1,3-Diselenetanes and 1,3-Dithietanes Derived from Camphor. Formation, Structure, Stereochemistry, and Oxidation to Selenoxide and Sulfoxide Products

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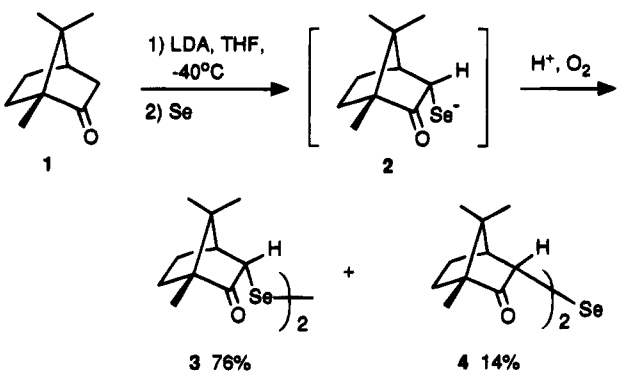
Received September 27, 1994®

The reaction of camphor enolate with elemental selenium, followed by aerial oxidation, afforded chiefly the *endo,endo*-dicamphoryl diselenide **3** and **4** selenide. However, in the presence of methyl iodide, the principal products were the *syn*- and *anti*-1,3-diselenetanes **5** and **6**, formed by the dimerization of the putative selenoketone intermediate **12**. The products **5** and **6** were also obtained by the base-catalyzed elimination of HCN from the camphoryl selenocyanate **14**, followed by dimerization of the same intermediate **12**. The reaction of camphor enolate with sulfur and methyl iodide did not produce the corresponding 1,3-dithietanes, but mainly a mixture of dicamphoryl sulfide and camphoryl methyl sulfide stereoisomers **15**–**18**. Base-catalyzed elimination of camphoryl thiocyanate **19** afforded the *anti*-1,3-dithietane **21** as the sole stereoisomer via thioketone **20**. Oxidation of **21** with $PhICl_2$ produced a single sulfoxide isomer **24**. Further oxidation of the latter with *m*-CPBA gave a mixture of bis-sulfoxides **25** and **26** and trioxide **27**, while exhaustive oxidation of **21** gave the bis-sulfone **29**. Treatment of the *syn*-1,3-diselenetane **5** with $PhICl_2$ resulted in oxidation of the *endo* and *exo* selenium atoms to afford selenoxides **30** and **31** in the ratio of 91:9, respectively. Similar oxidation of the *anti* isomer **6** produced the selenoxide **32** and a smaller amount of **30** by ring opening and reclosure. X-ray crystal structures of the *anti*-1,3-diselenetane and -dithietane **6** and **21** were determined.

Camphorthio compounds are well documented,[1] and several have useful synthetic applications based on the exploitation of the camphor moiety as a chiral auxiliary group. In contrast, analogous camphorseleno species are virtually unknown and have not been utilized in synthesis.[2] We therefore investigated the possibility of introducing selenium into the 3-position of camphor (**1**) by the direct selenenylation of its lithium enolate with the free element.[3] By analogy, Liotta and co-workers[4] had reported earlier that other, achiral enolates react with selenium to produce selenolate intermediates that were then alkylated *in situ* to afford the corresponding selenides. The similar generation of the desired camphor selenolate **2** would thus provide access to a series of chiral selenides, and to the diselenide **3**, by alkylation or aerial oxidation of **2**, respectively. We now report that this method not only permits the convenient preparation of diselenide **3** as planned, but under slightly different conditions results in the unexpected formation of 1,3-diselenetanes **5** and **6**. In this paper we describe our investigation of the latter compounds, some similar experiments leading to an analogous 1,3-dithietane, and the results of stepwise oxidations of these heterocycles to the corresponding selenoxides and sulfoxides.

Scheme 1



Formation of Camphor 1,3-Diselenetanes

When (1*R*)-(+)-camphor (**1**) was treated with LDA in THF, followed by elemental selenium at −40 °C, the selenolate **2** was generated *in situ*. Air oxidation of the reaction mixture then afforded the diselenide **3** and selenide **4** in yields of 76% and 14%, respectively, based upon correction for recovered starting material (Scheme 1). Typically, about half of the camphor is consumed in the reaction and the remainder is easily removed by vacuum sublimation and can be recycled. We next attempted to alkylate the selenolate **2** *in situ* with methyl iodide. However, the expected methyl selenide **7** was formed in only 12% yield, along with 15% of the selenoacetal **8**. The principal product was, surprisingly, a mixture of the corresponding *syn*- and *anti*-1,3-diselenetanes **5** and **6**, obtained in yields of 32% and 10%, respectively, after chromatographic separation (Scheme

® Abstract published in *Advance ACS Abstracts*, January 1, 1995.

(1) For recent examples, see: (a) Corey, E. J.; Chen, Z.; Tanoury, G. J. *J. Am. Chem. Soc.* **1993**, *115*, 11000. (b) Yang, T.-K.; Chen, R.-Y.; Lee, D.-S.; Peng, W.-S.; Jiang, Y.-Z.; Mi, A.-Q.; Jong, T.-T. *J. Org. Chem.* **1994**, *59*, 914. (c) Verdaguer, X.; Moyano, A.; Pericàs, M. A.; Riera, A.; Bernardes, V.; Greene, A. E.; Alvarez-Larena, A.; Piniella, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 2153. (d) Isobe, M.; Obeyama, J.; Funabashi, Y.; Goto, T. *Tetrahedron Lett.* **1988**, *29*, 4773. (e) Davis, F. A.; Reddy, R. T.; Han, W.; Carroll, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 1428. (f) Arai, Y.; Matsui, M.; Koizumi, T. *Synthesis* **1990**, 320. (g) Goodridge, R. J.; Hambley, T. W.; Haynes, R. K.; Ridley, D. D. *J. Org. Chem.* **1988**, *53*, 2881. (h) Hung, S.-M.; Lee, D.-S.; Yang, T.-K. *Tetrahedron Asymmetry* **1990**, *1*, 873.

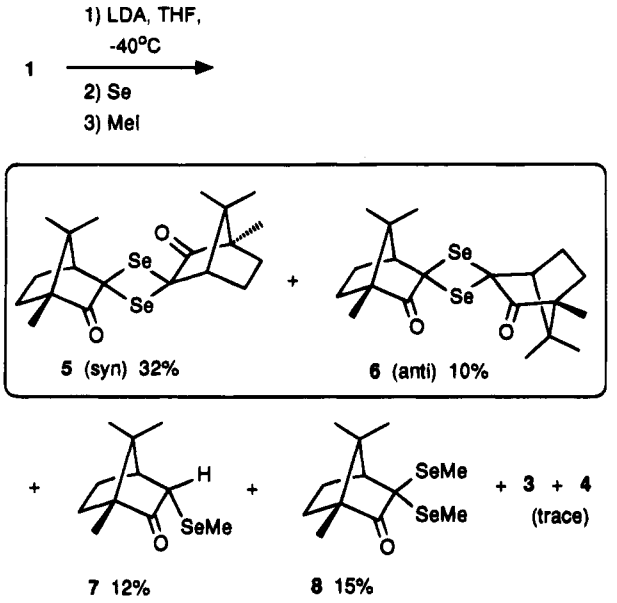
(2) A few 3-arylselenocamphor derivatives have been reported: (a) Barton, D. H. R.; Cussans, N. J.; Ley, S. V. *J. Chem. Soc., Chem. Commun.* **1978**, 393. (b) Nagao, Y.; Ochiai, M.; Kaneko, K.; Maeda, A.; Watanabe, K.; Fujita, E. *Tetrahedron Lett.* **1977**, 1345. (c) Brown, F. C.; Morris, D. G.; Murray, A. M. *Tetrahedron* **1978**, *34*, 1845.

(3) Preliminary communication: Back, T. G.; Dyck, B. P.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1994**, 515.

(4) Liotta, D.; Zima, G.; Barnum, C.; Saindane, M. *Tetrahedron Lett.* **1980**, *21*, 3643.

0022-3263/95/1960-0703$09.00/0

Scheme 2



2).[5] Only traces of diselenide **3** and selenide **4** were formed under these conditions. Similar results were observed when benzyl chloride was employed instead of methyl iodide. It is interesting to note that no detectable amounts of the diselenetanes were produced in the absence of the alkyl halide.

