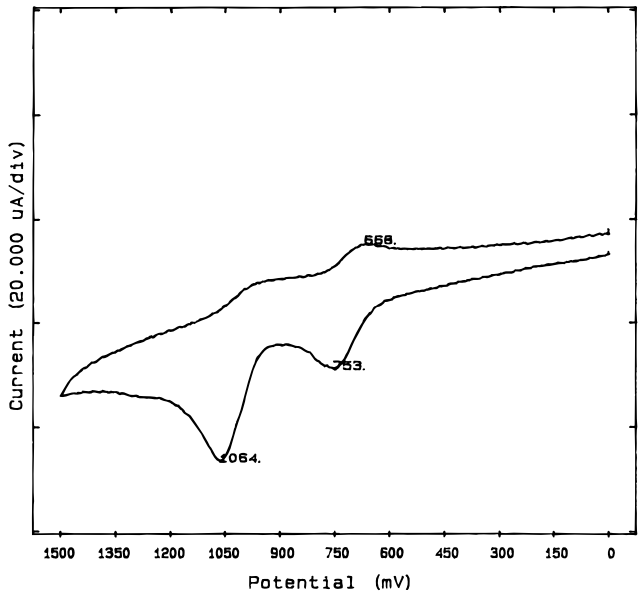


Figure 1. Cyclic voltammogram of 3,6-diphenyl-1,2-dithiin **1d** from 0 V → 1.5 V → 0 V. Compound **1d** was analyzed at 1.16 mM in 0.1 M *n*-Bu_4NPF_6/CH_3CN versus Ag/0.1 M $AgNO_3$ in CH_3CN with a Teflon-jacketed planar platinum working electrode. The scan was obtained at 200 mV/s.

There are major oxidations at 0.747 and 1.036 V. The oxidation at 0.747 V corresponds to a reduction at 0.700 V. There are additional weak oxidations at −0.432 and −1.024 V, as well as weak reductions at −0.156 and −0.677 V and a strong reduction at −1.710 V. 1,2-Dithiin (**1c**) showed a reversible oxidation peak, but no additional oxidation peak was observed up to a potential of 1.6 V. Two irreversible oxidation peaks were observed for thiarubrine A, **1a**. Selenium analogues **5** showed similar behavior, provided that glassy carbon was used as the working electrode. Erratic behavior was observed using platinum as the working electrode in contrast to the reproducible and well-defined cyclic voltammetric behavior of the 1,2-dithiins **1**. Parent 1,2-diselenin, **5a**, showed a markedly reduced cathodic peak associated with the oxidation at 0.53 V and an ill-defined irreversible second oxidation peak at ∼1.3 V. However, the cathodic peak currents corresponding to the oxidation at 0.61 V for **5b** and 0.57 V for **5e** were much higher and the second oxidation peaks at 0.99 and 1.1 V, respectively, better defined. Table 3 lists the peak potentials for these oxidations versus a Ag/0.1 M $AgNO_3$ in CH_3CN reference electrode.

Since 1,2-dithiins are known to decompose to thiophenes, the cyclic voltammograms of **3a** and **d** were also measured. In both CH_3CN and CH_2Cl_2 **3d** showed an apparently reversible oxidation with the peak potentials listed in Table 3. In CH_2Cl_2, **3a** shows an irreversible oxidation with a peak potential of 1.34 V versus Ag/0.1 M $AgNO_3$ in CH_3CN. To ascertain the HOMO energies for 1,2-dithiins **1c**, **e**−**h**, their photoelectron spectra were determined.[12] The lowest energy ionization potentials measured were 8.16, 7.78, 8.01, 7.65, and 7.67 eV, respectively, for these compounds. The ionization potentials for these compounds do not linearly correlate with their oxidation potentials. The lowest ionization potentials for 1,2-diselenins **5a**, **5b**, and **5e** were 7.93, 7.52, and 7.64 eV, respectively.

To provide more insight into the apparently reversible first oxidation of **1c**−**h**, the cyclic voltammetric behavior of **1d** and **1f** was studied in more detail (Figures 2 and 3, respectively). Cyclic voltammograms were measured over a range of scan rates (10−2000 mV/s) and concentrations (1.68−6.72 mM for **1d**, and 0.7−2.9 mM for **1f**). The data in both cases can be

Table 3. Peak Potentials for Compounds 1**a**,**c**−**g**,[a] 3**a**,**d**,[a] 5**a**,**b**,**e**,[b] Ph_2S_2,[a] and Ph_2Se_2[b] Determined by Cyclic Voltammetry

	CH_2Cl_2		CH_3CN		
cmpd	E_{P1},V	E_{P2},V	E_{P1},V	E_{P2},V	Ip[c], eV
1a	1.04	1.36	0.96	1.26	
1c	0.85	1.40	0.70	*d*	8.16
1d	0.80	1.23	0.75	1.04	
1e	0.82	1.13	0.58	1.23	8.01
1f			0.65	1.21	7.78
1g			0.61	0.99	7.65
1h			0.68	1.22	7.67
3a	1.34				
3d	1.14		1.04		
5a			0.53	1.3[e]	7.93
5b			0.61	0.99	7.52
5e			0.57	1.1	7.64
Ph_2S_2			1.29		
Ph_2Se_2			1.07		

[a] Peak potentials measured at a Pt electrode with scan rate of 100 mV/s versus a Ag/0.1 M $AgNO_3$ in CH_3CN reference electrode. [b] Peak potentials measured at a glassy carbon electrode with a scan rate of 100 mV/s versus a Ag/0.1 M $AgNO_3$ in CH_3CN reference electrode. [c] Lowest ionization potential determined by photoelectron spectroscopy. [d] No additional oxidation peak is observed up to +1.6 V. [e] Broad, poorly resolved peak.

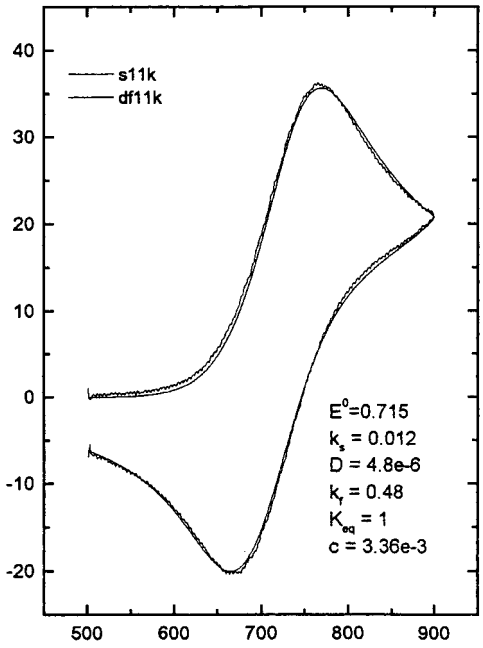
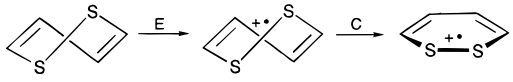


Figure 2. Experimental (wavy line) and simulated (smooth line) data for the reversible oxidation of 3,6-diphenyl-1,2-dithiin **1d**. Compound **1d** was analyzed at 3.36 mM in 0.1 M *n*-Bu_4NPF_6/CH_3CN versus Ag/0.1 M $AgNO_3$ in CH_3CN with a Teflon-jacketed planar platinum working electrode. The scan was obtained and simulated at 1 V/s. The axes are μA vs mV.

satisfactorily fitted in terms of an EC mechanism in which a chemical step follows the one-electron-transfer step. The parameters which provide the best fit are $E^{0\prime} = 0.716 \pm 0.003$ V, $k_s = 0.014 \pm 0.006$ cm/s, and $k_f = 0.318 \pm 0.027$ s^{-1} for **1d** and $E^{0\prime} = 0.575 \pm 0.001$ V, $k_s = 0.032 \pm 0.00$ cm/s, and $k_f = 0.468 \pm 0.033$ s^{-1} for **1f**, where k_s is the standard heterogeneous electron-transfer rate constant, and k_f is the first-order rate constant for the following chemical reaction. Typical



