2-Thiabicyclo[2.2.1]hept-5-ene and Its S-Oxides and 3-Alkyl Derivatives: Sulfine and Sulfene Cyclopentadiene Diels-Alder Adducts. Conversion of the Cyclopentadiene-Sulfine Adducts into 2-Oxa-3-thiabicyclo[3.3.0]oct-7-enes, Novel Bicyclic Sultenes[1]

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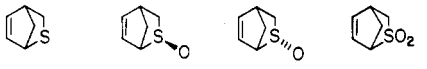
Reaction of (trimethylsilyl)methanesulfonyl chloride (**6a**) or -sulfonic anhydride (**6b**) with cesium fluoride in the presence of cyclopentadiene affords 2-thiabicyclo[2.2.1]hept-5-ene 2,2-dioxide (**4**) by way of sulfene $CH_2{=}SO_2$. Similar reaction of (trimethylsilyl)methanesulfinyl chloride (**7**) gave the unstable 2-thiabicyclo[2.2.1]hept-5-ene *endo*-2-oxide (**3**) via the intermediacy of sulfine $CH_2{=}SO$. Compound **3** can be oxidized to **4** and reduced to 2-thiabicyclo[2.2.1]hept-5-ene (**1**) and the latter oxidized to the stable 2-thiabicyclo[2.2.1]hept-5-ene *exo*-2-oxide (**2**). Fluorodesilylation of 1-(trimethylsilyl)propanesulfonic anhydride (**8**) in the presence of cyclopentadiene gave a 77/23 ratio of *endo*/*exo*-3-ethyl-2-thiabicyclo[2.2.1]hept-5-ene 2,2-dioxide (**9a**/**b**) by way of propanethial *S*,*S*-dioxide. The structure of the *major* isomer **9a** was established by an X-ray structure of the corresponding *exo*-epoxide **11a**, formed from **9a** by oxidation. Reaction of **4** with *n*-butyllithium followed by ethyl iodide gave a compound identical with minor isomer **9b**. Reaction of propanethial *S*-oxide with cyclopentadiene gave unstable *endo*-3-ethyl-2-thiabicyclo[2.2.1]hept-5-ene *endo*-5-oxide (**10a**). The structure of **10a** was established by oxidation to sulfone **9a**, by reduction and reoxidation to a stable *exo*-5-oxide **10b**, by its facile [2,3] sigmatropic rearrangement to *exo*-4-ethyl-2-oxa-3-thiabicyclo[3.3.0]oct-7-ene (**14c**), and by NMR spectroscopic methods. Compound **14c** was characterized by NMR spectroscopy and by its reactions. Oxidation of **14c** gave the *endo*/*exo*-3-oxides **15c**/**15c'** and the 3,3-dioxide **16c**. Reaction of **14c** with phenyllithium gave alcohol **17c**, which was desulfurized and oxidized to 5-propyl-2-cyclopentenone or was oxidized at both carbon and sulfur to give (*E*)-5-propylidene-2-cyclopentenone **21c** on gentle warming. Reaction of **14c** with *tert*-butyl alcohol gave *exo*-6-*tert*-butoxy-*exo*-3-ethyl-*syn*-7-hydroxy-2-thiabicyclo[2.2.1]heptane (**24**), characterized by further oxidation to crystalline hydroxy sulfone **25** and keto sulfone **26**. Mechanisms are proposed for the above series of reactions.

Cyclopentadiene has been widely employed to trap highly reactive thiocarbonyl compounds and give derivatives of 2-thiabicyclo[2.2.1]hept-5-ene (**1**).[2] Isolation of



1 2 3 4

the adducts provides evidence for the existence of short-lived precursors. We have used this approach to demonstrate a useful new synthesis of alkanethial *S*,*S*-dioxides (sulfenes)[3a] via fluorodesilylation of 1-(trimethylsilyl)alkanesulfonic acid derivatives and to ascertain the endo/exo preferences of sulfenes in the Diels-Alder reaction. Fluorodesilylation of (trimethylsilyl)methanesulfinyl chloride affords thioformaldehyde *S*-oxide (sulfine),[3a] which can also be trapped as its cyclopentadiene adducts, 2-thiabicyclo[2.2.1]hept-5-ene *exo*-*S*-oxide (**2**; minor) and 2-thiabicyclo[2.2.1]hept-5-ene *endo*-*S*-oxide (**3**; major). However, in contrast to the sulfene-cyclopentadiene adducts, which are stable at room temperature, the sulfine adduct is quite labile, rearranging even at 0 °C. Likewise, alkanethial *S*-oxides, including the onion lacrymatory factor propanethial *S*-oxide,[3b] react readily with cyclopentadiene, giving unstable adducts that rearrange. The sulfine adduct can be stabilized by oxidation to 2-thiabicyclo[2.2.1]hept-5-ene 2,2-dioxide (**4**). We have determined the stereochemistry and isomer ratios of the sulfine-cyclopentadiene adducts and their oxidation and reduction products. We have also elucidated the mechanism for rearrangement of these adducts. These stereochemical and mechanistic studies together provide useful information on the stereochemistry about the carbon-sulfur double bond in the sulfines as well as on their endo/exo preferences in the Diels-Alder reaction. We present herein a full report[4] of the determination of stereochemistry, by chemical as well as NMR and X-ray methods, of a series of previously unknown 3-alkyl-2-thiabicyclo[2.2.1]hept-5-enes and their *S*-oxides. We also describe the properties and uses of the novel heterocycles formed by rearrangement of the initial sulfine-cyclopentadiene adducts.

Results and Discussion

Cycloadducts of Thial *S*-Oxides and *S*,*S*-Dioxides with Cyclopentadiene. Fluorodesilylation of silyl compounds bearing a leaving group in the β-position represents a useful synthesis of olefins.[5] In connection with an investigation of the chemistry of 1-(triorganosilyl)alkanethiol derivatives **5**, and related compounds having both sulfur and silicon on the same carbon atom,[6] we wondered

† Fellow of the John Simon Guggenheim Memorial Foundation, 1984-1985.

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Table I. ^{1}H and ^{13}C NMR Chemical Shifts of 2-Thiabicyclo[2.2.1]hept-5-ene Derivatives

	compound										
ring posn	1[c]	4[d]	3	2	12a[e]	12b[e]	10a	10b	10c	9a	9b
1	50.5[a] (4.00 ex)[a]	64.4[a] (3.80)[a]	65.3	67.2[a]	54.1	54.4	65.6	76.8	67.0	65.8[a]	65.1
3	30.3[a] (3.17 ex, 2.20 en)[a]	47.3[a] (2.79 ex, 2.45 en)[a]	55.1	56.2[a]	51.5	50.8	63.5	67.5	60.7	59.1[a]	57.0
4	44.5 (3.44)	41.0 (3.40)	43.1	41.4	51.3	49.5	41.1[b]	44.5[b]	41.7[b]	44.6[b]	42.6[b]
5	130.8 (5.76)	140.6 (6.47)	139.9	145.3	128.8	133.0	137.8	142.7	145.2	137.8	141.5
6	135.6 (6.23)	129.2 (6.25)	127.8	126.6	137.4	136.9	129.7	127.0	126.7	130.0	129.5
7	49.9 (1.54 a, 1.36 s)	45.1 (2.51 a, 2.35 s)	44.7	43.8	48.4	47.4	47.5[b]	44.5[b]	45.8[b]	43.9[b]	45.8[b]
CH_2					27.7	30.4	18.3	22.9	23.3	23.0	23.3
CH_3					13.6	14.1	12.3	12.9	12.4	12.0	12.4

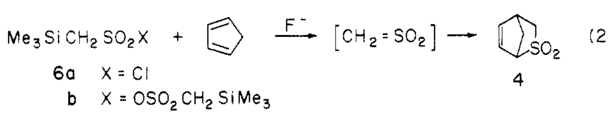
[a] Removed upon H/D exchange at C_1, C_3. [b] Assignment of pair may be interchanged. [c] Coupling constants (Hz): $J_{1,6} = 2.5$, $J_{3ex,3en} = 9.2$, $J_{3ex,4} = 4.0$, $J_{3en,7a} = 7.0$, $J_{4,5} = 3.1$, $J_{5,6} = 5.5$, $J_{7a,7s} = 9.1$. [d] Coupling constants (Hz): $J_{1,6} = 3.4$, $J_{3ex,3en} = 11.3$, $J_{3ex,4} = 4.3$, $J_{5,6} = 5.8$, $J_{7a,7s} = 14$. [e] Excellent agreement with published data of Krafft.[17]

whether fluorodesilylation could be used to form thiocarbonyl bonds (eq 1). We were delighted to find that it

$$R_3SiCHR'SO_nX \xrightarrow{F^-} R'CH{=}SO_n + R_3SiF + X^- \quad (1)$$

5, n = 0 - 2

could! Thus, when a solution of (trimethylsilyl)methanesulfonyl chloride (**6a**) or (trimethylsilyl)methanesulfonic anhydride (**6b**) was stirred in dry acetonitrile with an equivalent amount of cesium fluoride and an excess of cyclopentadiene, the adduct 2-thiabicyclo[2.2.1]hept-5-ene 2,2-dioxide (**4**) could be isolated as a colorless crystalline solid in 64% yield from **6a** or 75% yield from **6b** (eq 2). The known[7a] reagent **6a** could be



conveniently synthesized in 58% overall yield via chlorination of an aqueous solution of the isothiuronium salt formed by refluxing a mixture of chloromethyltrimethylsilane and thiourea in ethanol (eq 3). Compound **6b** could

$$Me_3SiCH_2Cl \xrightarrow[2)\ Cl_2,\ H_2O]{1)\ (NH_2)_2C=S} Me_3SiCH_2SO_2Cl \ (\mathbf{6a}) \quad (3)$$

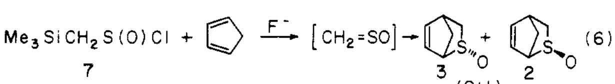
be prepared by sequential treatment of (trimethylsilyl)methanethiol[7b] with peracetic acid (giving the sulfonic acid) followed by phosphorus pentachloride (eq 4).

$$Me_3SiCH_2SH \xrightarrow[2)\ PCl_5]{1)\ CH_3CO_3H} (Me_3SiCH_2SO_2)_2O \ (\mathbf{6b}) \quad (4)$$

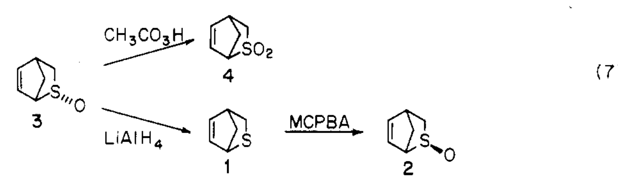
Fluorodesilylation of (trimethylsilyl)methanesulfinyl chloride (**7**), prepared as indicated in eq 5, in the presence

$$Me_3SiCH_2Cl \xrightarrow[2)\ Cl_2,\ Ac_2O]{1)\ AcSK} Me_3SiCH_2S(O)Cl \ (\mathbf{7}) \quad (5)$$

of cyclopentadiene at −20 °C gave in 90% crude yield a 9/1 mixture of the unstable 2-thiabicyclo[2.2.1]hept-5-ene *endo*-2-oxide (**3**) and the *exo*-2-oxide (**2**) (eq 6). This



mixture could be oxidized to **4** or reduced to the known[8] 2-thiabicyclo[2.2.1]hept-5-ene (**1**), which in turn could be oxidized giving a pure sample of the stable *exo*-2-oxide **2** (eq 7). ^{1}H and ^{13}C NMR data for compounds **1**–**4** are summarized in Table I.