The ^{1}H-NMR spectra of compounds **3**, **4**, and **7** were consistent with incorporation of selenium at the less hindered *endo* position at C(3) of camphor, as the coupling constants between H(3) and H(4) were all in the range of 4.2−4.6 Hz, which is typical of a 3-*exo* hydrogen.[1g,6] Diselenetanes **5** and **6** both exhibit C_2 symmetry. The *syn* isomer **5** has a C_2 axis passing through the two selenium atoms, while the *anti* isomer **6** has a similar axis perpendicular to the four-membered diselenetane ring. Consequently, both diselenetanes possess equivalent camphor residues, but only the *anti* isomer has equivalent selenium atoms. The selenium atoms in the *syn* isomer are not equivalent because one is *exo* to both camphor units while the other is *endo*. Thus, assignment of the *syn* and *anti* configurations to the major and minor isomers **5** and **6** was possible on the basis of their ^{77}Se-NMR spectra, in which the *syn* isomer **5** displayed two signals at δ 808.2 and 650.2 ppm (relative to Me_2Se), whereas **6** gave only one signal at δ 712.9 ppm. An X-ray crystal structure of **6** provided unambiguous proof of this assignment and is provided in the supplementary material.[24]

A plausible mechanism for the unexpected formation of diselenetanes **5** and **6** in the presence of methyl iodide is shown in Scheme 3, along with the more routine formation of diselenide **3** and selenide **4** in the absence of the alkyl halide. First, attack by camphor enolate upon gray selenium, which consists of essentially infinite chains, is expected to generate polyselenocamphor species **9** and polyselenolate anions. The further reaction of **9** with the enolate can then proceed via three different pathways. In path a, attack takes place at a remote (from the camphor moiety) selenium atom, producing a truncated polyselenocamphor **10** and the corresponding camphor polyselenolate **11**. The reaction of **10** and **11** with additional camphor enolate, and disproportionation of the various polyseleno species thus produced, ultimately degrades them to the simple selenolate **2**, which furnishes the diselenide **3** after aerial oxidation. On the other hand, attack by the enolate upon the selenium atom attached directly to the camphor residue affords the selenide **4** and polyselenolate anion, as shown in path b. The third possibility is given in path c. If proton abstraction from the acidic α-position of **9** by the more strongly basic camphor enolate[7] competes with attack by the latter at selenium (i.e., paths a and b), then an ensuing elimination would produce the selenoketone (selone) **12**.[8] Dimerization of selenobenzophenone[9a] and of certain selenocarbonyl fluorides[9b] has been previously observed to produce 1,3-diselenetanes. A similar process is postulated here to account for the formation of products **5** and **6**. Although direct observation of **12** was not possible, indirect evidence for its role as an intermediate in the formation of **5** and **6** is described below. The function of methyl iodide in this process remains speculative, but it probably serves by alkylating the polyselenolate byproducts formed during these reactions. It is entirely possible that the elimination reaction leading to **12** may be reversible with an unfavorable equilibrium resulting from the facile attack of the displaced polyselenolate anion upon the selenoketone selenium atom to regenerate the enolate of **9**.[10] Thus, under normal conditions, path c is not competitive with paths a and b. However, continuous removal of the polyselenolate species from the reaction mixture by alkylation could serve to drive the equilibrium toward **12**, ultimately producing the observed diselenetanes by improving the competitiveness of path c with the other routes. An alternative explanation is that prior Se-alkylation of intermediates such as **9**, **10**, and **11** facilitates the elimination step required for the formation of **12** by creating a better leaving group. The other products that were encountered in the presence of methyl iodide are the methyl selenide **7**, presumably formed by the direct alkylation of the simple selenolate **2**, and the selenoacetal **8**. Transselenenylations between α-seleno ketones and their enolates are well-known[11] and would account for the formation of **8**. Thus, attack by the enolate of **7** upon the selenium atom of another molecule of its conjugate acid (i.e., **7** itself) results in the displacement of camphor enolate and the formation of **8**. The above scheme therefore succeeds

(5) We refer to the 1,3-diselenetane **5** as syn because each of the two selenium atoms is on the same side (*exo* or *endo*) of both flanking camphor moieties. In the *anti* isomer **6**, each selenium atom is *exo* to one camphor unit and *endo* to the other.

(6) (a) Hutchinson, J. H.; Money, T. *Can. J. Chem.* **1984**, *62*, 1899. (b) Watanabe, Y.; Numata, T.; Oae, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1915. (c) Meinwald, J.; Meinwald, Y. C.; Baker, T. N., III. *J. Am. Chem. Soc.* **1963**, *85*, 2513.

(7) A selenium substituent in the α-position of a ketone stabilizes the conjugate base and so increases the acidity of the α-hydrogen atom. See: Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22.

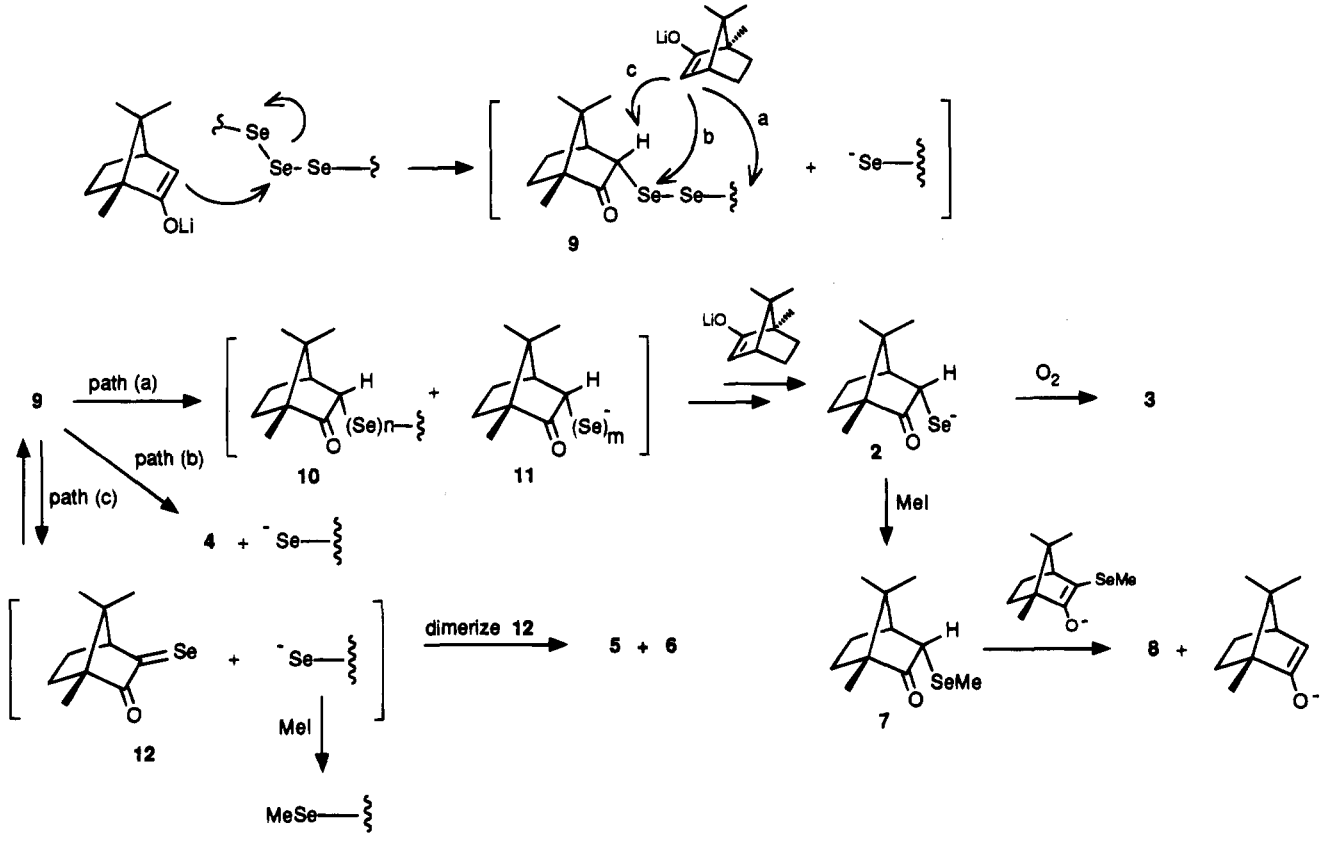
(8) For reviews of selones and related selenocarbonyl compounds, see: (a) Guziec, F. S., Jr. In *Organoselenium Chemistry*; Liotta, D., Ed.; Wiley: Chichester, 1987; Chapter 6. (b) Guziec, F. S., Jr. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; Wiley: Chichester, 1987; Volume 2, Chapter 4.

