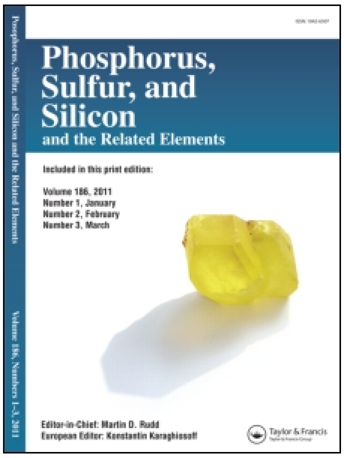

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HIGHLY DIASTEREOSELECTIVE OZONE-MEDIATED OXIDATIONS OF TWO SIX-MEMBERED RING VINYL SULFIDES APPENDED WITH A SPATIALLY PROXIMATE HYDROXYL GROUP

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HIGHLY DIASTEREOSELECTIVE OZONE-MEDIATED OXIDATIONS OF TWO SIX-MEMBERED RING VINYL SULFIDES APPENDED WITH A SPATIALLY PROXIMATE HYDROXYL GROUP

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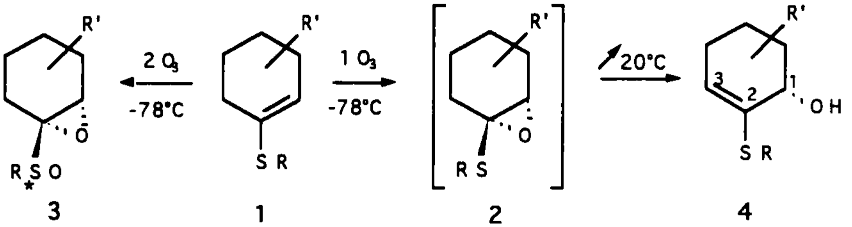
Ozone adds in high yield and stereoselectively to isomerically pure cyclohexenyl methyl sulfides **4a** and **4b** having a neighboring hydroxyl group as a result of conformational and stereoelectronic factors. Further diasteroselective self-induced oxidation of β'-hydroxy α,β-epoxysulfides intermediates to the corresponding sulfoxides **8a** and **8b**, respectively, is attributed to incipient hydrogen bonding between the substrate hydroxyl group and the ozone molecule. The configurational and conformational assignments of these hydroxy α,β-epoxysulfoxides are provided by spectroscopic studies.

Key words: Vinylsulfide, α,β-epoxysulfoxide, hydroxy-epoxysulfoxide, keto-epoxysulfoxide, ozonation, hydrogen bonding.

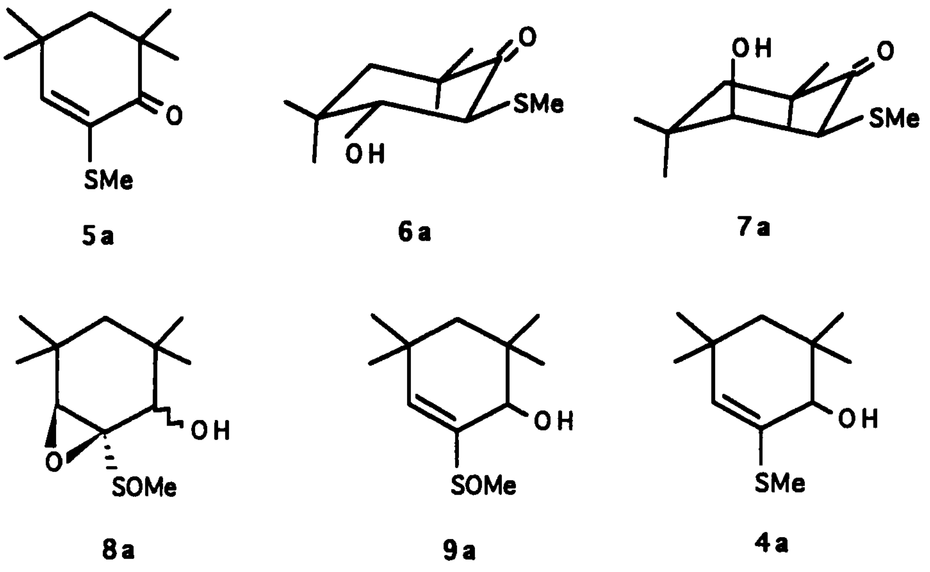
Reactions of unsaturated systems with ozone have extensively been studied and this topic has recently been reviewed by Bailey.[1] We earlier disclosed[2] that ozone reacted with six-membered ring alkenyl sulfides **1** affording selectively "partial cleavage"[3] products **2** or **3** in high yields (Equation 1). On the other hand, in that study, epoxidation as well as ozonolysis has been rationalized in terms of two competing mechanisms, both involving a polarized cyclic 1,2,3-trioxolane intermediate, also commonly known as a primary ozonide. The stereochemistry of the isomerically pure allylic alcohols **4** and diastereomeric α,β, epoxysulfoxides **3** has been established by ^{1}H NMR. The postulated structures of derivatives **3** have been confirmed later by X-ray analysis.[4]