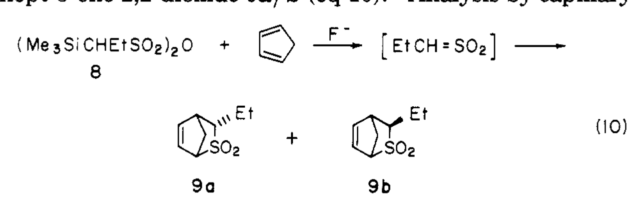
If **7** in acetonitrile is slowly added to 0.5 equiv of cesium fluoride in acetonitrile at −20 °C, *S*-chloromethyl (trimethylsilyl)methanethiosulfonate is formed in 97% yield. This reaction can be explained by postulating trapping of sulfine by **7** (eq 8) in analogy to the trapping of other sulfines by sulfinyl chlorides.[9]

$$Me_3SiCH_2S(O)Cl \ (\mathbf{7}) \xrightarrow{F^-} [CH_2{=}SO] \xrightarrow{\mathbf{7}} CH_2{=}\overset{+}{S}OS(O)CH_2SiMe_3\ Cl^- \longrightarrow ClCH_2SSO_2CH_2SiMe_3 \quad (8)$$

Having succeeded in our initial goal of demonstrating the feasibility of the fluorodesilylation route to sulfene and sulfine, we next sought to apply the procedure to substituted systems, e.g. **5** (R′ ≠ H). Fluorodesilylation of sulfonic anhydride **8** (the precursor to propanethial *S*,*S*-dioxide; eq 9) in the presence of cyclopentadiene afforded

$$Me_3SiCH_2Cl \xrightarrow[2)\ EtI]{1)\ sec\text{-}BuLi} Me_3SiCHEtCl \xrightarrow[2)\ OH^-;\ H^+]{1)\ (NH_2)_2C=S} Me_3SiCHEtSH \xrightarrow[2)\ PCl_5]{1)\ CH_3CO_3H} (Me_3SiCHEtSO_2)_2O \ (\mathbf{8}) \quad (9)$$

a 76% yield of *endo*/*exo*-3-ethyl-2-thiabicyclo[2.2.1]hept-5-ene 2,2-dioxide **9a**/**b** (eq 10). Analysis by capillary



GC indicated a 77/23 ratio of isomers. We also found that fluorodesilylation of 1-(trimethylsilyl)ethanesulfonic anhydride in the presence of cyclopentadiene gave a 68% yield of *endo*/*exo*-3-methyl-2-thiabicyclo[2.2.1]hept-5-ene 2,2-dioxide, which showed by GC analysis two isomers in the ratio 56/44. These alkanethial *S*,*S*-dioxide adducts could also be prepared by fluorodesilylation using the corresponding 1-(trimethylsilyl)alkanesulfonyl chlorides.[10]

(7) (a) Cooper, G. D. *J. Org. Chem.* **1956**, *21*, 1214. (b) Cooper, G. D. *J. Am. Chem. Soc.* **1954**, *76*, 2500. Decker, Q. W.; Post, H. W. *J. Org. Chem.* **1960**, *25*, 249.

(8) Johnson, C. R.; Keiser, J. E.; Sharp, J. C. *J. Org. Chem.* **1969**, *34*, 860.

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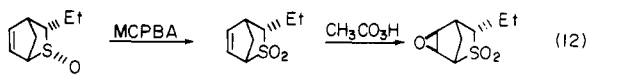
The basis for assignment of stereochemistry in the pairs of isomers **9a/b** will be indicated below.

Efforts to prepare 1-(trimethylsilyl)alkanesulfinyl chlorides were unsuccessful due to facile Si–C cleavage under chlorination conditions. Fortunately alkanethial *S*-oxides other than the parent sulfine can be directly prepared from the corresponding alkanesulfinyl chloride and trapped with cyclopentadiene. Thus, a solution of distilled propanethial *S*-oxide in Freon-11 was treated with excess cyclopentadiene at −78 °C, affording an adduct **10a** (eq 11). Compound **10a** was quite unstable, rearranging

(11)

10a

readily even at 0 °C. It could however be stored at −30 °C with little change occurring even after several weeks. Low-temperature NMR spectroscopy indicated that the adduct consisted of a single major component. Oxidation with *m*-chloroperbenzoic acid (MCPBA) gave material identical with the *major* product **9a** from fluorodesilylation of **8** in the presence of cyclopentadiene. In turn, oxidation of this product with peracetic acid gave a single, crystalline epoxy sulfone **11a** (eq 12), which was shown by X-ray

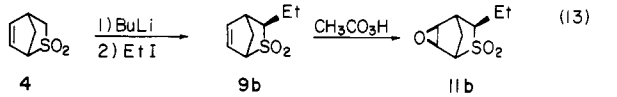


(12)

10a **9a** **11a**

crystallography to have an *endo*-ethyl group along with an *exo*-epoxy function (see Figure 1 for details). The propanethial *S*-oxide adduct **10a** must therefore also have an *endo*-ethyl group; the facile rearrangement as well as other data presented below indicate that the sulfoxide oxygen in this adduct also occupies the endo position.

Treatment of 2-thiabicyclo[2.2.1]hept-5-ene *S,S*-dioxide (**4**) with *n*-butyllithium followed by ethyl iodide gave a product identical with the *minor* adduct from **9b**. This upon further oxidation gave a noncrystalline epoxy sulfone **11b** *different* from **11a** (eq 13). Compound **11b** should

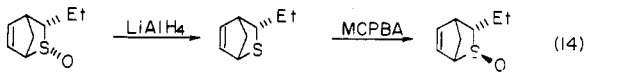


(13)

4 **9b** **11b**

have both the ethyl and epoxy groups in the exo positions. We have thus unequivocally established the stereochemistry of the major and minor propanethial *S,S*-dioxide adducts and the stereochemistry of the ethyl group in the propanethial *S*-oxide adduct **10a**.

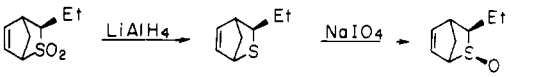
To complete the characterization of the adduct **10a**, it was reduced with lithium aluminum hydride to sulfide **12a** and reoxidized with MCPBA giving a *different* sulfoxide **10b** (eq 14) *which survived refluxing in deuteriotoluene*



(14)

10a **12a** **10b**

for 50 h without change. The product **9b** from treatment of **4** with *n*-butyllithium followed by ethyl iodide was reduced to the corresponding sulfide **12b** and reoxidized with sodium metaperiodate giving a sulfoxide **10c** *different* from either of the previously prepared isomers (eq 15). This



(15)

9b **12b** **10c**

sulfoxide also survived prolonged heating at 110 °C. The stereochemical assignments for **10a**, **10b**, and **10c** can be indicated as, respectively, the *endo*-ethyl *endo*-2-oxide, *endo*-ethyl *exo*-2-oxide, and *exo*-ethyl *exo*-2-oxide on the basis of (1) correlation with structure **11a**, (2) agreement of Eu(fod)$_3$ and aromatic solvent induced shift (ASIS) studies on these isomers with published studies on the two sulfoxides from 2-thiabicyclo[2.2.1]heptane (see the Experimental Section) as well as other NMR data on **10a–10c** and their corresponding sulfides and sulfones, (3) mechanistic information (see below) requiring that the sulfoxide oxygen in the *labile* adducts be endo, and (4) mechanistic expectations that oxidation of 2-thiabicyclo[2.2.1]hept-5-enes should lead preferentially to the *exo*-sulfoxides based on similar studies with 2-thiabicyclo[2.2.1]heptane.[11]

The stereoselective formation of adduct **3** provides unequivocal evidence for the generation of sulfine (thioformaldehyde *S*-oxide) in solution. The isolation of sulfine–methanesulfinyl chloride condensation products when the latter compound is treated with nitrogen bases has been reported by Freeman and Keindl.[12] We have pre-

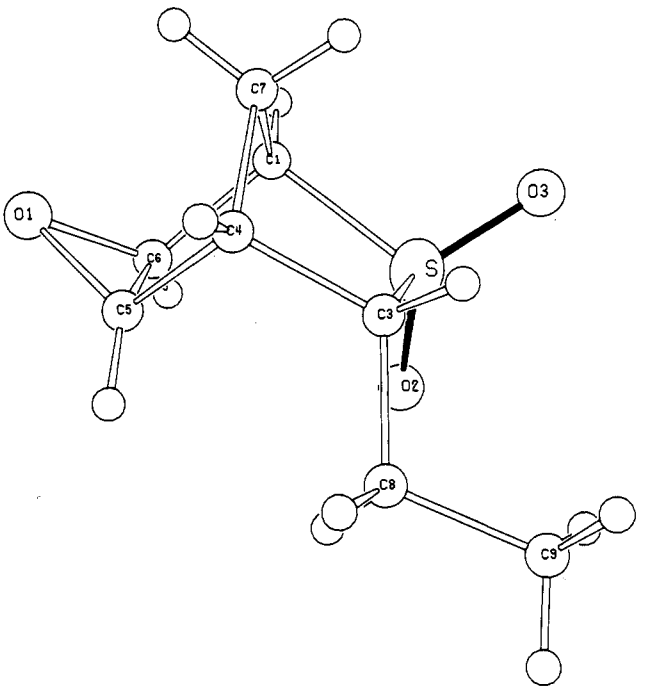


Figure 1. Perspective view of *exo*-5,6-epoxy-*endo*-3-ethyl-2-thiabicyclo[2.2.1]heptane 2,2-dioxide (**11a**) showing the atom-labeling scheme. The ethyl group occupies a position endo to the bicyclic ring while the epoxy oxygen is exo to the ring. Relevant bond distances and angles: S–O2, S–O3, 1.429 (3) Å; S–C1, 1.808 (4) Å; S–C3, 1.834 (4) Å; O1–C5, 1.447 (4) Å; O1–C6, 1.429 (5) Å; C5–C6, 1.454 (5) Å; C1–C7–C4, 98.1 (3)°; C5–O1–C6, 60.7 (2)°; O2–S–O3, 117.6 (2)°. Tables of crystal data, atomic coordinates and temperature factors, bond lengths and bond angles, anisotropic temperature factors, hydrogen atom positions, and observed and calculated structure factors for **11a** are found in ref 4f and as supplementary material in ref 4c.