(9) (a) Erker, G.; Hock, R.; Krüger, C.; Werner, S.; Klärner, F.-G.; Artschwager-Perl, U. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1067. (b) Boese, R.; Haas, A.; Spehr, M. *Chem. Ber.* **1991**, *124*, 51.

(10) The readdition of the polyselenolate nucleophile to the selenium atom of **12** (i.e., the reverse step of the elimination that produces **12**) may be especially facile in this case because of the unusually high positive character of the selenocarbonyl selenium atom. This is the expected result of enolate-like stabilization of negative charge on the selenocarbonyl carbon atom by the adjacent carbonyl group.

(11) For examples of related α- to α′-transselenenylations to ketone enolates, see: (a) Liotta, D.; Saindane, M.; Brothers, D. *J. Org. Chem.* **1982**, *47*, 1598. For a general discussion of these processes, see: (b) Back, T. G. In *Organoselenium Chemistry*; Liotta, D., Ed.; Wiley: Chichester, 1987; Chapter 1.

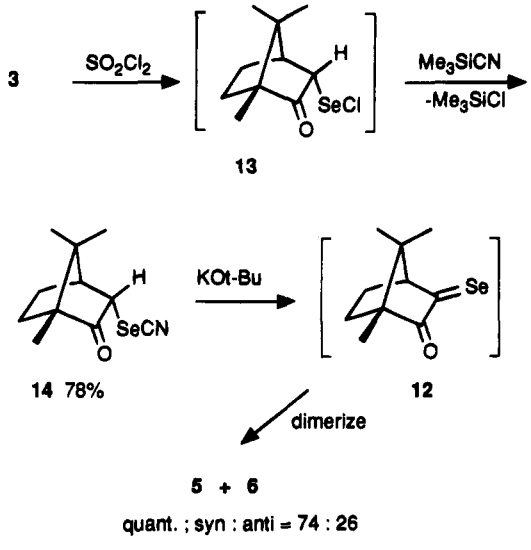
Scheme 3



in rationalizing the formation of all of the observed products, both in the absence and presence of methyl iodide.

Since the selenoketone **12** is a key intermediate in the postulated path c in Scheme 3, we desired further evidence that it is formed under the indicated conditions and that it is capable of dimerizing to the corresponding 1,3-diselenetanes. Unfortunately, all attempts at isolation or spectroscopic detection of **12** *in situ* failed, as did trapping experiments with dienes such as piperylene.[12] We therefore attempted to produce **12** by an independent method to see if it would dimerize in a similar manner. Efforts to regenerate the selenoketone by vacuum pyrolysis of the dimers **5** and **6** proved unsuccessful. However, Kirby[12a] and Krafft[12e,f] and their co-workers have demonstrated that selenoaldehydes and selenoketones can be produced by the base-catalyzed elimination of HCN from selenocyanates. Consequently, we prepared selenocyanate **14** by chlorinolysis of diselenide **3** with sulfuryl chloride, followed by the metathesis of the resulting selenenyl chloride **13** with trimethylsilyl cyanide (Scheme 4).[13] The stable, crystalline selenocyanate was then treated with potassium *tert*-butoxide in THF (Scheme 4) to afford a quantitative yield of the same 1,3-diselenetanes **5** and **6** that were obtained via Scheme 2, in a comparable ratio of 74:26 (vs 76:24 via Scheme 2).

Scheme 4



While this observation does not provide unequivocal evidence that **12** is also an intermediate in path c of Scheme 3, the very similar behavior provides strong support for this supposition.

Formation of a Camphor 1,3-Dithietane

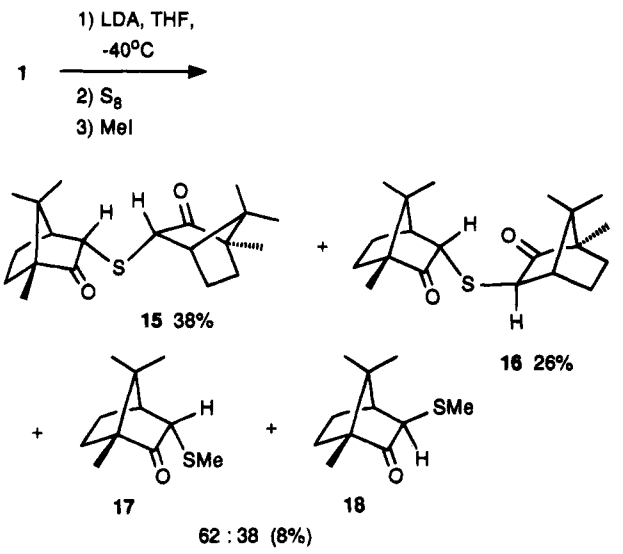
We next investigated whether camphor 1,3-dithietanes could be prepared in a manner similar to that of their selenium analogues.[14] The reaction of camphor enolate

(12) For examples of trapping of selenoketones and selenoaldehydes with 1,3-dienes, see: (a) Kirby, G. W.; Trethewey, A. N. *J. Chem. Soc., Chem. Commun.* **1986**, 1152. (b) Nakayama, J.; Akimoto, K.; Niijima, J.; Hoshino, M. *Tetrahedron Lett.* **1987**, *28*, 4423. (c) Erker, G.; Hock, R.; Nolte, R. *J. Am. Chem. Soc.* **1988**, *110*, 624. (d) Segi, M.; Koyama, T.; Nakajima, T.; Suga, S.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1989**, *30*, 2095. (e) Meinke, P. T. ; Krafft, G. A. *J. Am. Chem. Soc.* **1988**, *110*, 8671. (f) Meinke, P. T.; Krafft, G. A. *J. Am. Chem. Soc.* **1988**, *110*, 8679. (g) Okuma, K.; Kojima, K.; Kaneko, I.; Ohta, H. *Chem. Lett.* **1991**, 1053.

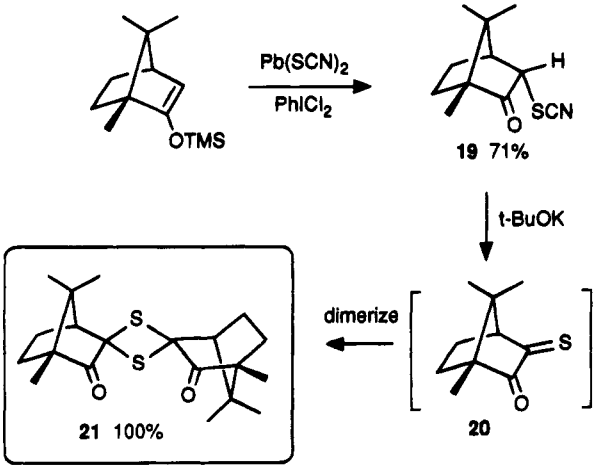
(13) Tomoda, S.; Takeuchi, Y.; Nomura, Y. *Chem. Lett.* **1981**, 1069.

(14) The dimerizations of thioketones and related compounds have been known for many years: (a) Schönberg, A.; Stephenson, A. *Chem. Ber.* **1933**, *66*, 567. For examples of these and related cycloadditions, see: (b) Block, E. In *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978; Chapter 7, pp 278–280.

Scheme 5



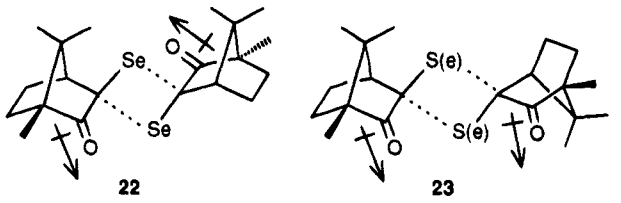
Scheme 6



with elemental sulfur (S_8) in the presence or absence of methyl iodide, with or without added HMPA,[4] failed to produce any detectable amounts of the corresponding dithietanes. Complex mixtures of products were obtained, from which we were able to isolate the *endo,endo*- and *endo,exo*-camphor sulfides **15** and **16** and a mixture of *endo*- and *exo*-methyl sulfides **17** and **18** as the only identifiable products (Scheme 5).