(1)

While exploring the chemical reactivity of α-sulfinyloxiranes **3** toward halides-based electrophilic reagents,[5] we felt that further reactions of ozone with stereochemically well defined α-sulfenyl allylic alcohols **4** should occur with high efficiency and an interesting stereochemical outcome. Here we wish to report our results on these reactions.

Initial investigations were carried out with the hydroxylated cyclohexenylsulfide **4a**. This cyclic system reacted smoothly with one molar equiv of ozone in dichlo-



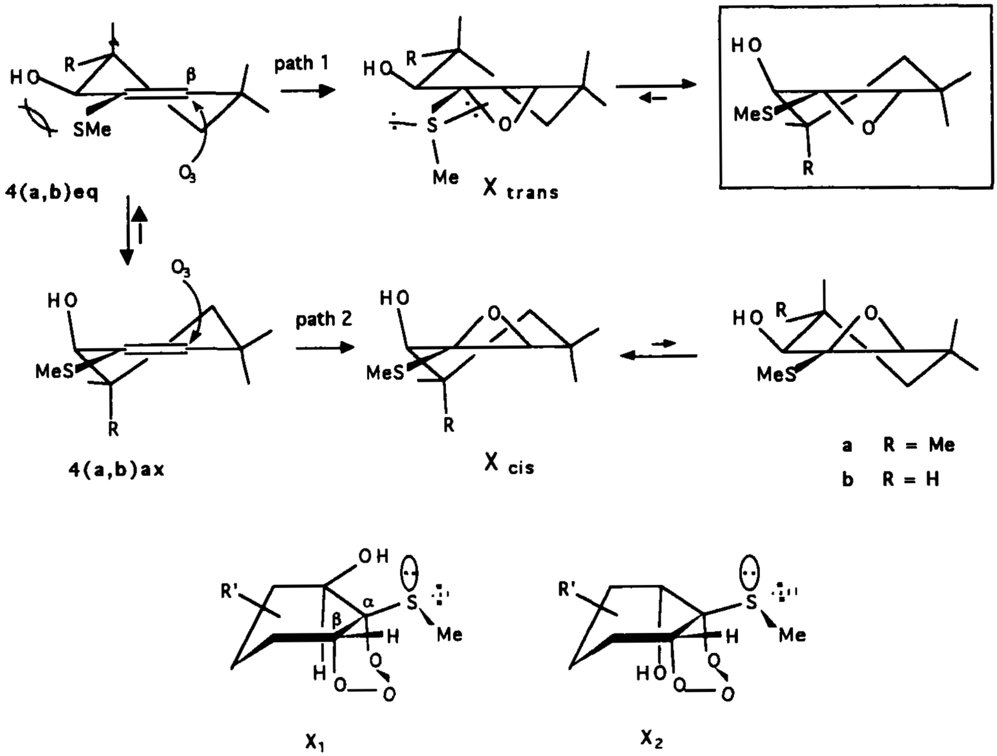
SCHEME I

romethane-pyridine solution at −78°C (method A) to lead, after preparative HPLC, to three major fractions: (1) the first eluted keto-vinylsulfide **5a**; (2) two epimeric β-hydroxy ketones **6a** and **7a**. Upon standing at room temperature or on silica gel, they were quantitatively dehydrated to **5a**. The structures of these products were assigned on the basis of NMR spectra[6]; (3) the spectroscopic properties of the most polar fraction indicated that hydroxy-epoxysulfoxide **8a** was also formed to some extent, along with some sulfinylated allylic alcohol **9a**.