(10) As indicated in eq 9, sulfonic anhydride **8** was prepared by addition of PCl_5 to 1-(trimethylsilyl)propanesulfonic acid and was characterized by spectroscopic methods including ^{13}C NMR, which indicated *two sets* of bands, as expected for a mixture of the *dl*- and *meso*-anhydride (see the Experimental Section). On the other hand, addition of the above sulfonic acid to PCl_5 gave 1-(trimethylsilyl)propanesulfonyl chloride showing only *three* distinct bands in its ^{13}C NMR spectrum at positions different from the bands for **8**.

(11) Johnson, C. R.; Diefenbach, H.; Keiser, J. E.; Sharp, J. C. *Tetrahedron* **1969**, *25*, 5649.

(12) Freeman, F.; Keindl, M. C. *J. Chem. Soc., Chem. Commun.* **1984**, 138.

viously characterized sulfine in the gas phase.[13] The stereoselective formation of 3-alkyl-2-thiabicyclo[2.2.1]-hept-5-ene *S,S*-dioxides by fluorodesilylation of 1-(triorganosilyl)alkanesulfonic acid derivatives represents unequivocal evidence for the generation of alkanethial *S,S*-dioxides (sulfenes) in solution and constitutes a particularly useful new approach to sulfenes. Efforts to produce cyclopentadiene–sulfene adduct 4 via reaction of methanesulfonyl chloride with triethylamine in the presence of cyclopentadiene failed,[14] presumably because the electrophilic sulfene as it is formed is captured by the triethylamine, affording a complex[15] faster than it reacts with cyclopentadiene.

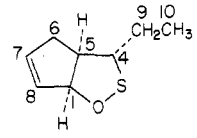
While π effects involving the sulfinyl group and the developing carbon–carbon double bond can be invoked to explain in part the preference of the alkanethial *S*-oxides for formation of the endo Diels–Alder adduct with cyclopentadiene, the preference of the sulfenes to form *endo*-cyclopentadiene adducts reflects steric effects or possibly secondary orbital overlap involving the alkyl groups. It is relevant to note than endo stereochemistry is favored in the Diels–Alder reactions of both 3,3,3-trifluoropropene and propene itself.[16]

Following initial publication of our results,[4] Krafft and Meinke reported that fluorodesilylation could also be used to synthesize thioaldehydes[17] [e.g., n = 0 in **5** (eq 1)] and selenoaldehydes.[18] In the cyclopentadiene adducts of ethanethial and propanethial,[17] Krafft found the endo to exo isomer ratios (assignments made by NOE experiments) to be 3.5/1 and 6/1; Krafft's ^{1}H and ^{13}C NMR data on *endo/exo*-3-ethyl-2-thiabicyclo[2.2.1]hept-5-ene are in excellent agreement with our own data on compounds **12a/12b**.

^{1}H and ^{13}C NMR Spectra of 2-Thiabicyclo[2.2.1]-hept-5-enes. While ^{1}H NMR data for 2-thiabicyclo-[2.2.1]hept-5-enes has been previously reported,[19] analogous ^{13}C NMR data have not. The assignment of proton and carbon chemical shifts in 1 and 4 is based on (1) 1,3,3-trideuteriation of 4 (3.5 equiv of *n*-butyllithium, then deuterium oxide) followed by conversion of 4-d_3 to 1-d_3 and 2-d_3; (2) proton–proton decoupling studies; and (3) APT and heteronuclear 2-D experiments on 1 and 4 at 300 MHz.[4f] In particular, the multiplet due to the olefinic C–H group at position 6 is identified by its simplification upon deuteriation at position 1.

The NMR spectra of the bicyclic unsaturated sulfur compounds show a change in proton or carbon chemical shifts at positions 5 and 6 on oxidation at sulfur, e.g. C-5 (H-5) is *downfield* from C-6 (H-6) in sulfides 1, **12a**, and **12b** while the situation is reversed upon oxidation to the corresponding sulfones **4**, **9a**, and **9b**. In the pairs **1/4**, **12a/9a**, and **12b/9b**, upon oxidation C-5 undergoes downfield shifts of 9.8, 9.0, and 8.5 ppm, respectively, while the corresponding *upfield shifts* at C-6 are 6.4, 7.1, and 7.4 ppm. In the case of oxidation to *endo*-sulfoxides, in the pairs **1/3** and **12a/10a**, upon oxidation C-5 undergoes downfield shifts of 9.1 and 9.0 ppm, respectively, while the corresponding *upfield shifts* at C-6 are 7.8 and 7.7 ppm. In the case of oxidation to *exo*-sulfoxides, in the pairs **1/2**, **12a/10b**, and **12b/10c**, upon oxidation C-5 undergoes downfield shifts of 14.5, 13.8, and 8.5 ppm, respectively, while the corresponding *upfield shifts* at C-6 are 9, 10.5, and 7.4 ppm. The above ^{13}C NMR shift data are similar to data reported for acyclic allylic sulfides, sulfoxides, and sulfones[20a,b] and 2-thiabicyclo[2.2.2]oct-5-enes and their *S*-oxides.[20c]

Table II. *exo*-4-Ethyl-2-oxa-3-thiabicyclo[3.3.0]oct-7-ene (14c): ^{1}H NMR Chemical Shifts and Coupling Constants[a]



14c

proton	chem shift,[c] ppm	coupling const, Hz
H-1	5.3 dt	$J_{8,1}$ = 2.3, $J_{7,1} \sim 0$, $J_{5,1}$ = 6.9, $J_{6en,1}$ = 2.2
H-4	3.3 ddd	($J_{8,4}$, $J_{7,4}$, $J_{1,4}$ = 0), $J_{5,4}$ = 2.0, $J_{9a,4} = J_{9b,4}$ = 5.6
H-5	2.9 tt	$J_{6en,5} \sim 5.3$, $J_{6ex,5} \sim 7.5$
H-6en	2.7 ddt	$J_{6ex,6en}$ = 14.5, $J_{8,6en}$ = 2.0, $J_{7,6en}$ = 2.2
H-6ex	2.3 ddq	$J_{8,6ex}$ = 2.2
H-7	6.1 ddd	$J_{8,7}$ = 5.5
H-8	5.7 dddd	$J_{7,8}$ = 5.5
H-9a	1.8 m[b]	$J_{10,9a}$ = 8.0
H-9b	1.8 m[b]	$J_{10,9b}$ = 8.0
H-10	0.9 t	

[a] In $CDCl_3$ with Me_4Si reference. [b] Precise assignment not possible. [c] Determined at 300 MHz.

Formation and Reactions of 2-Oxa-3-thiabicyclo-[3.3.0]oct-7-enes. We observed that the appearance of the NMR spectra of propanethial *S*-oxide–cyclopentadiene adduct **10a** underwent striking changes during the course of 24 h at room temperature. After a few hours a new signal appeared in the proton spectrum at 5.3 ppm while the olefinic multiplets originally at 6.28 and 6.05 ppm underwent a change in appearance and a shift to 6.1 and 5.7 ppm; analogous changes occurred in the ^{13}C NMR spectrum, e.g. appearance of a new signal at 95.1 ppm while the olefinic carbon signals shifted slightly. During this time period the sample had darkened. After 24 h at 25 °C the sample in the NMR tube had gelled. Spectra of the gelled sample showed only broadened upfield peaks; olefinic and other downfield peaks were absent from both the proton and carbon spectra.

A pure sample of the product from rearrangement of **10a** could be isolated in 50% yield by refluxing a 2% solution of **10a** in methylene chloride for 1.5 h, concentrating in vacuo at 0 °C, and molecular distillation [55 °C (0.001 mm)]. The products is a pale yellow liquid, homogeneous by capillary GC, showing a UV absorption at 310 nm (ϵ 60) and showing C=C but not S=O bands in its IR spectrum. On the basis of its ^{13}C and ^{1}H NMR spectra, its homonuclear correlated 2-D spectrum determined at 300 MHz, its other spectroscopic properties, and its transformations (see below) the structure of this rearranged product was determined to be *exo*-4-ethyl-2-oxa-3-thiabicyclo[3.3.0]oct-7-ene (**14c**), a rare example of an isolable sultene.[21] The adducts of cyclopentadiene with sulfine,

(13) Block, E.; Penn, R. E.; Olsen, R. J.; Sherwin, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 1264. Block, E.; Corey, E. R.; Penn, R. E.; Renken, T. L.; Sherwin, P. F.; Bock, H.; Hirabayashi, T.; Mohmand, S.; Solouki, B. *J. Am. Chem. Soc.* **1982**, *104*, 3119.
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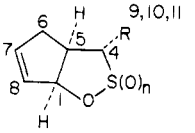
(17) Krafft, G. A.; Meinke, P. T. *Tetrahedron Lett.* **1985**, *26*, 1947.
(18) Krafft, G. A.; Meinke, P. T. *J. Am. Chem. Soc.* **1986**, *108*, 1314.
(19) Ohishi, J.; Tsuneoka, K.; Ikegami, S.; Akaboshi, S. *J. Org. Chem.* **1978**, *43*, 4013. Also see ref 8.
(20) (a) Bland, J. M.; Stammer, C. H. *J. Org. Chem.* **1983**, *48*, 4393. (b) Shapiro, M. J. *J. Org. Chem.* **1978**, *43*, 742. (c) Reich, H. J.; Trend, J. E. *J. Org. Chem.* **1973**, *38*, 2637.

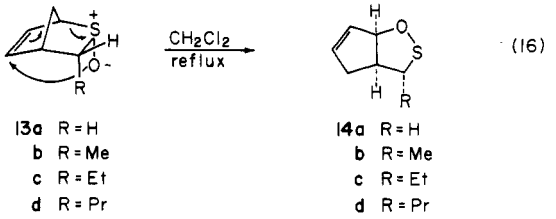
Table III. ^{13}C NMR Chemical Shift (ppm) Assignments for Bicyclic 1,2-Oxathiolanes



compd	position								
	C-1	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11
14a	95.6	45.0	43.9	39.7	137.9	128.2			
14b	95.6	56.7	53.1	38.7	136.6	128.3	19.9		
14c	95.0	64.8	51.0	39.3	136.7	128.1	27.2	12.8	
14d	95.6	63.0	51.7	39.3	136.9	128.5	36.4	21.9	13.8
15c/15c'[a]	101.8	79.9	46.3	40.0	136.3	129.2	23.7	12.4	
	98.4	77.7	43.0	36.8	133.9	130.1	20.8	13.1	
16c	87.9	63.3	42.5	38.1	137.2	127.6	21.9	11.3	

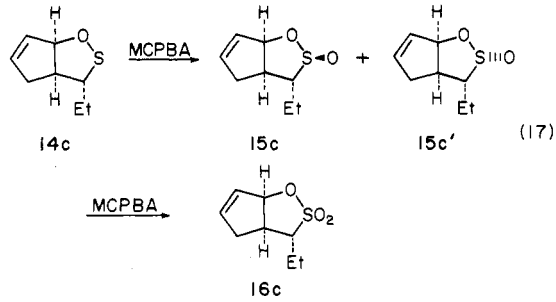
[a] Mixture of *endo/exo-S*-oxides. Isomers not identified.