In an experiment parallel to that shown in Scheme 4, the thiocyanate **19** was easily procured by treating the enol trimethylsilyl ether of camphor with lead thiocyanate and iodobenzene dichloride. This was subjected to elimination as in the case of the corresponding selenocyanate, and the 1,3-dithietane **21** was produced quantitatively as a unique stereoisomer (Scheme 6), presumably via the thioketone **20**. It is interesting to note that in contrast to the selenium series, where the *syn*-1,3-diselenetane was the major product in both Schemes 2 and 4, the sole 1,3-dithietane isomer was shown to possess the *anti*-configuration by X-ray crystallography (see supplementary material).

Although the precise mechanisms for the dimerizations of selenoketone **12** and thioketone **20** are unknown at present,[15] the difference in the observed stereochemistry can be explained by a consideration of steric effects and dipole repulsions. An examination of models suggests



Transition state leading to syn isomer **5** (carbonyl dipoles opposed)

Transition state leading to anti isomers **6** and **21** (carbonyl dipoles cumulative)

Figure 1. Transition states leading to *syn* and *anti* diselenetanes and dithietanes. The reaction may proceed via a stepwise rather than a concerted mechanism.

that the transition states **23** leading to the *anti* dimers are less crowded than those (**22**) leading to their *syn* isomers, regardless of whether a concerted or stepwise mechanism is assumed. On the other hand, opposing carbonyl dipoles are expected to favor the *syn* transition state (Figure 1). The X-ray structures of the *anti*-1,3-diselenetane **6** and the *anti*-1,3-dithietane **21** reveal that the C–S bonds in the latter compound are ca. 0.15 Å shorter than the C–Se bonds in the former. A table of selected bond lengths and bond angles of these two compounds is given in the supplementary material.[24] We propose that a tighter transition state, where steric effects dominate, leads to preferential formation of the *anti*-1,3-dithietane. In contrast, the relatively long C–Se bonds result in reduced steric effects and a greater role for dipole repulsions in determining the relative energies of the transition states for the two diselenetanes, resulting in preferential formation of the *syn* isomer.

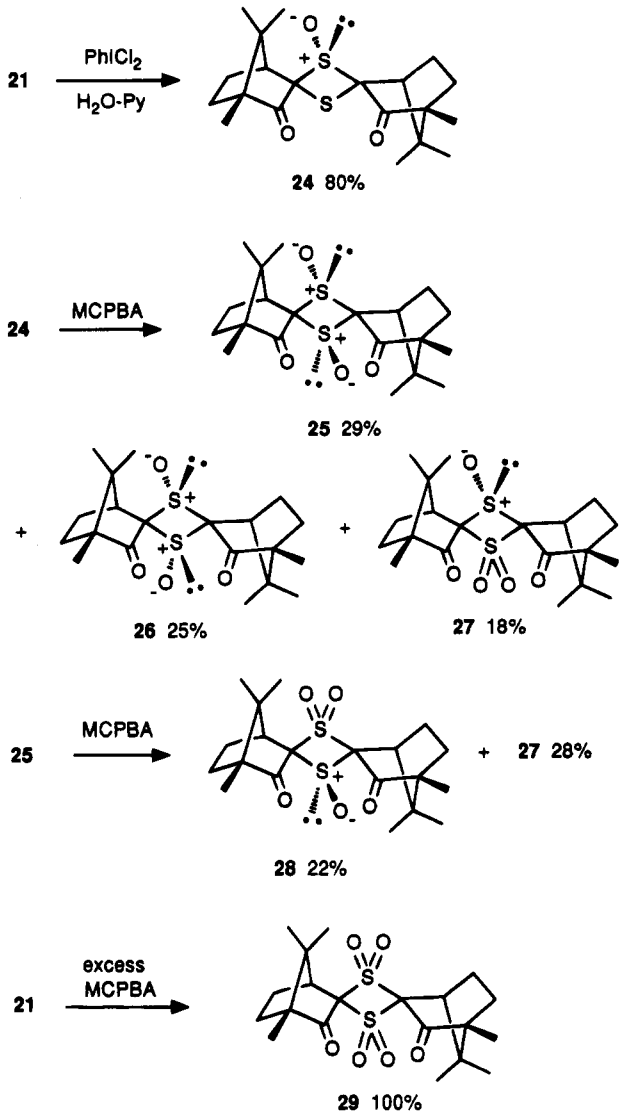
Oxidation of 1,3-Dithietanes and 1,3-Diselenetanes

The *anti*-1,3-dithietane **21**, like its selenium counterpart **6**, has equivalent sulfur atoms because of a C_2 axis of symmetry perpendicular to the four-membered ring. However, the two faces of this ring are not equivalent, and oxygen or other substituents on the sulfur atoms can be classified as *cis* or *trans* with respect to the carbonyl groups at the adjacent camphor carbon atoms. Two stereoisomeric monosulfoxides are therefore possible. Oxidation of **21** with 1 equiv of iodobenzene dichloride afforded essentially a single sulfoxide stereoisomer, isolated in 80% yield, along with a small amount of unreacted starting material. We assign this compound the *trans* configuration **24** on the basis of downfield shifts of the ^{1}H-NMR signals for H(4), H(4′), and *endo*-H(5) relative to the parent dithietane **21**.[16] It is also interesting that this sulfoxide is **less** polar (in some solvents)

(15) The mechanism for the dimerization of adamantanethione under photochemical conditions has been studied in detail: (a) Lawrence, A. H.; Liao, C. C.; de Mayo, P.; Ramamurthy, V. *J. Am. Chem. Soc.* **1976**, *98*, 3572. (b) Lawrence, A. H.; Liao, C. C.; de Mayo, P.; Ramamurthy. V. *J. Chem. Soc.* **1976**, *98*, 2219. Its acid-catalyzed dimerization has also been reported: (c) Greidanus, J. W. *Can. J. Chem.* **1970**, *48*, 3530. However, detailed mechanistic studies of the dimerization of other thio- and selenocarbonyl compounds appear to be lacking.

(16) The downfield shift of H(4) in both camphor moieties (from δ 2.53 in **21** to δ 2.84 and δ 2.71 and **24**) and of the *endo*-H(5) proton on one camphor unit (from δ < 1.88 to δ 2.58) is attributed to their location in the deshielding zone of the sulfoxide bond. For examples of similar effects caused by acetylene-like anisotropy of sulfoxides, see: (a) Buck, K. W.; Foster, A. B.; Pardoe, W. D., Qadir, M. H.; Webber, J. M. *J. Chem. Soc., Chem. Commun.* **1966**, 759. (b) Sataty, I. *Org. Magn. Reson.* **1974**, *6*, 8.

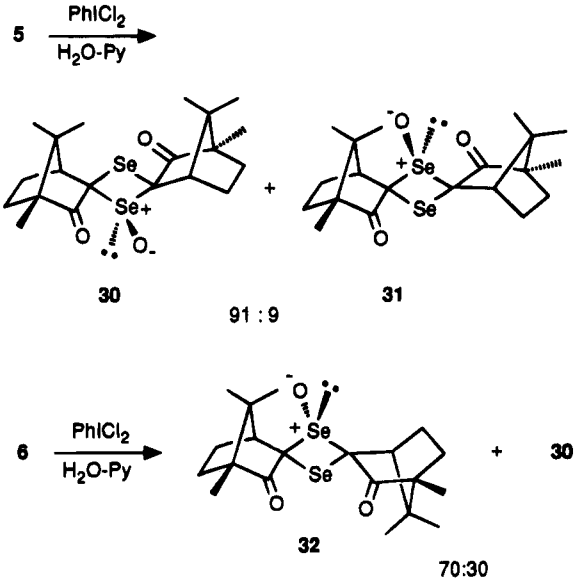
Scheme 7



than sulfide **21**, which we attribute to the partial cancellation of the two combined carbonyl dipoles by the new sulfoxide dipole. This also supports our assignment of the *trans* configuration to this sulfoxide. The further oxidation of **24** with 1 equiv of *m*-CPBA afforded comparable amounts of the corresponding *cis,trans*- and *trans,trans*-bis-sulfoxides **25** and **26** and a smaller amount of the *cis,trans,trans*-trioxide **27**. It was possible to easily distinguish between these three compounds because **25** has nonequivalent camphor units with six separate ^{1}H-NMR methyl signals,[17] while **26** has equivalent camphor residues. The trioxide **27** is, of course, distinct from **25** and **26** by virtue of its extra oxygen atom and greater molecular weight. Compound **27** and its *cis,trans,cis* trioxide isomer **28** were formed in comparable amounts by the similar oxidation of **25**, whereas exhaustive oxidation of the original dithietane **21** with excess *m*-CPBA afforded the bis-sulfone **29** in excellent yield. The greater downfield shifts for H-4 and H-4′ in the ^{1}H-NMR spectrum of **27** relative to **28** permit their assignments as the *cis,trans,trans* and *cis,trans,cis* trioxides, respectively. These processes are summarized in Scheme 7.