To shorten the purification procedure, and, at the same time, further obtain preparatively useful yield of enone derivative **5a**, a very simple "work-up" was devised. Thus, on addition of petroleum ether to the crude reaction mixture, the polar materials as **8a** and **9a** were precipitated. The resulting etheral solution was refluxed for a while and then concentrated. The ^{1}H NMR spectra of the oily residue definitely showed the presence of the enone **5a** in more than 90% purity. The overall process can be viewed as an oxidation of secondary allylic alcohols to the corresponding enones.

Since the method, as described above, was found somewhat troublesome and difficult to control, we next turned our attention to the reaction of the vicinal hydroxy vinylsulfide **4a** with two molar equiv of ozone (method B). Extension of this reaction to the trimethyl derivative **4b** likewise proved to be equally effective. The *cis*-stereochemistry of the compound **4b** has been previously assigned[2] on several grounds.

Surprisingly, the reaction produces a single hydroxylated α,β-epoxysulfoxide in each case. Both steps, *viz.* the carbon-carbon double bond epoxidation and oxidation at the sulfur atom are therefore highly stereoselective. The structures of α-sulfinyloxiranes **8a** and **8b** were deduced from their spectral data. While the relative configuration at the sulfinyl center in these compounds was easily identified, some doubt was remaining about the one of the allylic carbinol carbon until recently.



SCHEME II

The formation of **8a, b** can reasonably be rationalized by reference to Scheme II. In this scheme are depicted the two major conformations of the starting materials **4a** and **4b**. Conformers **4(a, b)ax** are assumed to be the more populated conformers. Such a strong bias for the pseudo-axial orientation of the hydroxyl group derives from an unfavorable "eclipsed relationship"[7] with the adjacent vinylic methylthio substituent.

At this stage, the first point of interest is how to reconcile the structural features of the epoxidation step with the scheme developed by us for ozone-vinylsulfides reactions.[2]

Accordingly, the reaction of ozone with α-sulfenyl allylic alcohols **4a** and **4b** might be expected to deliver 1,2,3-trioxolane intermediates of type X_1 or X_2. The mechanism involved, in each case, satisfies the stereoelectronic requirement for axial electrophilic attack at Cβ (maximum π-orbital overlap in the transition state leading to X). A near planar arrangement of the H—Cβ—Cα—S—Me fragment in these primary adducts would confer an orbital properly oriented on the sulfur atom for controlling the course of ozonide rearrangement to cis/trans epoxides. It is, therefore, reasonable to assume that ozone's approach in a plane perpendicular to the carbon-carbon double bond may be sensitive to steric effects. While the axial attack at C(β) on conformations **4(a, b)eq** (path 1) is free from 1,3 diaxial repulsive interactions, the attacking electrophile on conformers **4(a, b)ax** (path 2) experiences syn-diaxial steric repulsions by the pseudo-axial hydroxyl group. Apparently, X_2

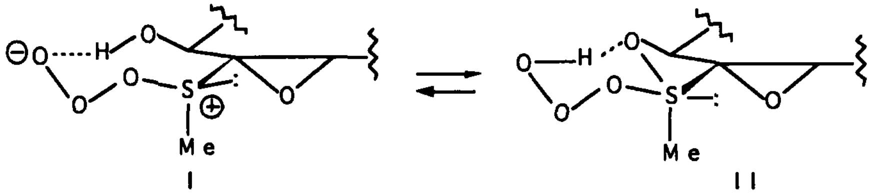
would be formed only if the OH group can behave as a coordinating group for the attacking species.