ethanethial *S*-oxide, and butanethial *S*-oxide (**13a**, **13b**, and **13d**, respectively) all rearranged in refluxing methylene chloride to afford in ca. 67% yield the corresponding 2-oxa-3-thiabicyclo[3.3.0]oct-7-enes **14a**, **14c**, and **14d**, respectively. ^1H NMR data (300 MHz) for compound **14c** and ^{13}C NMR data for compounds **14a–14d** are given in Tables II and III, respectively. The sultenes form by [2,3] sigmatropic rearrangement of the strained *endo*-sulfoxides (eq 16). A sultene has been proposed as an intermediate in reactions of a cyclic allylic sulfoxide.[22]



(16)

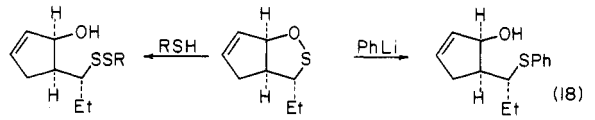
Treatment of sultene **14c** with 1 equiv of MCPBA at −30 °C gave a 1/1 mixture of sultines **15c** and **15c'**, *exo*-4-ethyl-2-oxa-3-thiabicyclo[3.3.0]oct-7-ene *endo/exo*-3-oxide (stereochemistry not assigned), while oxidation with 2-(phenylsulfonyl)-3-phenyloxaziridine[23] gave mainly one isomer (eq 17). Compounds **15c/15c'** showed a characteristic S=O band in the infrared at 1130 cm^{-1}; ^{13}C NMR data are given in Table III. We speculate that the major isomer formed in the latter oxidation has an exo S—O bond although this was not specifically determined. Sultines **15c/15c'** were thermally stable, in contrast to **14c**. Treatment of the **15c/15c'** mixture with 1 equiv of MCPBA afforded an unstable sultone, *exo*-4-ethyl-2-oxa-3-thiabicyclo[3.3.0]oct-7-ene 3,3-dioxide (**16c**), showing



(17)

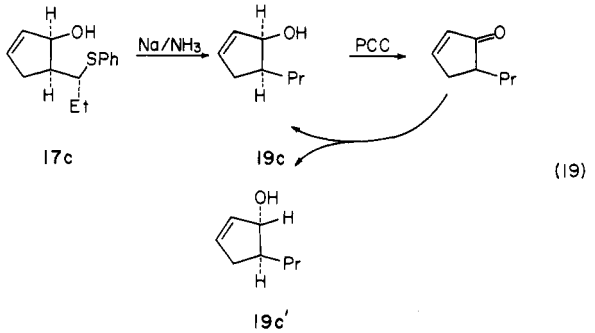
sulfonyl IR bands at 1170 and 1380 cm^{-1}; ^{13}C NMR data are given in Table III. The instability of this compound is not surprising since it is a tertiary, allylic sulfonate ester.

Sultene **14c** readily reacts with phenyllithium, giving alcohol **17c** in quantitative yield (eq 18). In order to



(18)

establish the structure of alcohol **17c**, it was desulfurized (Na/NH_3), giving unsaturated alcohol **19c** (eq 19), which



(19)

was oxidized (PCC)[24] to 5-propyl-2-cyclopentenone.[25] Alcohol **19c** formed from **17c** is identical with the major product of reduction of 5-propyl-2-cyclopentenone with sodium borohydride–cerium chloride.[26] Unsaturated alcohols related to **17c** could be formed in high yield by reaction of **14c** with methyllithium or *n*-butyllithium.[4f]

To demonstrate the synthetic utility of alcohol **17c**, we have subjected this compound to sequential oxidation at carbon (PCC) and then at sulfur (MCPBA, sodium metaperiodate) at 0 °C followed by flash distillation at 25 °C, giving directly (*E*)-5-propylidene-2-cyclopentenone (**21c**) by way of unstable sulfoxide **20c** (eq 20), in 42% overall yield from **14c**. In a similar manner (*E*)-5-ethylidene-2-cyclopentenone[27] could be prepared in 38% overall yield from sultene **14b**.

Sultene **14c** reacts rapidly with 2-methyl-2-propanethiol and other thiols[4f] giving unsaturated hydroxy disulfides such as **18c**. On the other hand the reaction with alcohols

(21) See papers cited in ref 4c, footnote 9.
(22) Yanagisawa, H.; Ando, A. *Tetrahedron Lett.* **1982**, *23*, 3379.
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(24) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647. Corey, E. J.; Boger, D. L. *Ibid.* **1978**, 2461.
(25) Agosta, W. C.; Smith, A. B. *J. Am. Chem. Soc.* **1971**, *93*, 5513.
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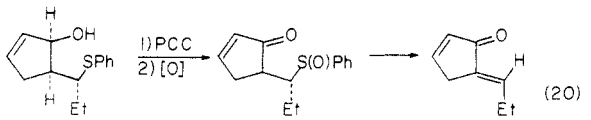
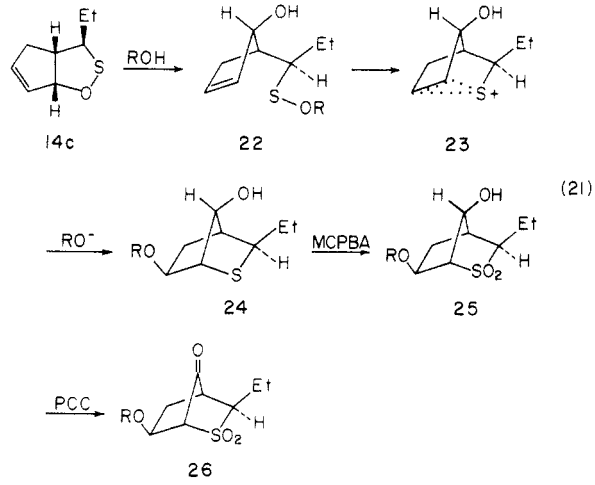
(27) Noyori, R.; Ohnishi, Y.; Kato, M. *J. Am. Chem. Soc.* **1972**, *94*, 5105.



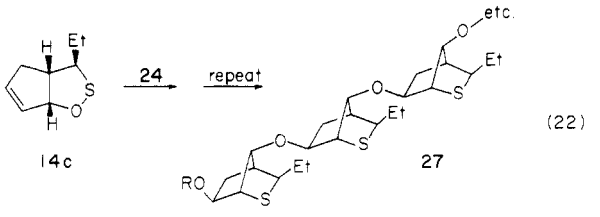
17c 20c 21c

leads to *exo*-6-alkoxy-*exo*-3-ethyl-*syn*-7-hydroxy-2-thiabicyclo[2.2.1]heptanes **24** (e.g. R = *t*-Bu, *i*-Pr, Et, Me; eq 21) all in quantitative yields. Alcohol adducts **24** may be



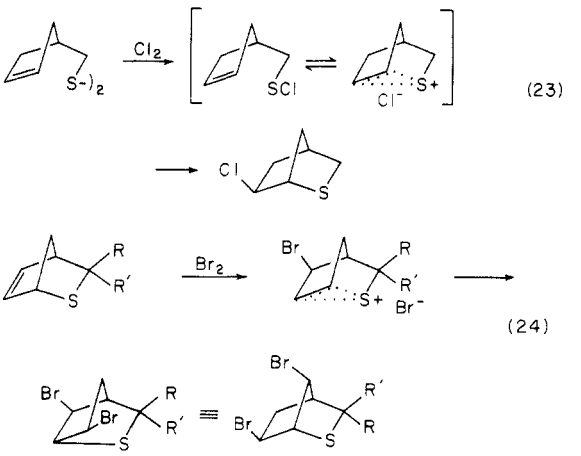
14c 22 23 24 25 26

formed by adding the distilled sultene **14c** to excess alcohol and heating at reflux for 2 h or by refluxing the initial Diels–Alder adduct **13c** with the alcohol for 3 h. While the adducts survived sublimation at 40–50 °C (0.001 mm), they underwent decomposition after 2 days in methylene chloride solution. Oxidation of **24** (R = *t*-Bu) with MCPBA gave a hydroxy sulfone **25** that proved to be more stable than the sulfide. The sulfone could be further oxidized to a keto sulfone **26**. The hydroxy sulfone and keto sulfone could be characterized, respectively, as *exo*-6-*tert*-butoxy-*exo*-3-ethyl-*syn*-7-hydroxy-2-thiabicyclo-[2.2.1]heptane 2,2-dioxide (**25**, R = *t*-Bu) and *exo*-6-*tert*-butoxy-*exo*-3-ethyl-7-oxo-2-thiabicyclo[2.2.1]heptane 2,2-dioxide (**26**, R = *t*-Bu). Compounds **25** and **26** were characterized by NMR spectroscopy at 300 MHz with comparison of NMR data on related 6,7-substituted 2-thiabicyclo[2.2.1]heptanes[28] and infrared spectroscopy (**26** has a strong carbonyl band at 1778 cm^{-1} which is closer to the carbonyl band at 1768 cm^{-1} in 7-norbornanone[29a] than the carbonyl band at 1745 cm^{-1} in 2-norbornanone[29b]). On the basis of the formation of **24** from **14c**, we suggest that the polymer formed from sultene **14c** has a structure **27** similar to **17** (eq 22; RO could be replaced by any nucleophilic group X).



14c 27

Formation of episulfonium ions related to **23** has been postulated in the chlorination of 3-cyclopentenylmethyl disulfide (eq 23).[19] Ring opening of episulfonium ions of type **23** to 6,7-disubstituted 2-thiabicyclo[2.2.1]heptanes has also been noted (eq 24).[28]



Experimental Section

General Procedures. Experimental procedures for representative compounds are given below. Certain preparations of known compounds are repeated here with modifications and spectral data not included in the earlier reports.[7,8,17] Details on the preparation of a variety of homologues of the compounds described herein as well as additional spectroscopic information including bond lengths and bond angles for compound **11a** may be found in ref 4f. Some of the compounds were too unstable for elemental analysis. NMR spectra were determined on a Varian EM360A or XL-300 or a Bruker WH-90 spectrometer using tetramethylsilane as internal standard; abbreviations used are s (singlet), d (doublet), t (triplet), and m (multiplet). Mass spectra were determined on an AEI-MS902 mass spectrometer or by GC–MS using a Hewlett-Packard 5890 capillary gas chromatograph with a Model 5970 mass selective detector. Elemental analyses were performed by MicroAnal Organic Microanalysis, Tucson, AZ. Analytical gas chromatography (GC) was performed on a Perkin-Elmer Sigma 2B gas chromatograph using a 50-m OV-101 capillary column. Ethyl ether, Freon-11, methylene chloride, and tetrahydrofuran were dried over lithium aluminum hydride. Cyclopentadiene, 1,2-methoxyethane, *tert*-butyl alcohol, and triethylamine were dried by distillation from calcium hydride. Acetonitrile was dried over phosphorus pentoxide.