(17) Only five methyl signals and one set of H-4 signals were observed because of fortuitous overlap.

Scheme 8



It will be recalled that, unlike the *anti* isomer, the *syn*-1,3-diselenetane **5** provides different environments for the two selenium atoms, as one resides *endo* to both camphor units, while the other is *exo*. However, the C_2 axis of symmetry that passes through the two heteroatoms renders the two faces of the four-membered ring equivalent. Thus, oxidation of compound **5** can produce regioisomeric, but not stereoisomeric, monoselenoxides. When diselenetane **5** was treated with 1 equiv of iodobenzene dichloride, a mixture of *endo*- and *exo*-selenoxides **30** and **31**, respectively, was obtained in the ratio of 91:9. The assignment of the *endo*-selenoxide structure to the major product is tentative and is based on the expected preference for oxidation of the more sterically accessible *endo* selenium atom (Scheme 8).

The *anti*-1,3-diselenetane **6**, where similar symmetry considerations apply as to those of the *anti*-1,3-dithietane **21**, afforded the *trans*-selenoxide **32** as the principal oxidation product, together with the *endo*-selenoxide **30**, previously obtained from the *syn*-1,3-diselenetane **5**. The formation of the latter compound indicates that C–Se bond cleavage occurs along with oxidation of the selenium atom (Scheme 8). The precise mechanism for the ring-opening and reclosure of the diselenetane ring needed to account for the formation of **30** is unclear at present. Further stepwise oxidation of the monoselenoxide products produced complex mixtures of relatively unstable products that were not investigated further.

Experimental Section

The ^{77}Se-NMR spectra were recorded using diphenyl diselenide or selenium dioxide as external standards. Chemical shifts are reported relative to dimethyl selenide (δ 0.0 ppm) by assuming that the signals from the standards are at δ 461.0[18a] and 1302.6[18b] ppm, respectively. Elemental analyses were performed by Ms. D. Fox of the Chemical Instrumentation Lab at the University of Calgary.

Iodobenzene dichloride was prepared by a literature procedure.[19a] This reagent has been previously employed in the oxidation of other sulfides to sulfoxides[19b,c] and selenides to selenoxides.[19d] The enol trimethylsilyl ether of camphor[20] was converted to the thiocyanate **19** by the method of Bacon

(18) (a) Chivers, T.; Doxsee, D. D.; Parvez, M. *Inorg. Chem.* **1993**, *32*, 2238. (b) Chivers, T.; Laitinen, R. S.; Schmidt, K. J. *Can. J. Chem.* **1992**, *70*, 719.

and Guy,[21] in which thiocyanogen chloride is generated in situ from lead thiocyanate and iodobenzene dichloride. *m*-CPBA was purified by washing with a pH 7.5 phosphate buffer[22] and was assumed to be 100% pure. Saturated aqueous solutions of NaCl, NH_4Cl, and other salts used in workup procedures were employed. (1*R*)-(+)-Camphor, selenium powder (100 mesh), and sulfur powder (100 mesh) were purchased from commercial sources and used without further purification. Other reagents and solvents were purchased and purified or dried by standard methods as required.

Chromatography was performed on silica gel (70–230 mesh) unless otherwise indicated.

Di(*endo*-3-camphoryl) Diselenide (3) and Di(*endo*-3-camphoryl) Selenide (4). *n*-Butyllithium (79.5 mmol) was added to a solution of diisopropylamine (13 mL, 93 mmol) and a few crystals of α,α-bipyridyl[4] in 100 mL of THF at −40 °C, and the resulting solution was stirred for 30 min. (1*R*)-(+)-Camphor (**1**) (9.99 g, 65.6 mmol) was added, and the solution was stirred for an additional 2 h. Selenium (6.65 g, 84.2 mmol) was added, and the suspension was stirred for 5 h at −40 °C. The reaction was quenched with aqueous NH_4Cl, the mixture was warmed to rt, and air was bubbled through it overnight. The mixture was then poured into 200 mL of ether, washed with aqueous NaCl, dried (Na_2SO_4), filtered (Celite), and concentrated *in vacuo*. The residue was heated at ca. 60 °C and 0.1 Torr in a vacuum desiccator equipped with a dry ice–acetone cooled trap overnight, thus recovering 5.07 g (51%) of sublimed camphor. The residue was chromatographed (elution with 10% ethyl acetate–hexanes) to afford 6.51 g of an unseparated mixture of **3** and **4** in the ratio of 84:16 (determined by NMR integration), which corresponds to yields of 76% and 14%, respectively, based on consumed camphor. Recrystallization of the mixture of **3** and **4** from methanol afforded yellow crystals of the pure diselenide **3**: mp 81–83 °C; IR (film) 1730, 1036 cm^{-1}; ^{1}H-NMR (400 MHz) δ 4.51 (dd, J = 4.6, 1.9 Hz, 2H), 2.41–2.39 (m, 2 H), 1.85–1.77 (m, 4 H), 1.70 (ddd, J = 12.2, 4.7, 4.7 Hz, 2 H), 1.40 (ddd, J = 13.7, 8.5, 5.4 Hz, 2 H), 1.04 (s, 6 H), 0.99 (s, 6 H), 0.94 (s, 6 H); mass spectrum *m/z* (relative intensity) 462 (25, M^+, $^{80}Se_2$), 382 (1), 311 (2), 231 (16), 151 (31), 123 (100). Anal. Calcd for $C_{20}H_{30}O_2Se_2$: C, 52.18; H, 6.57. Found: C, 51.98; H, 6.52. Concentration of the mother liquor and recrystallization from hexanes afforded the colorless selenide **4**: mp 160–164 °C; IR (film) 1734, 1042 cm^{-1}; ^{1}H-NMR (400 MHz) δ 4.30 (dd, J = 4.6, 2.0 Hz, 2 H), 2.34–2.32 (m, 2 H), 1.87–1.83 (m, 2 H), 1.75–1.66 (m, 4 H), 1.52–1.46 (m, 2 H), 1.02 (s, 6 H), 0.94 (s, 6 H), 0.93 (s, 6 H); mass spectrum *m/z* (relative intensity) 382 (42, M^+, ^{80}Se), 231 (50), 152 (63), 151 (41), 124 (100). Anal. Calcd for $C_{20}H_{30}O_2Se$: C, 62.98; H, 7.93. Found: C, 63.08; H, 7.99.