(2)

fits of the experimental and simulated cyclic voltammograms

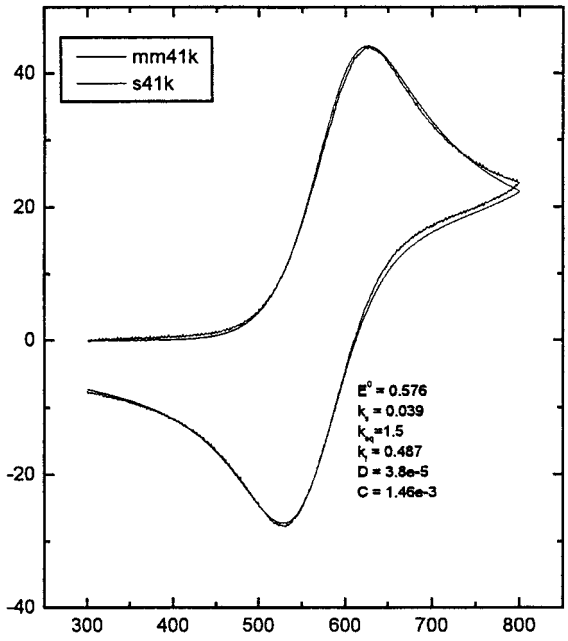


Figure 3. Experimental (wavy line) and simulated (smooth line) data for the reversible oxidation of 3,6-dimethyl-1,2-dithiin **1f**. Compound **1f** was analyzed at 1.46 mM in 0.1 M *n*-Bu_4NPF_6/CH_3CN versus Ag/0.1 M $AgNO_3$ in CH_3CN with a Teflon-jacketed planar platinum working electrode. The scan was obtained and simulated at 1 V/s. The axes are μA vs mV.

for **1d** and **1f** are shown in Figures 2 and 3, respectively; for **1d**, 1 V/sec and $c = 3.36 \times 10^{-3}$ M, while for **1f**, 1 V/sec and $c = 1.46 \times 10^{-3}$ M.

To investigate the nature of the C step in the theoretical fit of the cyclic voltammetric data, calculations were carried out on **1c**, **1f**, **5a** and their corresponding radical cations. The geometries were calculated by second-order many-body perturbation theory denoted as MP2 for closed shell and UMP2 for open shell systems. The inner core was kept frozen in the calculations. All electrons were considered in the calculations in all cases. To allow a good and consistent description of the sulfur bonds the valence double-ζ basis set used was augmented by a set of diffuse functions and polarization functions on non-hydrogen atoms (MP2/6-31+G*). For selenium it was necessary to employ a valence triple-ζ basis set with a diffuse function set added to non-hydrogen atoms and a set of polarization functions added to all atoms (MP2/6-311+G**). The minimum for **5a** was confirmed by frequency calculations with Pople's small split valence basis set. The calculations were performed by the GAUSSIAN 94 suite of programs.[31] While the parent 1,2-dithiin (**1c**) and 1,2-diselenin (**5a**) are puckered (C_2-symmetry), the corresponding cation radicals are flattened or planar (C_{2v}-symmetry), depending on the level of theory used. In addition, the bonds involving the heteroatoms are contracted in the cation radicals relative to the uncharged compounds. However, the CC-bond alternation is essentially maintained in the cation radicals. The geometry of the minimum energy conformation of **1c** agrees very well with that determined in the gas phase by microwave spectroscopy[9a,12] as shown in Table 4. For example, the CSSC dihedral angle is 53.9° as determined by microwave spectroscopy and 54.8° computationally. Furthermore, the calculated ionization potentials for **1c** and **1f** are 8.16 and 7.96 eV, respectively, and the observed values for the lowest ionization potentials are 8.16 and 7.78 eV, respectively. Treatment of **1d** with anhydrous $AlCl_3$ in CH_2Cl_2 resulted in the formation of the corresponding radical cation. This species was characterized by EPR spectroscopy, showing a broad singlet with $g_{av} \approx 2.0019$.

Discussion of Electrochemical Results. The interplay of redox chemistry and conformational processes has received considerable attention. Oxidation of tetraarylethylenes show two reversible cyclic voltammetric peaks to afford the corresponding radical cations and dications.[32] X-ray crystallographic structural analysis shows the substantial geometry changes that occur on oxidation. For example, for tetraanisylethylene the dihedral angle about the ethylenic bond increases from 4° to 31° to 62° on going from the neutral alkene to its radical cation to its dication. Similar geometry changes occur on reduction of bianthrone derivatives to their corresponding radical anions.[33] The electrochemical behavior in this case is interpreted in terms of a square scheme in which the planar bianthrone is first reduced to the planar anion radical. This species undergoes a conformational change to the more stable twist form. Oxidation of the twisted radical anion gives the twisted bianthrone which equilibrates to its more stable planar form.

Anodic oxidation of cyclic tetraalkylhydrazines shows remarkable temperature dependence.[34] Thus, 1,2-dimethylhexahydropyridazine undergoes a reversible oxidation at room temperature but shows two oxidation peaks at low temperature. The isomer with both methyl groups equatorial is reversibly oxidized to the planar radical cation, and the conformer with one methyl group equatorial and the other axial is irreversibly oxidized to the same radical cation at higher potential. The difference in oxidation potentials for the two conformers is ascribed to differences in heterogeneous rate constants. The heterogeneous rate constant for oxidation of the equatorial, axial isomer is smaller than that for the equatorial, equatorial isomer owing to the larger geometry changes on oxidation of the former than the latter. A triangular reaction scheme has been proposed involving the equilibrating conformational isomers and the same radical cation from either isomer.[35] Recent cyclic voltammetric studies on various 5,6-dihydrobenzo[*c*]cinnoline derivatives have led to the conclusion that they undergo oxidation via an E_iE-DISP mechanism in which electron transfer occurs simultaneously with conformational change. Such a mechanism has also been suggested[36] for the reduction of cyclooctatetraene. These studies have the added complication of multiple electron transfer and disproportionation.

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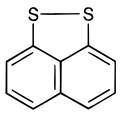
Table 4. Geometric Parameters for **1c**, **1f**, and **5a** and Their Cation Radicals[a]

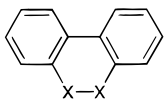
	1,2-dithiin (**1c**)		3,6-dimethyl-1,2-dithiin (**1f**)[b]		1,2-diselenin (**5a**)	
	uncharged (exp.)	cation radical	uncharged	cation radical	uncharged	cation radical
			Bond Length (Å)			
X−X	2.07 (2.05)	2.04	2.07	2.02	2.34	2.31
X−C	1.76 (1.76)	1.73	1.76	1.74	1.90	1.86
C═C	1.36 (1.35)	1.35	1.36	1.35	1.36	1.36
C−C	1.45 (1.45)	1.45	1.45	1.45	1.45	1.45
			Bond Angle (deg)			
X−X−C	97.8 (98.7)	106.4	98.3	107.7	94.1	102.2
X−C−C	122.0 (121.4)	128.1	119.5	123.7	123.5	130.3
C−C−C	123.9 (124.2)	125.4	125.3	127.6	125.8	127.5
			Torsion Angle (deg)			
C−X−X−C	54.8 (53.9)	6.3	56.6	14.2	52.1	0.0
X−X−C−C	−42.6 (−41.2)	−5.2	−43	−11.1	−42.4	0.0
X−C−C−C	1.6 (0.3)	0.8	1.5	1.2	1.3	0.0
C−C−C−C	28.0 (29)	2.3	28.4	5.8	31.1	0.0

[a] Experimental values ("exp.") from ref 9a; geometry optimized calculations using MP2/6-31+G* for **1c** and **1f** and MP2/6-311+G(d,p) for **5a**. The dihedral angle A−B−C−D is considered positive for a clockwise rotation of bond C−D with reference to bond A−B when viewed from atom B to atom C, and negative for a counterclockwise rotation. [b] For **1f** (**1f**$^{+\bullet}$), calculated value for C−Me = 1.50 (1.51) Å, for C−C−Me = 124.4° (124.7°), and for C−C−C−Me = 176.1° (177.6°).