(Trimethylsilyl)methanesulfonic Acid. Peracetic acid (15.6 g, 35%) was added to (trimethylsilyl)methanethiol[30] (2.7 g, 22.5 mmol) in methylene chloride (100 mL) while stirring at 0 °C; the solution was warmed to room temperature and stirring continued for 45 min. The solution was concentrated in vacuo (0.001 mm) at 30 °C, affording the title compound as a clear viscous liquid: 3.78 g (100% yield); IR (neat) 3700–2600 (br s), 1280–1020 (br s), 860 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 10.20 (s, 1 H), 3.75 (s, 2 H), 0.20 (s, 9 H) ppm; ^{13}C NMR ($CDCl_3$) 43.4, −1.4 ppm.

(Trimethylsilyl)methanesulfonyl Chloride (6a).[7a] Method 1. A solution of (trimethylsilyl)methanesulfonic acid (5.0 g, 30 mmol) in methylene chloride (60 mL) was added to phosphorus pentachloride (6.2 g, 30 mmol) in methylene chloride (150 mL) while stirring at 0 °C over a 45-min period; the solution was warmed to room temperature and stirred for 15 min. The solution was washed with cold 5% $NaHSO_3$ (2 × 200 mL), cold 5% $NaHCO_3$ (2 × 200 mL), and cold saturated NaCl (2 × 200 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. Flash distillation (0.001 mm) at 70–80 °C afford **6a** as a colorless liquid: 3.4 g (63% yield); ^1H NMR ($CDCl_3$) 3.47 (s, 2 H), 0.27 (s, 9 H) ppm; IR (neat) 2960 (m), 1395 (s), 1265 (s), 1185 (s), 865 (s), 740 (s) cm^{-1}; ^{13}C NMR ($CDCl_3$) 45.4, −1.4 ppm.

Method 2. A solution of chloromethyltrimethylsilane (24.0 g, 0.2 mol) and thiourea (30.4 g, 0.4 mol) in ethanol (500 mL) was refluxed for 48 h. Concentration in vacuo gave a solid that was dissolved in water (400 mL), cooled in ice, and treated with chlorine for 15 min at a temperature below 25 °C. Methylene

(28) Raasch, M. *J. Org. Chem.* **1975**, *40*, 161.
(29) (a) R. Zbinden, R.; Hall, H. K., Jr. *J. Am. Chem. Soc.* **1960**, *82*, 1215. (b) Gassman, P. G.; Pope, P. O. *J. Org. Chem.* **1964**, *29*, 160.
(30) Block, E.; Laffitte, J.-A.; Eswarakrishnan, V. *J. Org. Chem.* **1986**, *51*, 3428.

chloride (400 mL) was added, and chlorine was bubbled in for an additional 30 min. The organic layer was separated, and the aqueous layer was extracted with methylene chloride (2 × 200 mL). The combined organic layers were washed with cold 10% $NaHSO_3$ (2 × 300 mL), cold 10% $NaHCO_3$ (2 × 300 mL), and cold water (2 × 300 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. Distillation afforded **6a** as a colorless liquid: 21.6 g (58% yield); bp 50–52 °C (0.6 mm).

(Trimethylsilyl)methanesulfonic Anhydride (6b). A solution of phosphorus pentachloride (4.34 g, 20.8 mmol) in methylene chloride (100 mL) was added to a stirring solution of (trimethylsilyl)methanesulfonic acid (5.0 g, 29.8 mmol) in methylene chloride (250 mL) over a 45-min period, and stirring was continued for 30 min. The solution was washed with cold 5% $NaHSO_3$ (2 × 200 mL), cold 5% $NaHCO_3$ (2 × 200 mL), and cold saturated NaCl (2 × 200 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo (0.001 mm) at 70–80 °C, affording **6b** as a clear thick liquid: 2.68 g (38% yield); IR (neat) 2970 (m), 1395 (s), 1265 (s), 1185 (s), 865 (s), 740 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 3.05 (s, 4 H), 0.23 (s, 18 H) ppm; ^{13}C NMR ($CDCl_3$) 45.4, −1.4 ppm.

(Trimethylsilyl)methyl Thioacetate. Potassium hydroxide (22.4 g, 0.4 mol) was dissolved in absolute ethanol (250 mL). The flask was cooled in ice and thioacetic acid (30.45 g, 0.4 mol) was added dropwise. The reaction was stirred at room temperature for 0.5 h, and (chloromethyl)trimethylsilane (40.0 g, 0.4 mol) was added dropwise. After the addition was complete, the reaction mixture was heated at 50 °C overnight. Water (250 mL) was added, and the product was extracted with hexanes (2 × 200 mL). The combined hexane layer was washed with water (200 mL), separated, dried, and concentrated to give the title compound as an oil, 53.1 g (80%). Distillation gave a pale yellow oil: 46.2 g (71.2%); bp 85 °C (15 mm); IR (neat) 970 (m), 1700 (vs), 1260 (s), 1155 (s), 860 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) 2.25 (s, 2 H), 0.10 (s, 9 H) ppm; ^{13}C NMR ($CDCl_3$) 196.8, 30.0, 14.0, −2.0 ppm.

(Trimethylsilyl)methanesulfinyl Chloride (7). (Trimethylsilyl)methyl thioacetate, (7.5 g, 0.046 mol) was mixed with dry acetic anhydride (0.046 mol, 4.7 g). The reaction mixture was cooled to −40 °C, and chlorine (0.092 mol, 6.5 g) was bubbled in very slowly, keeping the flask temperature between −35 and −40 °C. After the addition of chlorine was complete, the reaction mixture was warmed up to room temperature. The flask was cooled to 0 °C, and acetyl chloride was removed under vacuum (2 mm). Trap-to-trap distillation (0.01 mmHg) of the crude material with the flask temperature at 30 °C gave **7** as a yellow oil: 6.4 g (72%); IR (neat) 1250 (s), 1135 (s), 850 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) 3.35 (d, 2 H), 0.30 (s, 9 H) ppm; ^{13}C NMR ($CDCl_3$) 57.9, −0.9 ppm.

2-Thiabicyclo[2.2.1]hept-5-ene 2,2-Dioxide (4). Cesium fluoride (2.0 g, 0.013 mol) was flame dried in place under vacuum and cooled under argon to 0 °C. After acetonitrile (60 mL) and cyclopentadiene (3 g, 0.05 mol) were added to the flask, a solution of **6b** (1.2 g, 0.0037 mol) in acetonitrile (8 mL) was added and the reaction mixture was stirred for 2 h at 0 °C and then for 1 h at room temperature. The solution was concentrated in vacuo and the residue dissolved in methylene chloride (75 mL). The organic layer was washed with 5% $NaHCO_3$ (2 × 50 mL) and once with saturated NaCl (50 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. Flash chromatography from ethanol and concentration in vacuo afforded **4** as a solid: 0.4 g (75% yield); mp 55 °C; IR (KBr) 1300 (s), 1140 (s), 1120 (ms) cm^{-1}; ^1H and ^{13}C NMR data, given in Table I. Substitution of **6a** for **6b** in the above procedure gave **4** in 63% yield. Compound **3** could also be oxidized to **4** with MCPBA.

2-Thiabicyclo[2.2.1]hept-5-ene (1).[8] A solution of **4** (0.48 g, 0.0033 mol) in ethyl ether (20 mL) was added to lithium aluminum hydride (0.64 g, 0.017 mol) in ethyl ether (30 mL) while stirring at 0 °C. The mixture was refluxed for 2 h. Sodium sulfate hydrate was added to the solution at room temperature until bubbling ceased. The mixture was filtered, concentrated in vacuo at 0 °C, and sublimed at atmospheric pressure to afford **1** as a waxy semisolid: 0.2 g (54% yield); IR (neat) 2970 (ms), 2940 (ms), 1335 (ms), 1255 (ms), 725 (s) cm^{-1}; ^1H and ^{13}C NMR data given in Table I. Compound **1** could also be prepared by lithium aluminum hydride reduction of **3**.[4f]

2-Thiabicyclo[2.2.1]hept-5-ene *exo*-2-Oxide (2). A solution of MCPBA (0.173 g, 0.85 mol) in methylene chloride (5 mL) was added to a stirring solution of **1** (0.1 g, 0.89 mmol) in methylene chloride (10 mL) at 0 °C, and the solution was stirred for 30 min at 0 °C and then for 2 h at room temperature. Ammonia was blown over the solution for 5 min followed by argon for 10 min. The solution was filtered and concentrated in vacuo, affording **2** as a pale yellow oil: 0.092 g (81%); IR (neat) 1045 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 6.2 (m, 1 H), 5.6 (m, 1 H), 4.1 (m, 1 H), 3.3 (m, 1 H), 3.0 (m, 1 H), 2.3 (m, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 145.3, 126.6, 67.2, 56.2, 43.8, 41.4 ppm.

2-Thiabicyclo[2.2.1]hept-5-ene *endo*-2-Oxide (3). Acetonitrile (60 mL) and cyclopentadiene (3 g, 0.05 mol) were added to cesium fluoride (1.0 g, 0.0065 mol), flame-dried in place under vacuum, and cooled under argon to −20 °C. A solution of **2** (0.5 g, 0.0029 mol) in acetonitrile (10 mL) was added to the stirring solution over a 15-min period, and stirring was continued at −20 °C for 2 h and then at 0 °C for 1 h. The solution was filtered through Celite and $MgSO_4$ and concentrated at 0 °C (0.001 mm) to yield the title compound as a thermally unstable, dark brown oil: 0.34 g (90%); IR (neat) 1038 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 6.2 (m, 1 H), 4.1 (m, 1 H), 2.9 (m, 3 H), 1.3 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$) 139.9, 127.8, 65.3, 55.1, 44.7, 43.1 ppm. Compound **2** (10%) was also present.

***S*-Chloromethyl (Trimethylsilyl)methanethiosulfonate.** Acetonitrile (60 mL) was added to cesium fluoride (0.5 g, 3.3 mmol) previously flame-dried in place under vacuum and cooled under argon. A solution of **7** (1.11 g, 6.5 mmol) in acetonitrile (8 mL) was added to the stirring solution at −20 °C over a 15-min period; the solution was stirred at −20 °C for 1 h and stored at −30 °C for 24 h. The solution was then filtered and concentrated on a vacuum pump (0.001 mm), affording the title compound as a yellow liquid: 0.67 g (97% yield); IR (neat) 2975 (m), 1335 (s), 1270 (s), 1143 (s), 870 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 5.20 (s, 2 H), 3.35 (s, 2 H), 0.30 (s, 9 H) ppm; ^{13}C NMR ($CDCl_3$) 59.3, 49.5, −0.8 ppm.