***syn*-1,3-Diselenetane 5 and *anti*-1,3-Diselenetane 6.** LDA (7.81 mmol) was prepared in 10 mL of THF as in the preceding procedure. (1*R*)-(+)-Camphor (**1**) (1.01 g, 6.63 mmol) was added, and the solution was stirred for 2 h at −40 °C. Selenium (0.582 g, 7.37 mmol) was added, and the suspension was stirred for 3 h at −40 °C and 1 h at −10 °C, followed by the dropwise addition of methyl iodide (0.88 mL, 14.1 mmol). The mixture was stirred for 45 min, during which time the reaction turned from a black suspension to a homogenous yellow solution. Aqueous NH_4Cl was cautiously added, and the mixture was allowed to warm to rt, poured into 100 mL of ether, washed with water and aqueous NaCl, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed to afford a less polar fraction (elution with 5% ethyl acetate–hexanes; *vide infra*), followed by 0.487 g (32%) of the *syn*-1,3-diselenetane **5** and 0.146 g (10%) of the *anti* isomer **6** as colorless powders (elution with 20% ethyl acetate–hexanes).

syn-Diselenetane **5**: R_f 0.30 (20% ethyl acetate–hexanes); mp 188–193 °C dec (from ethanol); IR (film) 1746, 1026, 1001 cm^{-1}; ^{1}H-NMR (200 MHz) δ 2.95 (d, J = 4.4 Hz, 2 H), 1.96–1.78 (m, 2 H), 1.63–1.48 (m, 4 H), 1.27–1.13 (m, 2 H), 1.00 (s, 6 H), 0.95 (s, 6 H), 0.68 (s, 6 H); ^{77}Se-NMR δ 808.2, 650.2; mass spectrum *m/z* (relative intensity) 460 (27, M^+, $^{80}Se_2$), 349 (29), 230 (20), 83 (100). Anal. Calcd for $C_{20}H_{28}O_2Se_2$: C, 52.41; H, 6.16. Found: C, 52.48, H, 6.24.

anti-Diselenetane **6**: R_f 0.15 (20% ethyl acetate–hexanes); mp 247–250 °C dec (from ethanol); IR (film) 1746, 1026, 1001 cm^{-1}; ^{1}H-NMR (200 MHz) δ 2.64 (d, J = 4.4 Hz, 2 H), 1.85–1.70 (m, 2 H), 1.68–1.52 (m, 2 H), 1.48–1.16 (m, 4 H), 0.96 (s, 6 H), 0.95 (s, 6 H), 0.73 (s, 6 H); ^{77}Se-NMR δ 712.9; mass spectrum *m/z* (relative intensity) 460 (11, M^+, ^{80}Se), 349 (12), 230 (31), 83 (100). Anal. Calcd for $C_{20}H_{28}O_2Se_2$: C, 52.41; H, 6.16. Found: C, 52.22; H, 6.03. Crystals suitable for X-ray diffraction were grown from absolute ethanol.

The less polar fraction that preceded **5** and **6** contained 3-(*endo*-methylseleno)camphor (**7**) and 3,3-bis(methylseleno)-camphor (**8**) in yields of 12% and 15% (by NMR integration), respectively, along with unidentified products. Further attempts at purification of **7** and **8** by chromatography were only partially successful, and their identification is tentative. Selenide **7**: ^{1}H-NMR (400 MHz) δ 3.65 (dd, J = 4.5, 1.6 Hz, 1 H), 2.20 (s, superimposed on m at δ 2.23–2.16, total 4 H), 1.86–1.77 (m, 2 H), 1.69 (ddd, J = 12.3, 4.1, 4.1 Hz, 1 H), 1.47 (ddd, J = 13.7, 8.7, 5.2 Hz, 1 H), 1.03 (s, 3 H), 0.93 (s, 3 H), 0.91 (s, 3 H). Selenoacetal **8**: ^{1}H-NMR (200 MHz) δ 2.28–2.26 (m, 1 H), 2.23 (s, 3 H), 2.13 (s, 3 H), 2.07–1.97 (m, 2 H), 1.83–1.71 (m, 2 H), 1.22 (s, 3 H), 1.04 (s, 3 H), 0.94 (s, 3 H).

3-(*endo*-Selenocyanato)camphor (14). Sulfuryl chloride (36 μL, 0.44 mmol) was added dropwise to an ice-cooled solution of diselenide **3** (204 mg, 0.443 mmol) in 2 mL of dichloromethane, and the resulting dark red solution was stirred at 0 °C for 15 min. This solution was added to trimethylsilyl cyanide (140 μL, 1.05 mmol) in 2 mL of dichloromethane, and the mixture was stirred at rt for 10 h. It was concentrated *in vacuo* and separated by chromatography (elution with 10% ethyl acetate–hexanes) to afford 177 mg (78%) of the pure selenocyanate **14** as a colorless solid: R_f 0.20 (10% ethyl acetate–hexanes); mp 61–62 °C (from hexanes); IR (film) 2149, 1742, 1030 cm^{-1}; ^{1}H-NMR (200 MHz) δ 4.65 (ddd, J = 4.6, 2.0, 0.6 Hz, 1 H), 2.45–2.40 (m, 1 H), 2.05–1.74 (m, 3 H), 1.43 (ddd, J = 13.6, 8.7, 5.0 Hz, 1 H), 1.11 (s, 3 H), 1.00 (s, 3 H), 0.99 (s, 3 H); mass spectrum *m/z* (relative intensity) 257 (12, M^+, ^{80}Se), 151 (45), 123 (43), 83 (100). Anal. Calcd for $C_{11}H_{15}NOSe$: C, 51.57; H, 5.90; N, 5.47. Found: C, 51.47; H, 5.91; N, 5.41.

Elimination of Selenocyanate 14 with Potassium *tert*-Butoxide. Potassium *tert*-butoxide (22 mg, 0.19 mmol) was added to a stirred solution of **14** (39 mg, 0.15 mmol) in 2 mL of THF, and the resulting solution was stirred at rt for 5 h. The mixture was poured into 10 mL of aqueous NH_4Cl and extracted with two 5 mL portions of ether. The combined ether extracts were washed with aqueous NaCl, dried (Na_2SO_4), and concentrated *in vacuo* to afford 35 mg (100%) of a 74:26 (by NMR integration) mixture of the diselenetanes **5** and **6**, identical to those obtained from the reaction of camphor enolate and selenium in the presence of methyl iodide.

Di(*endo*-3-camphoryl) Sulfide (15), *endo*-3-Camphoryl *exo*-3-Camphoryl Sulfide (16), 3-(*endo*-Methylthio)camphor (17), and 3-(*exo*-Methylthio)camphor (18). *n*-Butyllithium (7.76 mmol) was added to a solution of diisopropylamine (1.20 mL, 8.56 mmol) and a few crystals of α,α′-bipyridyl in 10 mL of THF at −40 °C, and the resulting solution was stirred for 45 min. Camphor (**1**) (1.01 g, 6.62 mmol) was added, and stirring was continued for 2 h. Sulfur (0.237 g, 7.40 mmol) was added, resulting in an orange color, followed by HMPA (3.50 mL, 20.1 mmol), which changed the color to dark green. The mixture was stirred at −40 °C for 1 h. Methyl iodide (0.90 mL, 14 mmol) was added, and the resulting solution turned yellow and was stirred at 0 °C for 45 min. Aqueous NH_4Cl was added, and the reaction was allowed to warm to rt. The mixture was poured into 100 mL of ether, washed three times with water and aqueous NaCl, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed (elution

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(21) Bacon, R. G. R.; Guy, R. G. *J. Chem. Soc.* **1960**, 318.

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with 10% ethyl acetate–hexanes) to afford three fractions. The first fraction contained 0.110 g (8%) of an unseparated mixture of *endo* and *exo* methyl sulfides **17** and **18** in the ratio of 62:38 (NMR integration), R_f 0.91 (10% ethyl acetate–hexanes), identified by comparison of the ^{1}H-NMR spectrum with that reported in the literature,[1g] and confirmed by GCMS: *m/z* (relative intensity) 198 (34, M^+), 170 (6), 155 (7), 123 (15), 87 (100).

The second fraction afforded 0.417 g (38%) of the *endo,endo* sulfide **15**:[23] R_f 0.36 (10% ethyl acetate–hexanes); mp 207–209 °C (from ethanol; sealed capillary); IR (Nujol) 1730, 1039, 781 cm^{-1}; ^{1}H-NMR (200 MHz) δ 3.99 (dd, J = 4.7 1.0 Hz, 2 H), 2.34–2.30 (m, 2 H), 1.90–1.63 (m, 6 H), 1.52–1.38 (m, 2 H), 1.01 (s, 6 H), 0.92 (s, 12 H); mass spectrum *m/z* (relative intensity) 334 (77, M^+), 306 (9), 223 (25), 183 (100), 124 (89). Anal. Calcd for $C_{20}H_{30}O_2S$: C, 71.81; H, 9.04. Found: C, 71.63; H, 9.03.