The cyclic voltammetric studies on the 1,2-dithiins reported in this paper avoid many of the complications involved in the previously reported work. Single electron transfer without disproportionation may be studied. Furthermore, there is only one conformer. Theoretical calculations show that the preferred geometry of the radical cation of 1,2-dithiins is planar or flattened compared with the parent 1,2-dithiin, **1c**. Since the energy calculated for planar **1c** is 9.7 kcal/mol greater than for the twisted form, oxidation of planar **1c** is not believed to play a role in the observed electrochemistry. Oxidation of the twisted **1c** directly to the planar radical cation *concerted* with geometry change is not believed to occur because the heterogeneous rate constant is not small but rather in the normal range. Consequently, it is proposed, as shown in eq 2, that the oxidation of the twisted **1c** produces the corresponding radical cation (E step), and then this radical cation undergoes a geometry change (C step) to the more stable planar or flattened radical cation. As shown in Figures 2 and 3, simulation of the cyclic voltammetric data could be achieved using an EC mechanism.

The electrochemical oxidation potential reflects the energy difference between the planar radical cation and twisted parent **1c**. However, the ionization potential determined by photoelectron spectroscopy reflects the energy required to ionize the twisted **1c** without change in geometry. Consequently, one expects that the vertical ionization potential obtained by photoelectron spectroscopy would not correlate with the electrochemical oxidation potential. In support of this inference naphtho[1,8-*c*,*d*]-1,2-dithiole, **45a**, undergoes a reversible one-electron oxidation in acetonitrile with $E_{1/2}$, determined polarographically, of 0.95 V vs SCE[37] (0.68 V vs Ag/AgCl[38]) which is comparable, when corrected for the 300 mV difference between SCE and Ag/Ag(I) reference electrodes, to that of **1c**. However, the lowest ionization potential of **45a** (7.14,[39] 7.15[40] eV) is 1 eV lower than that of **1c**. Since the geometry of **45a** is constrained, it serves as a model for disulfide oxidation without conformational change. This comparison reveals that the electrochemical oxidation potential of **1c** is anomalously low as compared to its ionization potential. Although this result supports the notion that oxidation of **1c** results in a conformational change, the result could also be due to a solvent[41] or ion-pairing effect.





45a, X = S
b, X = Se

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The electrochemistry of disulfides has not been extensively studied.[42] Typically, disulfides undergo irreversible oxidation with oxidation potentials in the range of 0.9−1.5 V versus a Ag/Ag(I) reference electrode. For example, diphenyl disulfide oxidizes at a peak potential of 1.29 V in acetonitrile under the conditions used for 1,2-dithiins, as shown in Table 2. The half-wave oxidation potentials, E_2, for diaryl diselenides are reported in the range of 0.89−1.45 V.[43] Under the conditions used for **5a** and **b**, diphenyl diselenide shows a peak potential at 1.07 V, as shown in Table 3. However, **46**,[37,38] derivatives of **45a**,[44] and related compounds[42] generally show reversible one-electron oxidations in CH_3CN. The voltammograms of **45a** and **45b** show two two-electron oxidations.[45] The first oxidation occurs by an ECE mechanism in which a chemical step occurs between the two one-electron transfers. This chemical step is attack by water on the radical cation. At faster scan rates and in dry CH_3CN the radical cation is detected electrochemically, with **45a**$^{+\bullet}$ more reactive toward water than **45b**$^{+\bullet}$. Comparison of these systems with the parent 1,2-dithiin **1c** and 1,2-diselenin **5a** indicates that the parent heterocycles undergo oxidation at lower potential

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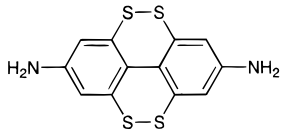
and the corresponding radical cations are more stable than their dibenzo[*c*,*e*] analogues. The radical cation of **1d**$^{+\bullet}$ was obtained on treatment of **1d** with anhydrous aluminum chloride in CH_2Cl_2. Bock and co-workers[46] reported that such treatment of compounds with ionization potentials of approximately 8 eV or less result in their oxidation. The EPR spectrum for **1d**$^{+\bullet}$ supports its structure, and the measured g_{av} value is in the range of that reported for other disulfide radical cations.[41] A number of stable planar π radical cations of heterocycles with formally a seven-electron count have been reported[47] and the planar, or nearly so, 1,2-dithiin and 1,2-diselenin radical cations appear to be related to them. Moreover, the radical cation of 1,4-dithiin bisannulated with bicyclo[2.2.2]octene has been shown computationally and by X-ray crystallographic studies to be planar.[47j] Persistent radical cations of 1,2-dithietes have also been reported,[46c,48] but it has been suggested[47a,e] that these species are 1,2,3-trithiolene radical cations, which are another example of seven-electron π radical cations.

The process associated with the second oxidation peak observed for **1c**−**e** in CH_2Cl_2 is unknown. Although the peak potential for **1d** in CH_3CN is the same as that for **3d**, these peaks are different in CH_2Cl_2; furthermore, this oxidation of **1d** is irreversible, but that for **3d** is reversible. Consequently, the second oxidation of **1d** in CH_3CN could be due to **3d**, but this is unequivocally ruled out in CH_2Cl_2. Comparison of the electrochemical behavior of **1d** and **3d** clearly eliminates the possibility that the reversible oxidation of **1d** is due to **3d** produced by rearrangement of **1d** to **3d** with loss of sulfur, which is a known photochemical reaction.[10a] The weak reduction peak for **1d** at −0.677 V in acetonitrile is ascribed to reduction of the disulfide moiety. This assignment is based on that reported for diphenyl disulfide[37] and **47**[49] which shows analogous reduction peaks.



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Experimental Section

General Methods. NMR spectra were obtained using Varian Gemini or XL-300 spectrometers at 300 MHz for ^{1}H, 75.3 MHz for ^{13}C and 57.1 MHz for ^{77}Se. Chemical shifts are reported in ppm relative to TMS or $CDCl_3$ (7.24 ppm; solvent unless otherwise indicated) for ^{1}H and $CDCl_3$ (77.0 ppm) for ^{13}C NMR spectra unless otherwise noted. ^{77}Se NMR spectra were obtained using the XL-300 spectrometer. Chemical shifts were measured with respect to MeSeSeMe (274 ppm) or Me_2Se (0.0 ppm) in $CDCl_3$. MS data were determined on either a Hewlett-Packard 5970 MSD (70 eV for EI) or a HP 5890 LC/GC/DI MS (70 eV for EI). For Se compounds, only the highest intensity peak of each multi-isotope cluster is given. IR spectra were obtained on a Perkin-Elmer model 1600 FT-IR. UV−vis spectra were obtained on a HP 8452. Elemental analyses were determined by NuMega Resonance Labs, Inc., San Diego, CA. THF and ethyl ether ("ether") were freshly distilled from sodium benzophenone ketyl. Hexane, methylene chloride, and ethyl acetate were distilled from CaH_2 before use. Baker silica gel (40 μm) was used for flash column chromatography. All flasks were dried by heating in an oven overnight and cooling under argon. Unless otherwise indicated, reactions were run under argon, and solutions were dried over anhydrous Na_2SO_4 or $MgSO_4$. Manipulations involving 1,2-dichalcogenins were done under dim or red light. Thiarubrine A was provided by Professor G. H. N. Towers and Jon Page of the University of British Columbia.

(*Z*,*Z*)-1,4-Bis(benzylthio)-1,3-butadiene (6a). To a solution of NaOMe, prepared by dissolving Na (2.44 g, 0.106 mol) in anhydrous MeOH (300 mL) at 0 °C, α-mercaptotoluene (34.8 g, 0.28 mol) was added dropwise with stirring, followed by 1,4-bis(trimethylsilyl)-1,3-butadiene (10 g, 0.052 mol). The resulting suspension was refluxed for 48 h and cooled to 0 °C, and the precipitate was collected by filtration and recrystallized from CH_2Cl_2−MeOH (1:5) to give the known[5] **6a** (12 g, 78%), mp 126−127.5 °C (lit.[5] 129 °C); ^{1}H NMR δ 7.0−7.7 (m, 10H), 6.31 (dd, J = 2.0, 6.5 Hz, 2H), 6.02 (dd, J = 2.0, 6.5 Hz), 3.88 (s, 4H); EI-MS, *m*/*z* 298 (M^+).