***endo*-3-Ethyl-2-thiabicyclo[2.2.1]hept-5-ene *endo*-2-Oxide (10a).** Triethylamine (10.1 g, 0.1 mol) was added to freshly distilled 1-propanesulfinyl chloride (12.7 g, 0.1 mol) in anhydrous Freon-11 (170 mL) while stirring under argon at −78 °C. The mixture was stirred for 4 h at −78 °C, warmed to −20 °C during 2 h, stored overnight at −15 °C, and then filtered under argon through a pad of $MgSO_4$. Fractional distillation at high vacuum into a liquid nitrogen cooled trap, slowly raising the pot temperature from −78 to 0 °C and following the composition of the fractions by ^1H NMR, gave 1.45 g [0.016 mol (16% yield)] of pure propanethial *S*-oxide: ^1H NMR ($CDCl_3$) 8.0 (t, 1 H), 2.4 (m, 2 H), 1.12 (t, 3 H) 1.12 ppm. This was dissolved in Freon-11 (75 mL) at −78 °C and treated during the course of 20 min with doubly distilled cyclopentadiene (5.3 g, 0.08 mol). Stirring was continued at −78 °C for 3 h, and then the temperature was raised to −10 °C during 3 h. The solution was filtered through a pad of $MgSO_4$ and concentrated at −78 to 0 °C (0.001 mm), affording **10a** as a colorless solid, 2 g (80% yield). The solid was stable when stored at −15 °C but decomposed rapidly at room temperature: IR (neat) 2960 (m), 1055 (s), 1035 (s, sh) cm^{-1}; ^1H NMR ($CDCl_3$) 6.28 (m, 1 H), 6.05 (m, 1 H), 4.35 (m, 1 H), 3.21 (m, 1 H), 2.75 (m, 1 H), 1.55 (m, 2 H), 1.15 (m, 2 H), 1.0 (m, 3 H) ppm; ^{13}C NMR ($CDCl_3$, −30 °C) 137.8, 129.7, 65.6, 63.5, 47.5, 41.1, 18.3, 12.3 ppm; MS, 156 (M^+), 91, 79, 74, 66.

***endo*-3-Ethyl-2-thiabicyclo[2.2.1]hept-5-ene 2,2-Dioxide (9a).** A solution of MCPBA (0.45 g, 2.2 mmol) in methylene chloride (40 mL) was added to a stirring solution of **10a** (0.32 g, 2.2 mmol) in methylene chloride (30 mL) at −78 °C, which was warmed to room temperature, and stirring continued for 2 h. The solution was washed with 5% $NaHSO_3$ (2 × 50 mL), 5% Na_2CO_3 (2 × 50 mL), and saturated NaCl (2 × 50 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo, affording **9a** as a pale yellow oil, 0.33 g (79% yield). Column chromatography gave an analytically pure yellow solid: mp 49–50 °C; IR (neat) 2975 (m), 1290 (s), 1125 (s), 750 (m) cm^{-1}; ^1H NMR ($CDCl_3$) 6.25 (dd, 1 H), 6.1 (m, 1 H), 3.8 (m, 1 H), 3.2 (m, 1 H), 2.6 (m, 1 H), 2.3 (m, 2 H), 1.15 (m, 2 H), 1.05 (t, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 137.8, 130.3, 65.8, 59.1, 44.6, 43.9, 23.0, 12.0 ppm; GC (195 °C) 8.56 min. Anal. Calcd for $C_8H_{12}O_2S$: C, 55.48; H, 7.02. Found: C, 55.48; H, 7.18.

***exo*-3-Ethyl-2-thiabicyclo[2.2.1]hept-5-ene 2,2-Dioxide (9b).** A hexane solution of *n*-butyllithium (5.8 mL, 1.55 M) was added to a stirring solution of **4** (1.3 g, 9.0 mmol) in tetrahydrofuran (150

mL) at −78 °C under argon, and the mixture was stirred for 30 min. Bromoethane (1.0 g, 9.3 mmol) was added to the stirring solution, which was warmed to room temperature. The solution was concentrated in vacuo; the residue was dissolved in methylene chloride (150 mL), washed with saturated NaCl (3 × 100 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo, affording **9b** as a light yellow oil: 1.2 g (78% yield); IR (neat) 2975 (m), 1300 (s), 1138 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 6.31 (dd, 1 H), 6.05 (dd, 1 H), 3.6 (m, 1 H), 3.0 (m, 1 H), 2.2 (m, 2 H), 1.7 (m, 3 H), 1.05 (t, 3 H), ppm; ^{13}C NMR ($CDCl_3$) 141.5, 129.5, 65.1, 57.0, 45.8, 42.6, 23.3, 12.4 ppm; GC (195 °C) 8.46 min.

***exo*-5,6-Epoxy-*endo*-3-ethyl-2-thiabicyclo[2.2.1]heptane 2,2-Dioxide (11a).** Peracetic acid (2.5 g, 12.0 mmol) was added to **9a** (0.2 g, 1.2 mmol) in acetic acid (2 mL) at 0 °C; the solution was warmed to room temperature and heated to 50 °C for 4 h. The solution was mixed with methylene chloride (50 mL), washed with 5% Na_2CO_3 (4 × 40 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. Recrystallization from ethanol afforded **11a** as white needles: 0.12 g (53% yield); mp 100 °C; IR (neat) 2980 (m), 1310 (s), 1140 (s), 860 (m) cm^{-1}; ^1H NMR ($CDCl_3$) 3.4 (m, 3 H), 2.8 (m, 2 H), 1.7 (m, 4 H), 0.91 (t, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 65.8, 60.4, 48.0, 46.8, 39.4, 23.2, 18.6, 12.3 ppm. Anal. Calcd for $C_8H_{12}O_3S$: C, 51.06; H, 6.38. Found: C, 51.23; H, 6.56.

***exo*-3-Ethyl-2-thiabicyclo[2.2.1]hept-5-ene (12b).**[17] A solution of **9b** (0.25 g, 1.45 mmol) in ethyl ether (8 mL) was added to lithium aluminum hydride (0.43 g, 11.6 mmol) in ethyl ether (15 mL) while stirring at 0 °C, and the solution was heated to reflux for 2 h. Sodium sulfate hydrate was added to the solution at room temperature until bubbling ceased. The solution was filtered and concentrated in vacuo, affording **12b** as colorless liquid: 0.18 g (88% yield); IR (neat) 2970 (s), 1465 (m), 740 (m) cm^{-1}; ^1H NMR ($CDCl_3$) 6.10 (dd, 1 H), 5.75 (dd, 1 H), 3.9 (m, 1 H), 3.0 (m, 1 H), 2.7 (m, 1 H), 1.7 (m, 2 H), 1.6 (m, 2 H), 1.05 (t, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 136.9, 133.0, 54.4, 50.8, 49.5, 47.3, 30.4, 14.1 ppm.

***exo*-3-Ethyl-2-thiabicyclo[2.2.1]hept-5-ene *exo*-2-Oxide (10c).** A solution of sodium periodate (0.24 g, 1.1 mmol) in water (5 mL) was added to a stirring solution of **12b** (0.16 g, 1.1 mmol) in methanol (10 mL), and stirring was continued for 18 h. The solution was filtered, the precipitate was extracted with methylene chloride (25 mL), and the filtrate and extract were combined, washed with dilute $Na_2S_2O_3$ (2 × 20 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo, affording **10c** as a colorless liquid: 0.11 g (63% yield); IR (neat) 2975 (s), 1018 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 6.15 (dd, 1 H), 5.60 (dd, 1 H), 4.0 (m, 1 H), 3.4 (m, 1 H), 3.0 (m, 1 H), 2.3 (m, 3 H), 1.7 (m, 2 H), 1.01 (t, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 145.2, 126.7, 67.0, 60.7, 45.8, 41.7, 20.3, 12.4 ppm.

***exo*-5,6-Epoxy-*exo*-3-ethyl-2-thiabicyclo[2.2.1]heptane 2,2-Dioxide (11b).** Peracetic acid (2.5 g, 12.0 mmol) was added to **9b** (0.2 g, 1.2 mmol) in acetic acid (2 mL) at 0 °C; the solution was warmed to room temperature and heated to 50 °C for 4 h. The solution was dissolved in methylene chloride (50 mL), washed with 5% Na_2CO_3 (4 × 40 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo, affording **11b** as a thick, pale yellow oil: 0.15 g (66% yield); IR (neat) 2980 (m), 1310 (s), 1140 (s), 860 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 3.5 (m, 3 H), 2.6 (m, 2 H), 1.8 (m, 4 H), 1.20 (t, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 63.7, 60.1, 50.3, 46.5, 41.2, 22.3, 21.8, 12.3 ppm.

***endo*-3-Ethyl-2-thiabicyclo[2.2.1]hept-5-ene (12a).**[17] A solution of **10a** (3.0 g, 21 mmol) in ethyl ether (25 mL) was added to a stirring solution of lithium aluminum hydride (1.7 g, 47 mmol) in ethyl ether (35 mL), which was heated to reflux for 2 h. Sodium sulfate hydrate was added to the solution until bubbling ceased. The mixture was filtered and concentrated in vacuo, affording **12a** as a colorless liquid: 1.3 g (48% yield); IR (neat) 2965 (s), 1465 (w), 820 (w), 745 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 6.17 (dd, 1 H), 5.5 (m, 1 H), 3.8 (m, 1 H), 3.5 (m, 1 H), 3.2 (m, 1 H), 1.6 (m, 2 H), 1.3 (m, 2 H), 0.90 (t, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 127.4, 128.8, 54.1, 51.5, 51.3, 48.4, 27.7, 13.6 ppm.

***endo*-3-Ethyl-2-thiabicyclo[2.2.1]hept-5-ene *exo*-2-Oxide (10b).** A solution of sodium periodate (0.76 g, 3.5 mmol) in water (10 mL) was added to a stirring solution of **12a** (0.5 g, 3.5 mmol) in methanol (20 mL), and stirring was continued for 18 h. The mixture was filtered, the precipitate was extracted with methylene chloride (75 mL), and the filtrate and extract were combined, washed with dilute $Na_2S_2O_3$ (2 × 50 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo, affording **10b** as a colorless liquid: 0.38 g (70% yield); IR (neat) 2960 (s), 1035 (s), cm^{-1}; ^1H NMR ($CDCl_3$) 6.17 (dd, 1 H), 5.71 (dd, 1 H), 4.1 (m, 1 H), 3.1 (m, 1 H), 2.4 (m, 3 H), 1.6 (m, 2 H), 1.01 (t, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 142.6, 126.9, 76.8, 67.5, 44.5, 44.5, 22.9, 12.9 ppm; MS, 156 (M^+), 91, 84, 74, 66.

(1-Chloropropyl)trimethylsilane. A cyclohexane solution of *sec*-butyllithium (0.18 mol, 141 mL, 1.3 M) was added to (chloromethyl)trimethylsilane (22.46 g, 0.18 mol) in tetrahydrofuran (600 mL) while stirring at −78 °C under argon over a 30–45-min period. Stirring was continued for 30 min at 78 °C. Bromoethane (19.9 g, 0.18 mol) was added to the solution, which was stirred for 20 min at −78 °C and warmed to room temperature. Ethyl ether (300 mL) was added; the solution was washed with water (5 × 400 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. Distillation afforded the title compound as a colorless liquid: 15.6 g (58% yield); bp 81–83 °C; IR (neat) 2965 (s), 1255 (s), 845 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 2.95 (dd, 1 H), 1.5 (m, 2 H), 0.90 (t, 3 H), 0.01, (s, 9 H) ppm; ^{13}C NMR ($CDCl_3$) 54.1, 26.7, 12.9, −3.4 ppm; MS, 150 (M^+), 135, 93, 73. Anal. Calcd for $C_6H_{15}ClSi$: C, 47.81; H, 10.03. Found: C, 48.40; H, 10.22.