The third fraction gave 0.286 g (26%) of the *endo,endo* sulfide **16**:[23] R_f 0.25 (10% ethyl acetate–hexanes); mp 210–212 °C (from ethanol, sealed capillary); IR (Nujol) 1730, 1038, 781 cm^{-1}; ^{1}H-NMR (200 MHz) δ 4.04 (dd, J = 4.5, 1.0 Hz, 1 H), 3.30 (s, 1 H), 2.26–2.22 (m, 1 H), 2.13 (d, J = 3.5 Hz, 1 H), 2.09–1.91 (m, 2 H), 1.86–1.25 (m, 6 H), 1.04 (s, 6 H), 0.94 (s, 9 H), 0.92 (s, 3 H); mass spectrum, *m/z* (relative intensity) 334 (84, M^+), 306 (10), 223 (74), 183 (100), 124 (77). Anal. Calcd for $C_{20}H_{30}O_2S$: C, 71.81; H, 9.04. Found: C, 71.69; H, 8.97.

3-(*endo*-Thiocyanato)camphor (19). Iodobenzene dichloride (3.32 g, 12.1 mmol) and lead(II) thiocyanate (1.96 g, 6.06 mmol) were stirred in dry dichloromethane at rt for 1 h. Camphor enol trimethylsilyl ether (2.60 mL, 10.6 mmol) was added, and the suspension was stirred for 2 h. The mixture was diluted with 100 mL of dichloromethane, washed twice with water and aqueous NaCl, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was chromatographed (elution with 10% ethyl acetate–hexanes) to afford 1.58 g (71%) of the thiocyanate **19** as a yellow oil: R_f 0.33 (10% ethyl acetate–hexanes); IR (neat) 2156, 1749, 1034 cm^{-1}; ^{1}H-NMR (200 MHz) δ 4.25 (dd, J = 4.6, 1.1 Hz, 1 H), 2.47–2.44 (m, 1 H), 1.99–1.87 (m, 2 H), 1.82–1.75 (m, 1 H), 1.49–1.36 (m, 1 H), 1.09 (s, 3 H), 0.99 (s, 3 H), 0.98 (s, 3 H); mass spectrum *m/z* (relative intensity) 209 (36, M^+), 181 (15), 151 (13), 123 (79), 83 (100). Anal. Calcd for $C_{11}H_{15}NOS$: C, 63.12; H, 7.22; N, 6.69. Found: C, 62.85; H, 7.05; N, 6.58.

***anti*-1,3-Dithietane 21.** Potassium *tert*-butoxide (242 mg, 2.16 mmol) was added to a stirred solution of thiocyanate **19** (409 mg, 1.95 mmol) in 5 mL of dry THF at −78 °C, and the resulting mixture was stirred for 2 h, during which time the initial orange color faded to a pale yellow. An additional 501 mg (4.46 mmol) of potassium *tert*-butoxide was added, and the solution was stirred at −78 °C for a further 30 min. Aqueous NH_4Cl was added, and the mixture was warmed to rt, poured into 50 mL of ether, washed with water and aqueous NaCl, dried (Na_2SO_4), and concentrated *in vacuo* to afford 361 mg (100%) of the dithietane **21** as a homogeneous (TLC, NMR) pale yellow powder: mp 262–263 °C (from ethanol, sealed capillary); IR (Nujol) 1767, 1004, 993 cm^{-1}; ^{1}H-NMR (200 MHz) δ 2.53 (d, J = 4.5 Hz, 2 H), 1.88–1.73 (m, 2 H), 1.65–1.41 (m, 4 H), 1.33–1.18 (m, 2 H), 0.97 (s, 6 H), 0.96 (s, 6 H), 0.76 (s, 6 H); mass spectrum *m/z* (relative intensity) 364 (13, M^+), 336 (9), 253 (23), 182 (97), 83 (100). Anal. Calcd for $C_{20}H_{28}O_2S_2$: C, 65.89; H, 7.74. Found: C, 66.19; H, 7.63. Crystals suitable for X-ray diffraction were grown from absolute ethanol.[24]

Oxidation of 1,3-Dithietane 21. Iodobenzene dichloride (209 mg, 0.76 mmol) was added to a stirred solution of dithietane **21** (264 mg, 0.72 mmol) and 10 drops of water in 10 mL of pyridine at −40 °C. The mixture was warmed to rt and stirred for 18 h. It was then poured into 50 mL of ether, washed three times with 5% HCl solution and aqueous NaCl, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was separated by chromatography (elution with 5% acetone–benzene) to afford 220 mg (80%) of the *trans*-sulfoxide **24** as a white powder: R_f 0.51 (elution with 5% acetone–benzene); mp 163–165 °C (from ethanol); IR (Nujol) 1766, 1755, 1085 cm^{-1}; ^{1}H-NMR (200 MHz) δ 2.84 (d, J = 3.9 Hz, 1 H), 2.71 (d, J = 4.1 Hz, 1 H), 2.58 (ddd, J = 12.4, 8.8, 3.3 Hz, 1 H), 2.12–1.98 (m, 1 H), 1.95–1.49 (m, 5 H), 1.36–1.22 (m, 1 H), 1.07 (s, 3 H), 1.02 (s, 3 H), 0.98 (s, 3 H), 0.97 (s, 3 H), 0.86 (s, 3 H), 0.79 (s, 3 H); mass spectrum *m/z* (relative intensity) 380 (0.1, M^+), 364 (2), 332 (3, M^+ − SO), 198 (9), 182 (92), 55 (100). Anal. Calcd for $C_{20}H_{28}O_3S_2$: C, 63.12; H, 7.42. Found: C, 63.23; H, 7.34.

Oxidation of *trans*-Sulfoxide 24. A solution of *m*-CPBA (95 mg, 0.55 mmol) in 1 mL of dichloromethane was added to a stirred solution of **24** (210 mg, 0.553 mmol) in 5 mL of dichloromethane at −78 °C, and the resulting suspension was stirred at this temperature for 5 h. The mixture was allowed to warm to rt and stirred for an additional 2 days. It was diluted with 25 mL of dichloromethane, washed twice with 1.5 M NaOH and aqueous NaCl, dried ($MgSO_4$), and concentrated *in vacuo* to afford 208 mg of a 25:30:26:19 (determined by NMR integration) mixture of unreacted starting material **24**, bis-sulfoxides **25** and **26**, and sulfone **27**, corresponding to yields of 24%, 29%, 25% and 18%, respectively. The mixture was separated by chromatography (elution with 30% ethyl acetate–hexanes) to afford unreacted **24**, R_f 0.42 (30% ethyl acetate–hexanes), identical to an authentic sample, followed by a mixture of the *trans,trans*-bis-sulfoxide **26** and the trioxide **27**, R_f 0.33 (30% ethyl acetate–hexanes), and the *cis,trans*-bis-sulfoxide **25**, R_f 0.15 (30% ethyl acetate–hexanes). The mixture of **26** and **27** was then separated by preparative TLC on silica gel with 5% acetone–benzene to afford **27**, R_f 0.46, and **26**, R_f 0.32.

cis,trans-Bis-sulfoxide **25**: mp 223–225 °C dec (from chloroform–ethanol); IR (Nujol) 1759, 1097, 1074, 1001 cm^{-1}; ^{1}H-NMR (400 MHz) δ 2.87 (d, J = 4.3 Hz, 2 H), 2.20–2.02 (m, 4 H), 1.88–1.80 (m, 2 H), 1.75–1.62 (m, 2 H), 1.15 (s, 3 H), 1.09 (s, 6 H), 1.035 (s, 3 H), 1.026 (s, 3 H), 0.99 (s, 3 H); mass spectrum *m/z* (relative intensity) 396 (M^+, 0.3), 198 (2), 182 (54), 170 (10), 139 (62), 83 (92), 55 (100). Anal. Calcd for $C_{20}H_{28}O_4S_2$: C, 60.58; H, 7.12. Found: C, 60.29; H, 7.11.

trans,trans-Bis-sulfoxide **26**: mp 194–196 °C dec (from ethanol); IR (chloroform) 1749, 1221, 1095, 1078, 1014 cm^{-1}; ^{1}H-NMR (400 MHz) δ 3.11 (d, J = 4.6 Hz, 2 H), 2.28–2.12 (m, 4 H), 1.85 (ddd, J = 14.0, 11.4, 4.8 Hz, 2 H), 1.70 (ddd, J = 14.0, 9.3, 5.8 Hz, 2 H), 1.06 (s, 6 H), 1.03 (s, 6 H), 1.00 (s, 6 H); mass spectrum *m/z* (relative intensity) 396 (M^+, 1), 198 (7), 182 (12), 170 (32), 153 (58), 83 (81), 55 (100). Anal. Calcd for $C_{20}H_{28}O_4S_2$: C, 60.58; H, 7.12. Found: C, 60.24; H, 6.78.