(*Z*,*Z*)-1,3-Butadiene-1,4-dithiol *S*,*S*-Diacetate (7). To a stirred suspension of Li ribbon (0.03 g, 4.3 mmol) in THF (20 mL) at −55 °C was slowly added 1-(*N*,*N*-dimethylamino)naphthalene (0.74 g, 4.32 mmol). The blue-green solution of LDMAN was stirred for 4 h and was then cooled to −75 °C. Compound **6a** (0.26 g, 0.88 mmol) in THF (2.5 mL) was added dropwise. The resulting solution was stirred for 0.5 h, quenched (MeOH), and then treated with excess acetyl chloride (1 mL). The mixture was warmed to room temperature and stirred for 15 min, solvent was removed in vacuo, and the residue was transferred to a separatory funnel with CH_2Cl_2 and water. The aqueous layer was extracted with ether (2 × 30 mL), the combined organic layers were washed with 10% HCl solution (3 × 20 mL) and brine (2 × 20 mL) and were dried, filtered, and concentrated. The solid residue was purified by flash column chromatography (1:9 ethyl acetate−hexanes) to give the known[5] **7** as a colorless solid (0.17 g, 96%), mp 148 °C, ^{1}H NMR δ 6.78 (AA′BB′, J = 11.2, 9.8, 1.2, −1.2 Hz, 2H), 6.37 (AA′BB′, J = 11.2, 9.8, 1.2, 1.1 Hz, 2H), 2.42 (s, 6H); ^{13}C NMR δ 190.48, 124.78, 120.94, 30.88; GC−MS *m*/*z* 202 (M^+).

1,2-Dithiin (1c). Compound **7** (5.96 g, 0.03 mol) was suspended in MeOH (350 mL) and treated with KOH (3.32 g, 0.06 mol) at 0 °C, giving a yellow solution. Iodine (12.78 g, 0.05) in MeOH (100 mL) was added slowly with stirring. The dark red solution was stirred for 20 min and then partitioned between pentane−ether (4:1 v/v, 200 mL) and water (100 mL). The aqueous layer was extracted with pentane−ether (4 × 50 mL), the combined organic layers were washed with $Na_2S_2O_3$ solution (2 × 150 mL), NH_4Cl (1 × 150 mL), brine (2 × 150 mL), and water (2 × 150 mL) and were dried and filtered. The solvent was removed by atmospheric pressure distillation using a Vigreux column to give the known[5] **1c** as a red-orange, heat- and light-sensitive oil (2.5 g, 73%), best stored in the dark at −78 °C until used: ^{1}H NMR δ 6.29 (H4,5, AA′XX′, J = 9.3, 5.6, 1.8, −0.1 Hz, 2H), 6.07 (H3,6, AA′XX′, J = 9.3, 5.8, 1.6, −0.1 Hz, 2H); ^{13}C NMR δ 129.74 (C4,5), 119.43 (C3,6); UV−vis (CH_2Cl_2) λ_{max} 452 (ϵ 90), 279 (ϵ 2000), and 248 (ϵ 1500); EI-GC−MS *m*/*z* 116 (M^+, 100%), 71 (84), 58 (28), 45 (64).

1,2-Dithiin 1-Oxide (37c). To a solution of **1c** (58 mg, 0.5 mmol) in CH_2Cl_2 (10 mL) was added *m*CPBA (150 mg, 57−86%) at 0 °C. The mixture was stirred at 0 °C for 30 min, warmed to 25 °C, concentrated, and chromatographed (5:2 hexane−EtOAc) giving **37c** as a light brown oil (43 mg, 65% yield); ^{1}H NMR δ 7.18 (H6, dd, J = 9.5, 1.1 Hz, 1H), 7.03−7.08 (H3,4, m, 2H), 6.98 (H5, J = 9.5, 4.7 Hz,

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1H); ^{13}C NMR δ 126.39, 121.70, 120.30, 119.11; CI LC−MS *m*/*z* 133 ($M^+ + 1$); IR (ν_{max}, neat) 1593 (m), 1515 (m), 1319 (m), 1074 (s; S═O) cm^{-1}.

1,2-Dithiin 1,1-Dioxide (38c). To a solution of **1c** (58 mg, 0.5 mmol) in CH_2Cl_2 (15 mL) was added *m*CPBA (450 mg, 57−86%) in CH_2Cl_2 (30 mL) at 0 °C. The mixture was stirred overnight at 25 °C, concentrated, and chromatographed (5:2 hexane−EtOAc) giving **38c** as a light brown oil (33 mg, 44% yield); ^{1}H NMR δ 7.14 (H6, dd, ^3J = 9.9, 1.0 Hz, 1H), 6.94 (H4, dd, ^3J = 10.5, 6.5 Hz, 1H), 6.83 (H3, dd, ^3J = 10.5, 1.0 Hz, 1H), 6.76 (H5, dd, ^3J = 9.9, 6.5 Hz, 1H); ^{13}C NMR δ 134.56, 128.79, 126.81, 121.54; IR (ν_{max}, neat) 3056 (m), 1590 (m), 1534 (m), 1326 (s; SO_2), 1127 (s; SO_2) cm^{-1}; UV−vis (CH_3CN) λ_{max} 316 nm.

***(Z,Z)*-1,4-Bis(benzylseleno)-1,3-butadiene (6b).** A suspension of dibenzyl diselenide (2.0 g, 5.9 mmol) in EtOH (25 mL) at 0 °C was treated with $NaBH_4$ (0.88 g, 23.6 mmol) in small portions, 1,4-bis-(trimethylsilyl)-1,3-butadiene (**1b**; 0.57 g, 2.94 mmol) was added, and the mixture was refluxed for 4 h, cooled to 0 °C, and filtered. The precipitate was dissolved in CH_2Cl_2, filtered, concentrated, washed with EtOH, and dried, giving **6b** (0.92 g, 80%), as off-white plates; mp 124−125 °C; ^{1}H NMR δ = 3.92 (s, 4H), 6.44 (dd, 2H, $^3J_{cis}$ = 7 Hz, ^5J = 1.9 Hz), 6.52 (dd, $^3J_{cis}$ = 7 Hz, ^5J = 1.9 Hz, 2H), 7.2 (m, 10H); ^{13}C NMR δ 30.15, 124.16, 127.01, 128.41, 128.59, 128.85, 138.44; ^{77}Se NMR δ 315; MS (70 eV) *m*/*z* 394 (M^+). Anal. Calcd for $C_{18}H_{18}Se_2$: C, 54.83; H 4.60. Found: C, 54.30; H, 4.75.

1,2-Diselenin (5a). To liquid NH_3 (70 mL) in a 100 mL three-necked flask at −78 °C was added **6b** (0.98 g, 2.8 mmol) followed by lithium (0.2 g, 28 mmol) in small pieces. The blue solution was stirred for 1.5 h at −60 °C, quenched (MeOH), and evaporated. Under argon the residue was dissolved in degassed aqueous 10% KOH solution (150 mL) which was extracted with degassed hexane (3 × 20 mL) to remove toluene. The aqueous solution was then covered with hexane (70 mL), oxygen was carefully bubbled through the solution until the hexane phase turned red. The extraction process was repeated twice with fresh hexane (2 × 70 mL). After drying the hexane extract, hexadecane (15 mL) was added, hexane was evaporated (water pump vacuum, 15 °C), $CDCl_3$ (2 mL) was added, and the volatiles were transferred at 0.02 Torr to a liquid nitrogen cooled "flash distillation" trap.[8b] Yield of **5a**, 68% (deep red solution; by NMR with 1,4-dioxane standard); ^{1}H NMR δ 6.10 (m, 2H, H3,6), 6.27 (m, 2H, H4,5, AA′BB′ multiplets with $^3J_{3,4/5,6}$ = 9.1, $^4J_{3,5/6,4}$ = 0, $^3J_{4,5}$ = 5.1, $^5J_{3,6}$ = 1.9 Hz); ^{13}C NMR δ 112.78 (C3,6), 132.22 (C4,5); ^{77}Se NMR δ 119 (vs Me_2Se); UV−vis (hexane) λ_{max} = 504 (ϵ 107), 312 (ϵ 1294), 234 (ϵ 1189), 214 (ϵ 1076) nm; GC−MS (70 eV) *m*/*z* 212 (M^+; 57%), 132 (100%).