1-(Trimethylsilyl)propanethiol. A solution of (1-chloropropyl)trimethylsilane (14.2 g, 94.7 mmol) and thiourea (15.2 g, 0.2 mol) in ethanol (500 mL) was refluxed for 48 h. Concentration in vacuo gave a solid that was dissolved in water (250 mL) and treated with 40% NaOH (50 mL) for 10 min. The solution was extracted with ethyl ether (2 × 150 mL), and the organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. Distillation afforded the title compound as a colorless liquid: 6.1 g (45% yield); bp 65 °C (31 mm); IR (neat) 2960 (s), 1255 (s), 845 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 1.6 (m, 3 H), 1.0 (m, 4 H), 0.05 (s, 9 H) ppm; ^{13}C NMR ($CDCl_3$) 27.0, 13.2, −3.0 ppm.

Treatment of the title compound with *n*-butyllithium in THF followed by acetyl chloride gave 1-(trimethylsilyl)propyl thioacetate. Anal. Calcd for $C_8H_{18}OSSi$: C, 50.47; H, 9.53. Found: C, 50.65, H, 9.88.

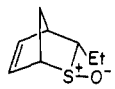
1-(Trimethylsilyl)propanesulfonic Acid. Peracetic acid (21.7 g, 35%) was added to 1-(trimethylsilyl)propanethiol (5.0 g, 33.7 mmol) in methylene chloride (100 mL) while stirring at 0 °C. The mixture was then warmed to room temperature, and stirring was continued for 45 min. The solution was concentrated in vacuo and then concentrated (0.001 mm) at 30 °C for 25 min, affording the title compound as a clear thick liquid: 6.6 g (100% yield); IR (neat) 2960 (br s), 1260 (s), 1140–1180 (br s), 860 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 10.40 (s, 1 H), 2.40 (t, 1 H), 1.8 (m, 2 H), 1.03 (t, 3 H), 0.10 (s, 9 H) ppm; ^{13}C NMR ($CDCl_3$) 55.2, 20.1, 14.3, −1.8 ppm.

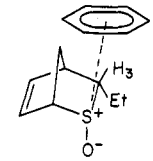
Aromatic Solvent Induced Shift (ASIS) and Europium Shift Studies of Isomeric Sulfoxides 10a and 10b. The ^1H NMR spectra of **10a** and **10b** were determined in C_6D_6 and in $CDCl_3$ in the presence and absence of 0.33 equiv of the shift reagent $Eu(fod)_3$. The data are given below (ppm). In the case of the ASIS, compound **10a** shows a larger shift in the position of proton H-3 but a smaller shift for protons H-5 and H-6 than compound **10b**, in line with expectations (see Table IV). The calculated pseudocontact shift (PS) seen in the $Eu(fod)_3$ studies is largest for proton H-3 or the *exo*-sulfoxide **10b**, as expected since this proton is cis to the sulfoxide group. The larger shift experienced for protons H-5 and H-6 in **10a** compared to **10b** is also reasonable since the sulfoxide oxygen should be closer to the double bond in **10a** compared to **10b**. The observations made here agree with results of a similar NMR study of 2-thiabicyclo[2.2.1]heptane 2-oxides.[31]

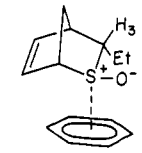
1-(Trimethylsilyl)propanesulfonic Anhydride (8). Phosphorus pentachloride (2.0 g, 9.5 mmol) in methylene chloride (150 mL) was added to a stirring solution of 1-(trimethylsilyl)-propanesulfonic acid (1.2 g, 6.2 mmol) in methylene chloride (100 mL) over a 45-min period while stirring. Stirring was continued for 30 min. The solution was washed with cold 5% $NaHSO_3$ (2 × 200 mL), cold 5% $NaHCO_3$ (2 × 200 mL), and cold saturated NaCl (2 × 200 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo* (0.001 mm), affording **8** as a clear thick liquid: 0.4 g (38%

(31) Fraser, R. R.; Durst, T.; McClory, M. R.; Viau, R.; Wigfield, Y. Y. *Int. J. Sulfur Chem., Part A* **1971**, *1*, 133.

Table IV. Aromatic Solvent-Induced Shift and Europium Shift Data for Sulfoxides 10a and 10b

compd	proton	$\delta(CDCl_3)$	$\delta(C_6D_6)$	$\Delta\delta(C_6D_6)$	δ + 0.33 equiv of Eu(fod)$_3$	PS
	H-1	4.3	3.9	−0.4	6.0	+2.7
	H-3	2.7	2.2	−0.5	4.2	+1.6
	H-4	3.2	2.7	−0.5	4.2	+1.0
	H-5	6.2	5.8	−0.4	8.8	+2.6
	H-6	5.9	5.8	−0.1	7.9	+2.0
10a						
	H-1	3.9	3.5	−0.4	6.7	+2.8
	H-3	2.3	2.1	−0.2	6.0	+3.7
	H-4	3.0	2.4	−0.6	4.1	+1.1
	H-5	6.1	5.5	−0.6	7.1	+1.0
	H-6	5.6	5.1	−0.5	6.5	+0.9
10b						





yield); IR (neat) 2975 (s), 1385 (s), 1260 (s), 1175 (s), 858 (s), 705 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) 3.2 (m, 2 H), 2.0 (m, 4 H), 1.25 (t, 6 H), 0.38 (s, 18 H) ppm; ^{13}C NMR ($CDCl_3$) 58.0, 57.5, 20.3, 20.2, 13.8, 13.6, −1.7 ppm.

1-(Trimethylsilyl)propanesulfonyl Chloride. A solution of 1-(trimethylsilyl)propanesulfonic acid (2.5 g, 128 mmol) in methylene chloride (50 mL) was added during 45 min to a stirring solution of phosphorus pentachloride (2.67 g, 14.8 mmol) in methylene chloride (50 mL) at 0 °C. The solution was warmed to room temperature, stirred for 15 min, washed with cold 5% $NaHSO_3$ (2 × 75 mL), cold 5% $NaHCO_3$ (2 × 75 mL), and cold saturated NaCl (2 × 75 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. Flash distillation at 70–80 °C (0.001 mm) afforded the title compound as a colorless liquid: 1.6 g (59% yield); IR (neat) 2970 (m), 1375 (s), 1260 (s), 1175 (s), 855 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) 3.05 (t, 1 H), 2.05 (m, 2 H), 1.17 (t, 3 H), 0.30 (s, 9 H) ppm; ^{13}C NMR ($CDCl_3$) 71.6, 21.6, 13.4, −1.4 ppm.

***endo*/*exo*-3-Ethyl-2-thiabicyclo[2.2.1]hept-5-ene 2,2-Dioxide (9a/b).** Cesium fluoride (0.47 g, 3.1 mmol) was flame-dried in place under vacuum and cooled under argon to 0 °C. After acetonitrile (20 mL) and cyclopentadiene (0.44 g, 6.2 mmol) were added, a solution of 8 (0.47 g, 1.3 mmol) in acetonitrile (8 mL) was added while stirring and the solution was stirred for 2 h at 0 °C and then for 1 h at room temperature. The solution was concentrated in vacuo and the residue dissolved in methylene chloride (100 mL). The organic layer was washed with 5% $NaHCO_3$ (2 × 100 mL) and saturated NaCl (100 mL), dried over $MgSO_4$, filtered and concentrated in vacuo. Flash chromatography from ethanol afforded **9a/9b** as a light yellow oil: 0.17 g (76% yield); ^{1}H and ^{13}C NMR spectroscopy indicated a mixture of **9a** and **9b** with the former as the major component; GC (195 °C) indicated a 77/23 **9a/9b** mixture.

***exo*-4-Ethyl-2-oxa-3-thiabicyclo[3.3.0]oct-7-ene (14c).** Compound **10a** (4.5 g, 28.8 mmol) in methylene chloride (250 mL) was heated to reflux for 1.5 h, concentrated in vacuo, and distilled, affording **14c** as a light yellow liquid: 2.3 g (51% yield); bp 55 °C (0.001 mm); IR (neat) 2965 (s), 2934 (s), 1356 (m), 939 (m) cm^{-1}; ^{1}H and ^{13}C NMR data given in Table II.

***exo*-4-Ethyl-2-oxa-3-thiabicyclo[3.3.0]oct-7-ene *endo*/*exo*-3-Oxide (15c/15c'). Method 1.** A solution of 2-(phenylsulfonyl)-3-phenyloxaziridine (0.27 g, 1.0 mmol) in chloroform (15 mL) was added to a stirring solution of **14c** (0.16 g, 1.0 mmol) in chloroform (15 mL) at 0 °C. The solution was warmed to room temperature and stirred for 2 h. The solution was filtered and concentrated in vacuo to afford **15c** as a pale yellow oil: 0.14 (79%); ^{1}H NMR ($CDCl_3$) 5.8 (m, 3 H), 3.2 (m, 1 H), 2.8 (m, 2 H), 2.5 (m, 1 H), 1.8 (m, 2 H), 1.10 (t, 3 H) ppm; IR (neat) 2965 (m), 1130 (s) cm^{-1}; ^{13}C NMR ($CDCl_3$) 136.3, 129.2, 101.8, 79.9, 46.4, 40.0, 23.7, 12.4 ppm.

Method 2. A solution of MCPBA (0.52 g, 2.6 mmol) in methylene chloride (30 mL) was added to a stirring solution of **14c** (0.4 g, 2.6 mmol) in methylene chloride (35 mL) at 0 °C over a 30-min period, warmed to room temperature, and stirred for 1.5 h. The solution was cooled to −40 °C, filtered, and concentrated in vacuo to 0.5 mL. Preparative thin-layer chromatography from methylene chloride afforded **15c/15c'** as a pale yellow oil: 0.1 g (22% yield); ^{1}H NMR ($CDCl_3$) 5.8 (m, 3 H), 3.2 (m, 1 H), 2.8 (m, 2 H), 2.5 (m, 1 H), 1.8 (m, 2 H), 1.10 (t, 3 H) ppm; IR (neat) 2965 (m), 1130 (s) cm^{-1}; ^{13}C NMR ($CDCl_3$) 136.3,* 133.9, 130.0, 129.2,* 101.8,* 98.4, 79.9,* 77.7, 46.4,* 43.0, 40.0,* 36.8, 23.7,* 20.8, 131.1, 12.4* ppm (isomer **15c** indicated by *); GC (125 °C) 9.88 (76%), 10.12 min (24%).

***exo*-4-Ethyl-2-oxa-3-thiabicyclo[3.3.0]oct-7-ene 3,3-Dioxide (16c).** A solution of MCPBA (0.24 g, 1.2 mmol) in methylene chloride (20 mL) was added to a stirring solution of **15c/15c'** (0.2 g, 1.2 mmol) in methylene chloride (25 mL) at 0 °C. The solution was warmed to room temperature and stirred for 2 h. The solution was cooled to −40 °C, filtered three times, and then concentrated in vacuo, affording **16c** as a thick semisolid: 0.1 g (44% yield); IR (neat) 2970 (m), 1380 (s), 1170 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) 6.0 (m, 1 H), 5.7 (m, 1 H), 5.2 (m, 1 H), 2.7 (m, 4 H), 1.8 (m, 2 H), 1.10 (t, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 137.2, 127.6, 87.9, 63.3, 42.6, 38.1 ppm. This compound was quite unstable, rapidly turning black at room temperature.