cis,trans,trans-Trioxide **27**: mp 270–274 °C dec (from ethanol); IR (chloroform) 1763, 1342, 1159, 1093 cm^{-1}; ^{1}H-NMR (400 MHz) δ 3.15 (d, J = 4.2 Hz, 1 H), 3.06 (d, J = 4.2 Hz, 1 H), 2.40–2.25 (m, 2 H), 2.24–2.11 (m, 2 H), 1.91–1.82 (m, 3 H), 1.74 (ddd, J = 14.3, 9.0, 5.6 Hz, 1 H), 1.16 (s, 3 H), 1.11 (s, 3 H), 1.09 (s, 3 H), 1.06 (s, 3 H), 1.05 (s, 3 H), 1.04 (s, 3 H); mass spectrum *m/z* (relative intensity) 412 (4, M^+), 384 (1), 348 (5), 278 (22), 199 (43), 182 (25), 153 (77), 83 (95), 55 (100); exact mass calcd for $C_{20}H_{28}O_5S_2$ 412.1378, found 412.1377.

Oxidation of *cis,trans*-Bis-sulfoxide 25. *m*-CPBA (18 mg, 0.10 mmol) was added to a solution of **25** (40 mg, 0.10 mmol) in 10 mL of THF at −78 °C. The mixture was stirred for 3 h at −78 °C and then for 2 days at rt and at reflux for 1 day. Some starting material persisted, an additional 7 mg (0.04 mmol) of *m*-CPBA was added, and the mixture was refluxed for 2 days. It was cooled to rt, washed twice with 1.5 M NaOH and aqueous NaCl, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was separated by preparative TLC on silica gel with 5% ethyl acetate–hexanes to afford 12 mg (28%) of *cis,trans,trans*-trioxide **27**, R_f 0.56 (identical to an authentic sample from the preceding procedure), and 9 mg (22%) of the *cis,trans,cis*-trioxide **28**: R_f 0.28; mp 251–256 °C dec (from ethanol); IR (chloroform) 1768, 1340, 1159, 1109 cm^{-1}; ^{1}H-NMR (400 MHz) δ 2.90 (d, J = 4.3 Hz, 1 H), 2.80–2.79 (m, 1 H), 2.27–2.09 (m, 4 H), 1.85–1.78 (m, 3 H), 1.63 (ddd, J = 14.4,

(23) Sulfide **15** or **16** of unspecified stereochemistry with mp 197–199 °C was reported previously: Reznik, P. E. *Nekotorye Voprosy Farmatsii, Sbornik Nauch. Trudov Vyssh. Ucheb. Zavedenii Ukr. S.S.R.* **1956**, 124; *Chem. Abstr.* **1959**, *53*, 9267g.

(24) The authors have deposited atomic coordinates for structures **6** and **21** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB3 1EZ, UK.

8.8, 5.7 Hz, 1 H), 1.15 (s, 3 H), 1.13 (s, 3 H), 1.09 (s, 3 H), 1.08 (s, 3 H), 1.05 (s, 3 H), 1.04 (s, 3 H); mass spectrum *m/z* (relative intensity) 412 (1, M^+), 348 (5), 300 (8), 278 (30), 182 (24), 153 (68), 83 (90), 55 (100); exact mass calcd for $C_{20}H_{28}O_5S_2$ 412.1378, found 412.1339.

Bis-sulfone 29. Dithietane **21** (67 mg, 0.18 mmol) and *m*-CPBA (50–60%, 1.30 g, ca. 3.8 mmol) were stirred in 5 mL of chlorobenzene at 110 °C for 4 h. The mixture was cooled and poured into 50 mL of ether, washed six times with 1.5 M NaOH and aqueous NaCl, dried (Na_2SO_4), and concentrated *in vacuo* to afford 80 mg (100%) of the bis-sulfone **29**, as an off-white powder: mp 226–231 °C dec (from dichloromethane-ethanol); IR (Nujol) 1766, 1756, 1375, 1085 cm^{-1}; ^{1}H-NMR (200 MHz) δ 3.18 (dd, J = 2.5, 2.5 Hz, 2 H), 2.24–2.14 (m, 4 H), 1.83–1.74 (m, 4 H), 1.06 (s, 12 H), 1.05 (s, 6 H); mass spectrum *m/z* (relative intensity) 428 (59, M^+), 400 (18), 336 (12), 151 (30), 83 (100). Anal. Calcd for $C_{20}H_{28}O_6S_2$: C, 56.05; H, 6.59. Found: C, 55.69; H, 6.37.

Oxidation of *syn*-Diselenetane 5. Iodobenzene dichloride (61 mg, 0.22 mmol) was added to a solution of **5** (100 mg, 0.22 mmol) and 10 drops of water in 10 mL of pyridine at −40 °C, and the resulting mixture was stirred at this temperature for 4 h. It was warmed to rt, poured into 50 mL of ether, washed three times with 5% aqueous HCl and aqueous NaCl, dried (Na_2SO_4), and concentrated *in vacuo* to afford 92 mg of a 91:9 mixture of *endo* and *exo* selenoxides **30** and **31**, respectively, as a white powder that could not be separated further: IR (Nujol) 1742, 1024, 1003, 859 cm^{-1}; ^{1}H-NMR (200 MHz) attributed to the *endo*-selenoxide **30** δ 3.67 (d, J = 4.4 Hz, 1 H), 2.70 (ddd, J = 14.1, 9.6, 4.3 Hz, 1 H), 2.48 (d, J = 4.2 Hz, 1 H), 2.11–1.92 (m, 2 H), 1.80–1.57 (m, 4 H), 1.55–1.44 (m, 1 H), 1.04 (s, 3 H), 1.03 (s, 3 H), 1.00 (s, 3 H), 0.97 (s, 3 H), 0.83 (s, 3 H), 0.74 (s, 3 H); ^{77}Se-NMR δ 1106.7, 575.7; ^{1}H-NMR (200 MHz) assigned to the *exo*-selenoxide **31** δ 3.21 (d, J = 4.6 Hz, 1 H), 2.67 (d, J = 4.5 Hz, 1 H), 1.08 (s, 3 H), 1.07 (s, 3 H), 0.99 (s, 3 H), 0.95 (s, 6 H), 0.80 (s, 3 H); ^{77}Se-NMR δ 1130.5, 463.5. Other ^{1}H-NMR signals of **31** were masked by those of the major isomer **30**.

Oxidation of *anti*-Diselenetane 6. The oxidation of **6** (103 mg, 0.23 mmol) with iodobenzene dichloride (63 mg, 0.23 mmol) was performed as in the preceding procedure to afford a 70:30 mixture of selenoxides **32** and **30** as a white powder that could not be separated further: IR (Nujol) 1743, 1023, 1002, 856 cm^{-1}; ^{1}H-NMR (400 MHz) attributed to the *trans*-selenoxide **32** δ 2.87 (d, J = 4.6 Hz, 1 H), 2.78 (d, J = 4.4 Hz, 1 H), 2.30 (ddd, J = 14.5, 9.8, 4.6 Hz, 1 H), 2.04–1.90 (m, 2 H), 1.80–1.43 (m, 3 H), 1.36–1.19 (m, 2 H), 1.03 (s, 3 H), 0.992 (s, 3 H), 0.987 (s, 3 H), 0.97 (s, 3 H), 0.82 (s, 3 H), 0.76 (s, 3 H); ^{77}Se-NMR δ 1209.7, 606.3. The presence of selenoxide **30** was inferred from the observation of ^{1}H- and ^{77}Se-NMR signals matching those of the sample prepared in the preceding procedure.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support. B.P.D. thanks NSERC for a Postgraduate Scholarship.

Supplementary Material Available: ORTEP diagrams of *anti*-1,3-diselenetane **6** and *anti*-1,3-dithietane **21**, a table of selected bond lengths and bond angles from their X-ray structures,[24] and the ^{1}H-NMR spectra of dithietane trioxides **27** and **28** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9418691