1,2-Diselenin 1-Oxide (39a). *Due to the instability of the title compound, the following manipulations were conducted at −50 to −20 °C.* A solution of **5a** (∼3 mg) in CD_2Cl_2 (0.7 mL) and 1,4-dioxane as internal standard (4.7 mg) were added to an NMR tube, cooled to −50 °C, treated with *m*CPBA (∼4 mg), and shaken to achieve homogeneity; ^{1}H NMR (CD_2Cl_2, −38 °C) δ 6.87 (dd, ^3J = 10.2 Hz, ^5J = 0.9 Hz, SeC*H*═CH, 1H); 6.95 (dd, ^3J = 10.2, 7.2 Hz, SeCH═C*H*, 1H); 7.11 (dd, ^3J = 10.2, 7.2 Hz, Se(O)CH═C*H*, 1H); 7.24 (dd, ^3J = 10.2 Hz, ^5J = 0.9 Hz, Se(O)C*H*═CH, 1H).

***(Z,Z)*-1-Benzylseleno-4-benzylthio-1,3-butadiene (6c).** As for **6b**, BnSeNa (from 8.55 g, 25 mmol BnSeSeBn) and BnSNa (from 6.2 g, 50 mmol α-toluenethiol and 150 mmol NaOMe in 120 mL MeOH) were refluxed with 1,4-bis(trimethylsilyl)-1,3-butadiene (7.0 g, 36 mmol) for 24 h. A precipitate containing 1:1:2 **6a**:**6b**:**6c** (10.8 g) formed at 0 °C. Oxidation of 1.22 g of this solid in THF (11 mL) with 30% H_2O_2 (0.6 mL) at 25 °C for 2 h precipitated (*Z*,*Z*)-1,4-bis(benzylseleno)-1,3-butadiene *Se*,*Se*-bis-oxide **10** (0.33 g), ^{77}Se NMR (δ 878) and IR (ν_{max}, neat) 785 cm^{-1} (Se═O); ^{1}H NMR δ 6.87 (dd, ^3J = 10.2 Hz, ^5J = 0.9 Hz, SeC*H*═CH, 1H); 6.95 (dd, ^3J = 10.2, 7.2 Hz, SeCH═C*H*, 1H); 7.11 (dd, ^3J = 10.2, 7.24 Hz, Se(O)CH═C*H*, 1H); 7.24 (dd, ^3J = 10.2 Hz, ^5J = 0.9 Hz, Se(O)C*H*═CH, 1H). Chromatography of the filtrate (silica gel; CH_2Cl_2:MeOH 19:1) gave solid (*Z*,*Z*)-1-benzylseleno-4-benzylthio-1,3-butadiene *Se*-oxide **9**, 400 mg, yield 61%); ^{77}Se NMR, δ 867; IR (ν_{max}, neat) 802 cm^{-1}; ^{1}H NMR δ 6.81 (d, ^3J = 8.4 Hz, SC*H*═CH, 1H); 7.01 (dd, ^3J = 8.4, 9.6 Hz, SCH═C*H*, 1H); 7.22 (d, ^3J = 9 Hz, Se(O)C*H*═CH, 1H); 7.36 (dd, ^3J = 9, 9.6 Hz, Se(O)CH═C*H*, 1H). For comparison the monosulfoxide of **6a,** (*Z*,*Z*)-1,4-bis-(benzylthio)-1,3-butadiene *S*-oxide, was prepared and showed ^{1}H NMR δ 6.98 (dd, ^3J = 9.5, 4.7 Hz, S(O)CH═C*H*, 1H); 7.03−7.08 (m, SC*H*═C*H*, 2H); 7.18 (dd, ^3J = 9.5 Hz, ^5J = 1.1 Hz, S(O)C*H*═CH, 1H). Sodium thiosulfate (0.7 mL, 1 M) in MeOH (10 mL) reduction of **9** (1.1 mmol) for 16 h gave **6c** (292 mg, yield 77%), off-white needles, mp 120−121 °C. ^{1}H NMR δ 3.89 (s, 2H, SCH_2Ph), 3.92 (s, 2H, SeCH_2-Ph), 6.05 (d, 1H, ^3J = 9.6 Hz, SC*H*═CH), 6.17 (dd, 1H, ^3J = 10.3, 9.6 Hz, SCH═C*H*), 6.40 (d, 1H, ^3J = 9.4 Hz, SeC*H*═CH), 6.64 (dd, 1H, ^3J = 10.3, 9.4 Hz, SeCH═C*H*), 7.2−7.3 (m, 10H); ^{13}C NMR δ 30.08 (SCH_2Ph), 38.09 ($SeCH_2Ph$), 124.56 (SCH═*C*H), 126.80 (SeCH═*C*H), 127.68 (S*C*H═CH), 128.31 (Se*C*H═CH), 128.58, 128.78, 128.84 (Ph); ^{77}Se NMR δ 312; MS (70 eV) *m*/*z* 346 (M^+). Anal. Calcd for $C_{18}H_{18}$-SSe: C, 62.42; H, 5.24. Found: C 61.95, H 5.37.

2-Selenathiin (5c). The synthesis of **5a** was followed, using sodium. Yield of **5c**, 56% (orange solution; by NMR, 1,4-dioxane standard); ^{1}H NMR δ 6.00 (dd, $^3J_{cis}$ = 7.9 Hz, ^5J = 1.7 Hz, 1H), 6.26−6.29 (m, 3H); ^{13}C NMR δ 113.76 (Se*C*H═CH), 119.25 (S*C*H═CH), 129.67 (SCH═*C*H), 131.97 (SeCH═*C*H); ^{77}Se NMR δ 228; UV−vis (hexane) λ_{max} = 488 nm; GC−MS (70 eV) *m*/*z* 164 (M^+, 20%), 84 (100%), 58 (100%).

2-Selenathiin 2-Oxide (39c). *Due to the instability of the title compound, the following manipulations were conducted at −50 to −20 °C.* The synthesis of **39a** was followed using a solution of **5c** (2.6 mg, 0.02 mmol) in CD_2Cl_2, 1,4-dioxane as internal standard, and a slight excess of *m*CPBA; ^{1}H NMR (CD_2Cl_2) δ 6.81 (d, ^3J = 8.4 Hz, SC*H*═CH, 1H); 7.01 (dd, ^3J = 8.4, 9.6 Hz, SCH═C*H*, 1H); 7.22 (d, ^3J = 9 Hz, Se(O)C*H*═CH, 1H); 7.36 (dd, ^3J = 9, 9.6 Hz, Se(O)CH═C*H*, 1H).

1,4-Bis(benzylthio)-1,3-butadiyne (15). Benzylthioethyne (8 g, 60 mmol) was slowly added to a stirred solution of CuCl (0.27 g) and TMEDA (0.41 mL) in acetone (40 mL) at 25 °C into which oxygen was bubbled. After 3 h, the mixture was concentrated and treated with dilute ice cold HCl solution (0.3 mL concentrated HCl diluted to 50 mL). The suspension was extracted with ether (2 × 50 mL), the combined ether layers were washed with brine (2 × 50 mL) and water (35 mL), dried, and concentrated in vacuo affording **15** as a yellow solid (7.7 g, 97%) of good purity. An analytical sample of **15** prepared by flash chromatography (1:9 CH_2Cl_2−hexanes) had mp 38−39 °C; ^{1}H NMR δ 7.4−7.2 (m, 10H), 3.96 (s, 4H); ^{13}C NMR δ 135.99, 129.07, 128.79, 128.05, 82.43, 74.22, 40.98; GC−EI-MS *m*/*z* 294 (M^+); IR (ν_{max}, neat) 2075 cm^{-1} (C≡C). Anal. Calcd for $C_{18}H_{14}S_2$: C, 73.43; H, 4.79. Found: C, 73.46; H, 4.86.