***cis*-5-[1-(Phenylthio)propyl]-Δ^2-cyclopentenol (17c).** A hexane solution of phenyllithium (4.58 mL, 2.0 M) was added to **14c** (1.43 g, 9.1 mmol) in tetrahydrofuran (200 mL) while stirring at −78 °C. The mixture was stirred for 30 min at −78 °C and then warmed to room temperature. Water (500 mL) was added, and the solution was extracted with ethyl ether (2 × 100 mL). The organic extracts were washed with water (2 × 500 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. Flash chromatography (ethanol) afforded **17c** as a yellow oil: 1.81 g (84% yield); IR (neat) 3200–3600 (br s), 3065 (s), 2980 (s), 2950 (sh m), 1600 (w), 1492 (m), 1450 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.1 (m, 5 H), 5.7 (m, 2 H), 4.6 (m, 1 H), 3.5 (m, 1 H), 3.2 (m, 1 H), 2.3 (m, 1 H), 2.1 (m, 2 H), 1.6 (m, 2 H), 0.90 (t, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 135.7, 132.4, 132.2, 128.9, 128.7, 127.1, 75.7, 50.9, 45.4, 35.6, 25.3, 9.9 ppm.

***cis*-5-*n*-Propyl-Δ^2-cyclopentenol (19c). Method 1.** Sodium (0.1 g, 4.3 mmol) was added to **17c** (0.98 g, 4.2 mmol) in ammonia (100 mL) while stirring at −78 °C until the blue color persisted for 15 min. The reaction mixture was then warmed to room temperature, the ammonia was evaporated, and the residue was dissolved in methylene chloride (100 mL), washed with water (4 × 100 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. Distillation afforded **19c** as a colorless liquid: 0.41 g (77% yield); bp 76 °C (6 mmHg); IR (neat) 3200–3600 (br s), 2948 (s), 1622 (w), 1065 (m), 922 (m), 744 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) 5.8 (m, 2 H), 4.5 (m, 1 H), 2.2 (m, 3 H), 1.4 (m, 5 H), 1.0 (m, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 135.9, 133.2, 76.8, 42.5, 36.8, 31.3, 21.8, 14.4 ppm.

Method 2. To a stirring solution of cerium trichloride heptahydrate (1.68 g, 4.5 mmol) in methanol (3 mL) was added 5-propyl-2-pentenone[4f,25] (0.57 g, 4.5 mmol). Sodium borohydride (0.17 g, 4.5 mmol) was added within 2 min while stirring. The solution was stirred for 3–5 min, treated with water (20 mL), extracted with ethyl ether (2 × 20 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. Flash distillation [25 °C (0.001 mm)] afforded **19c** as a colorless liquid: 0.31 g (56% yield); IR (neat) 3100–3600 (br s), 2955 (s), 2930 (s), 1055 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) 5.7 (m, 2 H), 4.4 (m, 1 H), 2.0 (m, 3 H), 1.4 (m, 6 H), 0.9 (m, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 135.9*, 133.6, 133.2, 83.5, 76.8*, 48.0, 42.5*, 37.6, 36.7*, 36.6, 31.2*, 21.7*, 21.2, 14.3*, 14.2 ppm

(* = major isomer); GC (100 °C) 4.80 (79%), 5.31 min (21%).

***cis*-5-[1-(Phenylthio)propyl]-Δ^2-cyclopentenone.** A solution of **17c** (2.0 g, 8.5 mmol) in methylene chloride (5 mL) was added rapidly to pyridinium chlorochromate (2.76 g, 12.8 mmol) in methylene chloride (10 mL) while stirring. The solution was stirred for 2 h. Ethyl ether (50 mL) was added, the solution decanted, and the black residue washed with ethyl ether (2 × 20 mL); the filtrates were combined, filtered through Celite/$MgSO_4$/Florisil, and concentrated in vacuo. Flash chromatography (ethanol) afforded the title compound as a yellow oil: 1.8 g (92% yield); IR (neat) 2965 (m), 1705 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 7.4 (m, 1 H), 7.1 (m, 5 H), 5.9 (m, 1 H), 3.5 (m, 1 H), 3.0 (m, 1 H), 2.5 (m, 2 H), 1.4 (m, 2 H), 1.0 (m, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 165.3, 164.4*, 135.2, 134.5*, 132.1, 131.7*, 129.0*, 128.7, 127.1, 126.9*, 54.5, 48.6*, 45.5, 38.9, 31.6*, 25.6, 22.8*, 12.5* ppm (for both isomers) (* = major isomer). Anal. Calcd for $C_{14}H_{16}OS$: C, 72.37; H, 6.94. Found: C, 73.04; H, 7.19.

(*E*)-5-Propylidene-Δ^2-cyclopentenone (21c). A solution of MCPBA (1.4 g, 6.8 mmol) in methylene chloride (35 mL) was added to a stirring solution of *cis*-5-[1-(phenylthio)propyl]-Δ^2-cyclopentenone (1.6 g, 6.8 mmol) in methylene chloride (50 mL) while stirring at 0 °C, and the solution was stirred at room temperature for 2 h. Ammonia was bubbled in for 5 min followed by argon for 10 min. The solution was filtered and concentrated in vacuo. The residue was stored in a sealed flask at room temperature for 48 h. Flash distillation (0.001 mm) at room temperature yielded **21c** as a bright yellow-orange oil: 0.43 g (51% yield); IR (neat) 2980 (m), 1710 (s), 1660 (s), 1215 (m) cm^{-1}; ^1H NMR ($CDCl_3$) 7.3 (m, 1 H), 6.35 (t, 1 H), 6.2 (m, 1 H), 3.1 (m, 2 H), 2.1 (m, 2 H), 1.05 (t, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 196.4, 160.3, 156.6, 136.7, 136, 31.8, 22.9, 12.7 ppm.

***cis*-5-[1-(*tert*-Butyldithio)propyl]-Δ^2-cyclopentenol (18c).** A stirring solution of **14c** (0.5 g, 3.2 mmol) in 2-methyl-2-propanethiol (10 mL) was heated to reflux for 5 h and concentrated in vacuo, affording **18c** as a light yellow oil, 0.64 g (80% yield). Preparative TLC (CH_2Cl_2) followed by distillation using a Kugelrohr apparatus gave an analytically pure sample of **18c** as a clear, colorless oil: IR (neat) 3200–3600, 2955 (s), 1460 (m), 1360 (m), 1135 (m), 1020 (m) cm^{-1}; ^1H NMR ($CDCl_3$) 5.9 (m, 2 H), 4.7 (m, 1 H), 3.0 (m, 1 H), 2.5–2.0 (m, 4 H), 1.9 (m, 1 H), 1.6 (m, 1 H), 1.33 (s, 9 H), 0.97 (t, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 135.3, 132.4, 75.2, 54.3, 48.3, 34.9, 30.0 (3 C), 27.9, 10.5 ppm. Anal. Calcd for $C_{12}H_{22}OS_2$: C, 58.49; H, 9.00. Found: C, 58.30; H, 9.03.

***exo*-3-Ethyl-*exo*-6-*tert*-butoxy-*syn*-7-hydroxy-2-thiabicyclo[2.2.1]heptane (24).** A stirring solution of **14c** (0.5 g, 3.2 mmol) in *tert*-butyl alcohol (10 mL) was heated to reflux for 2.5 h and concentrated in vacuo. The residue was dissolved in methylene chloride (50 mL), washed with saturated NaCl (2 × 50 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo, affording **24** as a thick colorless liquid: 0.68 g (92% yield); IR (neat) 3100–3600 (br m), 2975 (s), 1180 (s), 1040 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 4.3 (m, 1 H), 3.7 (m, 1 H), 2.9 (m, 1 H), 2.6 (m, 1 H), 2.2 (m, 2 H), 1.6 (m, 4 H), 1.05 (s, 9 H), 0.85 (t, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 77.9, 74.4, 73.7, 56.3, 53.9, 44.8, 40.5, 29.8, 28.3 (3 C), 13.2 ppm. This compound underwent polymerization on standing at room temperature or upon chromatography.

***exo*-3-Ethyl-6-*tert*-butoxy-*syn*-7-hydroxy-2-thiabicyclo[2.2.1]heptane 2,2-Dioxide (25).** A solution of MCPBA (1.23 g, 6.0 mmol) in methylene chloride (50 mL) was added to a stirring solution of **24** (0.69 g, 2.9 mmol) in methylene chloride (75 mL) at 0 °C; the resultant mixture was warmed to room temperature and stirred for 2 h. Ammonia was bubbled through the solution for 9 min followed by argon for 10 min. The mixture was filtered and concentrated in vacuo, affording **25** as a white solid: 0.65 g (80% yield); mp 67–69 °C; IR (KBr) 3100–3500 (br m), 2970 (s), 1300 (s), 1185 (s), 1150 (s), 1070 (m) cm^{-1}; ^1H NMR ($CDCl_3$) 4.7 (m, 1 H), 4.40 (dd, 1 H), 3.3 (m, 1 H), 3.1 (m, 1 H), 2.65 (dd, 1 H), 2.61 (ddt, 1 H), 2.2 (m, 1 H), 2.10 (dd, 1 H), 1.77 (dd, 1 H), 1.8 (m, 1 H), 1.17 (s, 9 H), 1.10 (t, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 78.0, 74.4, 73.3, 56.4, 53.9, 44.8, 40.5, 29.9, 28.3 (3 C), 13.2 ppm. Anal. Calcd for $C_{12}H_{22}O_4S$: C, 54.96; H, 8.40. Found: C, 54.50; H, 8.21.

***exo*-3-Ethyl-*exo*-6-*tert*-butoxy-7-keto-2-thiabicyclo[2.2.1]heptane 2,2-Dioxide (26).** A solution of **25** (0.5 g, 1.9 mmol) in methylene chloride (10 mL) was added rapidly to a stirring solution of pyridinium chlorochromate (0.5 g, 2.2 mmol) in methylene chloride (15 mL), and stirring was continued for 2 h. Ethyl ether (75 mL) was added, the solution decanted, the black residue washed with ethyl ether (2 × 50 mL), and the filtrate combined, filtered through Celite/$MgSO_4$/Florisil, and concentrated in vacuo. Chromatography using chloroform afforded **26** as a white solid: 0.1 g (20% yield); IR (neat) 2975 (s), 1760 (s), 1315 (s), 1140 (s), 1070 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 4.3 (m, 1 H), 3.1 (m, 1 H), 2.9 (m, 1 H), 2.5 (m, 2 H), 1.7 (m, 3 H), 1.1 (s, 9 H), 0.95 (t, 3 H) ppm.

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