***(E,E)*-1,4-Bis(benzylthio)-1,4-bis(triphenylstannyl)-1,3-butadiene (16).** Tetrakis(triphenylphosphine)palladium(0) (0.20 g, 0.17 mmol) was added to a stirred solution of **15** (1.47 g, 5 mmol) in hexane−CH_2Cl_2 (600 mL, 4:1). Triphenyltin hydride (4.38 g, 12.5 mmol) was added dropwise to the solution at −50 °C. After 10 min, the mixture was slowly allowed to warm. A precipitate appeared at −30 to −20 °C and was collected at 25 °C, giving **16** as a yellow solid (1.74 g, 35%), mp 157−159 °C; ^{1}H NMR δ 7.7−6.8 (m, 42H), 3.68 (s, 4H); ^{13}C NMR δ 141−136 (several), 129.5−126 (several), 40.54. Anal. Calcd for $C_{54}H_{46}S_2Sn_2$: C, 65.10; H, 4.62. Found: C, 65.08; H, 4.77. The structure of **16** was determined by X-ray crystallography.[6]

***(E,E)*-1,4-Bis(benzylthio)-1,4-diiodo-1,3-butadiene (17).** Iodine (122 mg, 0.48 mmol) in CH_2Cl_2 (3 mL) was added during 1.5 h at 0 °C to a stirred solution of **16** (200 mg, 0.20 mmol) in CH_2Cl_2 (9 mL) using a syringe pump. The solution was stirred overnight at 25 °C and then washed ($NaHSO_3$ [2 × 20 mL] and KF [20 mL]), dried, filtered, concentrated, and chromatographed (1:6 CH_2Cl_2−hexanes) giving **17** as a pale yellow solid (110 mg, 100% yield) with mp 111−112 °C; ^{1}H NMR δ 7.35−7.20 (m, 10H), 7.17 (s, 2H), 3.85 (s, 4H); ^{13}C NMR δ 145.25, 136.36, 129.18, 128.63, 127.69, 95.10, 42.77. Anal. Calcd for $C_{18}H_{16}S_2I_2$: C, 39.29; H, 2.93. Found: C, 39.50; H, 3.13.

***(E,E)*-2,4-Bis(benzylthio)-2,4-hexadiene (18).** Methyllithium in ether (1.5 M, 1.33 mL, 2 mmol) was added to a stirred suspension of Cu_2I_2 (0.190 g) in ether (1 mL) at −15 °C. The solution was cooled to −78 °C, **17** (55 mg, 0.1 mmol) in ether was added, and stirring was continued for 1 h at −78 °C. At 25 °C, the solution was quenched with NH_4Cl solution (2.5 mL) and extracted with ether, and the ether layers were washed with brine and water and were dried, filtered, concentrated, and chromatographed (1:9 CH_2Cl_2−hexanes) to afford **18** as a yellow solid (20.5 mg, 63% yield); ^{1}H NMR δ 7.29 (m, 10H),

6.50 (s, 2H), 3.92 (s, 4H), 2.06 (s, 6 H); ^{13}C NMR δ 137.95, 131.92, 128.71, 128.59, 128.37, 126.95, 36.09, 24.58; EI-GC−MS *m*/*z* 326 (M^+, 5%), 235 (25%), 91 (100%), 65 (15%), 45 (6%).

3,6-Dimethyl-1,2-dithiin (1f). 1-*N*,*N*-Dimethylaminonaphthalene (0.85 g, 5 mmol), Li (0.24 g, 35 mmol), and THF (10 mL) were stirred at −55 °C for 5 h. The green solution was cooled to −85 °C, and **18** (0.25 g, 0.76 mmol) in THF (10 mL) was added dropwise. The dark solution was stirred for 1.5 h, quenched by addition of several drops of MeOH followed by acetyl chloride (1 mL), slowly warmed to 25 °C, and concentrated in vacuo. The mixture was placed in a separatory funnel with the aid of small portions of water and CH_2Cl_2 and extracted with ether. The combined organic layers were washed with HCl solution (10%) and brine, dried, filtered, concentrated, and chromatographed (17:1 hexanes−EtOAc) to give (*Z*,*Z*)-2,4-hexadiene-2,4-dithiol *S*,*S*-diacetate (**19**; 0.13 g, 74%) as a colorless solid, EI-MS *m*/*z* 332 (M^+, 100%). Compound **19** from several syntheses (60 mg, 0.26 mmol) was suspended in MeOH (6 mL) with stirring and treated with KOH (30 mg in 1 mL MeOH) at 0 °C. Iodine (132 mg, 52 mmol) in MeOH (2 mL) was slowly added to the resultant yellow solution which was then stirred for 20 min, diluted with water (2 mL), and extracted with hexane (3 × 5 mL), and the combined organic layers were washed (sequentially with $Na_2S_2O_3$, NH_4Cl, brine, water), dried, filtered, concentrated in vacuo, and chromatographed (hexane) to afford **1f** (25 mg, 67%) as a light-sensitive red liquid, ^{1}H NMR δ 6.05 (s, 2H), 2.03 (s, 6H); ^{13}C NMR δ 128.47, 125.93 (=CH), 22.95 (Me); EI-LC−MS *m*/*z* 144 (M^+, 53%), 111 (54%), 59 (100%); UV−vis (CH_3CN) λ_{max} 202 (45,000), 268 (22,000), 334 (360), 422 (47) nm.

***(Z,Z)*-1,4-Bis(thiocyanato)-1,4-bis(*t*-butyl)-1,3-butadiene (25a).** To a stirred solution of Ti(O*i*-Pr)$_4$ (9.0 mmol, 2.4 mL) in ether (100 mL), was successively added 3,3-dimethyl-1-butyne (**20a**; 15 mmol, 1.9 mL) and *i*-PrMgCl ((18 mmol, 9.0 mL, 2.0 M in ether) in this order at −78 °C. The solution was stirred at −78 °C for 1 h and at −30 °C for 2 h, cooled to −78 °C, and treated with dropwise addition of thiocyanogen (15 mmol) in CH_2Cl_2 (45 mL) [prepared immediately before use by adding Br_2 (15 mmol, 2.4 g) in CH_2Cl_2 (15 mL) dropwise to a suspension of lead thiocyanate (17 mmol, 5.4 g) in CH_2Cl_2 (30 mL) at 0 °C, stirring the mixture until Br_2 was discharged, and removing the solid by filtration under argon]. The reaction mixture was warmed to 25 °C over 1.5 h, stirred for 0.5 h, cooled to 0 °C, slowly quenched with 1 N HCl, and extracted with pentane and ether (1:1). The organic layer was washed ($NaHSO_3$, $NaHCO_3$ and brine solutions), dried, and concentrated in vacuo. Chromatography (hexane−ether, 80:20) gave **25a** (1.45 g, 67%), a yellow solid, mp 76−77 °C; ^{1}H NMR δ 1.30 (s, 18H), 7.13 (s, 2H); ^{13}C NMR δ 28.88, 40.40, 110.32, 131.15, 142.91; GC−MS *m*/*z* 280 (M^+), 265, 222, 166; IR (ν_{max}, neat) 2155 cm^{-1}. Anal. Calcd for $C_{14}H_{20}N_2S_2$: C, 59.96; H, 7.19. Found: C, 59.88; H, 7.53.

***(Z,Z)*-1,4-Bis(*tert*-butyl)-1,3-butadiene-1,4-dithio-*S*,*S*-diacetate (24a). Method I.** As in the synthesis of **7**, **23a** (2.0 mmol, 0.42 g) in THF (6 mL) was reacted with LDMAN [from 1-*N*,*N*-dimethylaminonaphthalene (10 mmol, 2.0 mL) and Li (10.0 mmol, 70 mg) in THF (10 mL)] followed by quenching wih excess AcCl. Chromatography (8:2 hexane: ether) gave **24a** (140 mg, 82%), mp 164−165 °C; ^{1}H NMR δ 1.09 (s, 18H), 2.37 (s, 6H), 6.86 (s, 2H); ^{13}C NMR δ 28.84, 30.90, 38.97, 132.16, 143.12, 192.73; GC−MS *m*/*z* 314 (M^+), 271, 215, 196, 181, 159, 57; IR (ν_{max}, neat) 1708 cm^{-1}.

Method II. To a well-stirred suspension of $LiAlH_4$ (2.0 mmol, 76 mg) in ether (5 mL) was added at −78 °C a solution of **25a** (0.5 mmol, 144 mg) in THF/ether (5 mL, 1:4). The reaction mixture was warmed gradually to 25 °C over 2 h, cooled to −78 °C again, and acetyl chloride (excess) was added very carefully. After the addition was completed, the mixture was warmed to room temperature and stirred for 30 min. The reaction was quenched with dilute HCl solution and extracted with ether, and the ether solution was washed ($NaHCO_3$ and brine solution), dried, and concentrated. Pure **24a** (130 mg, 83%) was obtained by recrystallization (hexane).

3,6-Bis(*tert*-butyl)-1,2-dithiin (1g). Method I. 24a (0.64 g, 2.0 mmol) was suspended in MeOH (80 mL) at 0 °C. A solution of NaOMe (4.0 mmol, from Na and MeOH) in MeOH was added slowly to the suspension over 30 min, followed by stirring at 0 °C for 2 h, whereupon the solution turned yellow. Iodine (0.55 g, 2.0 mmol) in MeOH (20 mL) was added dropwise, the mixture was stirred for 0.5 h, warmed to 25 °C, poured into ice water and extracted with hexane, and the combined organic layers were washed (cold $Na_2S_2O_3$, NH_4Cl, and brine solutions), dried, filtered, and concentrated in vacuo. Chromatography (hexane) gave **1g** (0.29 g, 64%) as a light-sensitive red solid, mp 76−77 °C; ^{1}H NMR δ 1.20 (s, 18H), 6.16 (s, 2H); ^{13}C NMR δ 28.74, 37.72, 122.02 (=CH), 146.52; EI-GC−MS *m*/*z* 228 (M^+, 23%), 181 (31%), 172 (30%), 157 (100%), 57 (50%); UV−vis (CH_2Cl_2) λ_{max} 406 (ϵ 175), 294 (ϵ 896), 236 nm (ϵ 980). Anal. Calcd for $C_{12}H_{20}S_2$: C, 63.10; H, 8.83. Found: C, 63.23; H, 8.74.

Method II. A solution of **25a** (0.5 mmol, 140 mg) in THF (5 mL) was added slowly to a deep blue solution of SmI_2 (1.1 mmol, 0.1 M solution) in THF (50 mL) over a period of 0.5 h at 0 °C. After the addition was completed, the mixture was warmed to 25 °C, stirred for 0.5 h, diluted with ether, filtered through silica gel, and concentrated. Chromatography (hexane) gave **1g** (0.96 g, 85% yield).

Method III. TBAF (0.55 mmol, 0.55 mL, 1.0 M in THF) was added slowly to **25a** (0.25 mmol, 70 mg) in THF (12 mL) at 0 °C. The mixture was stirred at 25 °C for 2 h, quenched (saturated NH_4Cl), diluted (Et_2O), washed (NH_4Cl and NaCl solutions), dried, and concentrated. Chromatography (hexane) gave **1g** (53 mg, 93%).

Method IV. As in the synthesis of **22a**, sulfur monochloride (1.0 mmol, 60 μL) was slowly added at −100 °C to a solution prepared from Ti(O*i*-Pr)$_4$ (1.2 mmol, 0.40 mL) in ether (35 mL), 3,3-dimethyl-1-butyne (**1b**; 2.0 mmol, 0.25 mL) and *i*-PrMgCl (2.4 mmol, 1.2 mL, 2.0 M in ether). After workup, chromatography (hexane) gave a mixture of **1g** and 2,5-bis(*tert*-butyl)thiophene (**3g**)[17a] (4:1 ratio by ^{1}H NMR; yield 80%).

3,6-Bis(*tert*-butyl)-1,2-dithiin 1-Oxide (37g). *m*CPBA (100%, 0.18 mmol, 30 mg) in 2 mL of CH_2Cl_2 was slowly added to the solution of **1g** (0.15 mmol, 34 mg) in CH_2Cl_2 (5 mL) at 0 °C. The mixture was stirred for 15 min at 0 °C, warmed to 25 °C and concentrated. The residue was dissolved in ether, washed (KI, Na_2SO_3, and brine solutions), dried, and concentrated in vacuo. Chromatography (ether−hexane) gave **37g** (28 mg, 77%), a light yellow solid, mp 85−86 °C; ^{1}H NMR δ 1.28 (s, 9H), 1.35 (s, 9H), 6.64 (d, J = 7.7 Hz, 1H), 6.69 (d, J = 7.7 Hz, 1H); ^{13}C NMR δ 29.61, 30.27, 36.83, 37.83, 116.21 (=CH), 120.01 (=CH), 138.42, 145.70. UV−vis (CH_2Cl_2) λ_{max} 242 (ϵ 984), 266 (ϵ 1036), 314 (ϵ 1128) nm.

***(Z,Z)*-1,4-Bis(thiocyanato)-1,4-bis(trimethylsilyl)-1,3-butadiene (25c).** As in the synthesis of **25a**, thiocyanogen (6.0 mmol) in CH_2Cl_2 (15 mL) was added dropwise at −78 °C to a solution prepared from Ti(O*i*-Pr)$_4$ (3.6 mmol, 1.2 mL) in ether (30 mL), (trimethylsilyl)acetylene (**20c**; 6.0 mmol, 0.85 mL) and *i*-PrMgCl (7.2 mmol, 3.6 mL, 2.0 M in ether) at −78 °C. After workup, chromatography (hexane−ether, 80: 20) afforded **25c** (0.52 g, 56%) as a light yellow solid, mp 78−79 °C; ^{1}H NMR δ 0.35 (s, 18H), 7.20 (s, 2H); ^{13}C NMR δ 1.36, 110.19, 136.19, 138.26; GC−MS *m*/*z* 312 (M^+), 297, 254, 213, 198, 166, 116, 91, 73; IR (ν_{max}, neat) 2153 cm^{-1}.

3,6-Bis(trimethylsilyl)-1,2-dithiin (1i). Method I. As in the synthesis of **1g**, method II, **25c** (0.5 mmol, 166 mg) in THF (5 mL) was treated with SmI_2 (1.1 mmol) in THF (50 mL). After workup, chromatography (hexane) gave **1i** as a red solid (70 mg, 54%); ^{1}H NMR δ 0.18 (s, 18H), 6.43 (s, 2H); ^{13}C NMR δ −2.20, 135.47 (=CH), 139.08; EI-GC−MS *m*/*z* 260 (M^+, 25%), 245 (18%), 73 (100%); UV (CH_2Cl_2) λ_{max} 478 (ϵ 520), 348 (ϵ 4890), 236 (ϵ 4768) nm.

Method II. To a well-stirred suspension of $LiAlH_4$ (2.0 mmol, 76 mg) in ether (25 mL) was added at −78 °C a solution of **25c** (0.4 mmol, 125 mg) in THF−ether (5 mL, 1:4). The reaction mixture was warmed to room temperature over 2 h, and then the flask was cooled to −30 °C. Several drops of ethyl acetate were added to quench the excess $LiAlH_4$, and then iodine (0.5 mmol, 127 mg) in ether (10 mL) was added dropwise. The flask was slowly warmed to room temperature and stirred for an additional 40 min. The reaction mixture was diluted with ether and washed (NH_4Cl, brine solutions), dried, and concentrated in vacuo. Chromatography (hexane) gave **1i** and 2,5-bis(trimethylsilyl)-thiophene[17b] (**3i**) (1:2 ratio by ^{1}H NMR; overall yield 65%).

Method III. As in the synthesis of **1g**, method IV, S_2Cl_2 (1.0 mmol, 60 μL) was slowly added at −100 °C (MeOH−liquid N_2) to a solution prepared from Ti(O*i*-Pr)$_4$ (1.2 mmol, 0.40 mL) in ether (35 mL), 3,3-dimethyl-1-butyne (**20a**, 2.0 mmol, 0.30 mL) and *i*-PrMgCl (2.4 mmol,

1.2 mL, 2.0 M in ether). After workup, chromatography (hexane) afforded a mixture of **1i** and **3i** (1:1 ratio by ^{1}H NMR; yield 65%).

***(Z,Z)*-1,4-Bis(selenocyanato)-1,4-bis(*t*-butyl)-1,3-butadiene (33).** As in the synthesis of **25a**, selenocyanogen (12 mmol) [Selenocyanogen was prepared immediately before use by adding I_2 (10 mmmol, 2.5 g) to a solution of anhydrous AgSeCN (20 mmol, 4.3 g; dried at 60 °C for 24 h at 1 Torr) in THF (30 mL) at 0 °C and stirring at 0 °C for 30 min until a clear, bright yellow solution was obtained; the reaction was then cooled to −78 °C and filtered, and the filtrate was collected in a flask maintained at −78 °C.] in THF (25 mL) was added dropwise to a solution prepared from Ti(O*i*-Pr)$_4$ (7.2 mmol, 2.3 mL) in ether (60 mL), 3,3-dimethyl-1-butyne (**20a**; 12 mmol, 1.5 mL), and *i*-PrMgCl (14.4 mmol, 7.2 mL, 2.0 M in ether) at −78 °C. After workup and concentration, recrystallization (hexane) gave **33**, a light yellow solid (1.2 g, 54%), mp 134−135 °C; ^{1}H NMR δ 1.30 (s, 18 H), 7.05 (s, 2 H); ^{13}C NMR δ 29.30, 40.81, 100.83, 133.23, 145.38; GC−MS *m*/*z* 374 (M^+), 270, 229, 214, 149, 133, 107, 91, 77, 57; IR (ν_{max}, KBr) 2148 cm^{-1}. Anal. Calcd for $C_{14}H_{20}N_2Se_2$: C, 44.93; H, 5.39. Found: C, 44.97; H, 5.52.

3,6-Bis(*tert*-butyl)-1,2-diselenin (5b). Method I. As in the synthesis of **1g**, method II, **33** (1.4 mmol, 532 mg) in THF (5 mL) was treated with SmI_2 (3.0 mmol) in THF (100 mL). After workup, chromatography (hexane) gave **5b**, a red solid (0.2 g, 83%), mp 84−85 °C; ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 18H), 6.22 (s, 2H); ^{13}C NMR δ 29.23, 38.64, 124.69 (=*C*H), 144.18; ^{77}Se NMR δ 165.2; EI-LC−MS *m*/*z* 324 (M^+, 40%), 268 (30%), 253 (65%), 229 (60%), 91 (100%); UV (CH_2Cl_2) λ_{max} 448 (ϵ 235), 290 (ϵ 1380), 232 nm (ϵ 1470). Anal. Calcd for $C_{12}H_{20}Se_2$, C, 44.73; H, 6.26. Found, C, 44.84; H, 6.12.

Method II. As in the synthesis of **1g**, method III, **33** (0.50 mmol, 188 mg) in THF (25 mL) was treated with TBAF (1.1 mmol, 1.1 mL, 1.0 M TBAF solution in THF). Chromatography (hexane) gave **5b** (146 mg, 90%).

3,6-Bis(*tert*-butyl)-1,2-diselenin 1-Oxide (39b). *Due to the instability of the title compound, all of the following manipulations were conducted at −40* °C. Compound **5b** (15 mg) and CD_2Cl_2 (0.8 mL) were added to an NMR tube and cooled to −40 °C. A slight excess of peracetic acid was added, and the NMR tube was shaken for 10 min (yield 60% by ^{1}H NMR). ^{1}H NMR (CD_2Cl_2) δ 1.29 (s, 9H), 1.30 (s, 9H), 6.56 (d, J = 8.0 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H); ^{13}C NMR (CD_2Cl_2) δ 29.62, 32.68, 37.70, 38.98, 119.56, 123.75, 139.43, 144.70. UV (CH_2Cl_2) λ_{max} 266.

***(Z,Z)*-1,4-Bis(thiocyanato)-1,4-bis(isopropyl)-1,3-butadiene (25b).** As in the synthesis of **25a**, thiocyanogen (15 mmol) in CH_2Cl_2 (45 mL) was added dropwise at −78 °C to a solution prepared from Ti(O*i*-Pr)$_4$ (2.8 mL, 9.0 mmol) in ether (100 mL), 3-methyl-1-butyne (**20b**, 1.02 g, 15.0 mmol), and *i*-PrMgCl (9 mL, 18 mmol, 2.0 M in ether) at −78 °C. Chromatography (4:1 hexane−ether) gave **25b** as a yellow solid (0.28 g, 15% yield), mp 77−78 °C; ^{1}H NMR δ 1.27 (d, J = 7.02 Hz, 12H), 2.83 (septet, 2H), 6.78 (s, 2H); ^{13}C NMR δ 21.59, 36.81, 109.23, 127.47, 138.72; GC−MS *m*/*z* 252 (M^+), 167, 152, 136, 125, 121, 119, 77, 69, 65, 59; IR (ν_{max}, KBr) 2155 cm^{-1} (SC≡N).

3,6-Bis(isopropyl)-1,2-dithiin (1h). As in the synthesis of **1g**, method III, **25b** [crude material containing 0.521 g (2.07 mmol) **25b** by NMR analysis] in THF (30 mL) was treated with TBAF (4.14 mL, 4.14 mmol, 1 M in THF). Chromatography (hexane) gave **1h**, a red-orange liquid (0.351 g, 85%; based on amount of **25b** used, by NMR analysis); ^{1}H NMR δ 1.16 (d, J = 6.84 Hz, 12H), 2.53 (m, 2H), 6.08 (s, 2H); ^{13}C NMR δ 21.21 (CH_3), 35.75 (Me_2CH), 122.78 (=*C*H), 142.06; EI-GC−MS *m*/*z* 200 (M^+, 15%), 153 (61%), 143 (100%); UV (CH_2Cl_2) λ_{max} 292, 420 nm.

Cyclic Voltammetry. Voltammograms were measured on degassed solutions approximately 10^{-3} M in substrate and 0.1 M in tetra-*n*-butylammonium hexafluorophosphate, which served as supporting electrolyte, in CH_3CN or CH_2Cl_2 as solvent versus a Ag/0.10 M $AgNO_3$ in CH_3CN reference electrode. A 0.3-cm^2 platinum flag, which was heated to incandescence in a flame prior to each run, a 1.6 mm diameter Teflon-jacketed planar platinum electrode or a 3 mm diameter glassy planar carbon electrode for **5a** and **5b** served as the working electrode, and the scan rates were varied from 10 to 2000 mV/s. A 0.5 mm diameter platinum wire was used as the counter electrode in all cases. All electrochemical experiments were performed under rigorously anaerobic conditions in a Vacuum Atmospheres model HE-493 drybox or sealed electrochemical cell under red light. A Cypress Systems electrochemical data acquisition system model CYSY-1 was used to acquire and process the data. The detailed electrochemical studies were done in the same manner as reported above using CH_3CN as solvent. A 1.6 mm diameter Teflon-jacketed planar platinum electrode was used as the working electrode and was polished with alumina on an emery pad prior to each run. In addition, blank runs on the supporting electrolyte solution were done to be able to subtract the residual current in the detailed analysis.

Electrochemical Simulations. Simulations of the cyclic voltammograms were carried out using the fast implicit finite difference algorithm employed in Digisim 2.1 (Bioanalytical Systems). Two possible mechanisms were considered:

$$\text{Model 1: } a - e^- \rightleftharpoons b; \quad b \rightleftharpoons c \quad K = [c]/[b] = 1$$

$$\text{Model 2: } a - e^- \rightleftharpoons b; \quad 2b \rightleftharpoons c$$

The experimental current−voltage curves were first background current-corrected. The simulations were then allowed to proceed to obtain the best fit, allowing the formal potential ($E^{0'}$), the heterogeneous rate constant k_s, and the forward rate constant of the following chemical reaction k_f, to vary. Other experimental parameters such as electrode area and scan rate were held constant as was the electron-transfer coefficient, a = 0.5. Simulations were compared with experimental data over a wide range of scan rates and concentrations, and the range of values reported is consistent with the best fit over all of these conditions. The data were observed to be consistent with Model 1 since there was no significant effect of concentration on the curve-fitting parameters, which would be expected for a second-order following chemical reaction. It also was not possible to obtain satisfactory fits for a simple one-electron transfer mechanism.

Theoretical Calculations. The B3LYP exchange correlation functional was used in all of the ^{77}Se NMR spectroscopic calculations. The GIAO calculations were performed on geometries obtained by DFT B3LYP/6-31+G(d) as well as MP2/6-311+G(2d,p) calculations. All other calculations were made with Gaussian 94 revision E.2.[31] The Hartree−Fock method with second-order Moeller−Plesset corrections was implemented as found in Gaussian 94, using the 6-31G basis set with one additional set of both polarization and diffuse funcions (MP2/6-31+G*). Optimized geometries were found for the neutral and cation radical species of each compound investigated. The energy of the un-ionized species was then calculated as a single point at the optimized ionized geometry, and vice versa. Each single-point calculation was also performed as an optimization to verify that the un-ionized minima do not represent minima on the ionized potential energy surface, and vice versa. All geometries found fell into the expected cases of twist or planar ring geometries. These calculations were performed on a Silicon Graphics Origin 2000 Octane 32-processor machine.

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Supporting Information Available: Experimental details for compounds **1d**, **3g**−**i**, **5d**, **e**, **8**, **11c**, **20b**, **22a**, **23a**, **29a**,**b**, **30**−**34**, **36**, **37f**, **38e**,**f**, **40**, and benzylthioethyne (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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