As solvent polarity effects have no influence on the reaction outcome,[9] the formation of the trans 1,2,3-trioxolane intermediates X_1 was therefore assumed to compete favorably. The structure of X_1 is also seen to be a compromise between the minimization of steric interactions and the lone pair-lone pair repulsions. Once X_1 are formed, β'-hydroxy-α,β-epoxysulfides[10] with a trans stereochemistry can result.

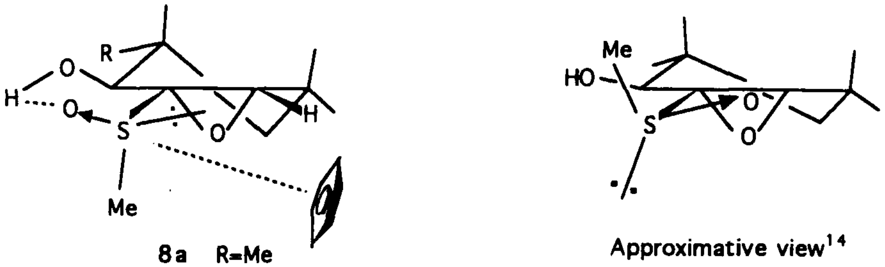
The next step is concerned with the oxidation of these labile species, noted X trans in Scheme II, by a second molecule of ozone at the electron-rich and sterically accessible sulfenyl center. The high diastereoselectivity observed is likely due to the directing effect of the properly positioned hydroxyl group.

With oxidants that hydrogen bond, selective oxygen transfer to the sulfur atom in functionalized sulfides is well documented. Stereoselective conversion of suitable hydroxylated sulfides to the corresponding sulfoxides with certain oxidizing agents has been either attributed to incipient hydrogen bonding between the reactants[11] or demonstrated to occur by hydrolysis of cyclic oxysulfonium salts.[12] In the light of these conclusions, the formation of an eight-membered ring transition state of type I in which hydrogen bonding between the hydroxylic hydrogen and the nucleophilic end of ozone can be reasonably envisioned (Scheme III). Moreover, electrostatic stabilization of the positive sulfur center can be provided by the hydroxyl oxygen atom, a bridged sulfurane intermediate like II would then result. We believe that the transient structures I and II describe the essential features of this reaction.

The best piece of spectral evidence for determining the relative configuration at the sulfinyl center in sulfinyloxiranes **8a** and **8b** possessing a proximate OH group was gathered from analysis of aromatic solvent induced shifts (ASIS) in ^{1}H NMR spectroscopy. Significant upfield shifts induced by benzene coordination to the positive end of the S → O dipole were observed for the nearby epoxidic proton on the spectra ($\delta CDCl_3$—δC_6D_6 = 0.25 ppm for **8a** and **8b**). In the case at hand, the S—O bond is rigidly constrained toward the side of the hydroxyl group by hydrogen bonding in solution. Infrared data were also useful for confirming these stereochemical assignments. The compounds **8a** and **8b** exhibited in dilute CCl_4 solution two distinct hydroxyl bands: the narrow fundamental "free-OH" and the wide hydrogen-bonded OH bonds fall at 3310 and 3360 cm^{-1} respectively. These were not altered on dilution even to 10^{-3} M. Similar studies related to the ability of the sulfoxide-oxygen atom to act as a proton acceptor in intramolecular hydrogen bonding have been repeatedly conducted.[13]



SCHEME III



8a R=Me
b R=H

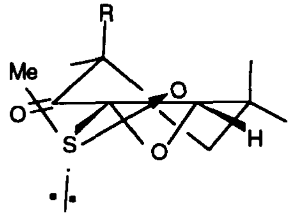
Approximative view[14] of **8a** in the solid state

SCHEME IV

These spectroscopic results have been recently confirmed by X-ray diffractometry on the adduct **8a**.[14] The structure of **8a** is configurationally identical but conformationally different in the solid state as can be seen in Scheme IV.

Experimentally, a one-pot preparation of bicyclic methylsulfinyl oxiranes **8a, b** with an adjacent hydroxyl group emerges by simply applying method A to cycloalkenyl methyl sulfides **1a, b** and then submitting the resulting allylic alcohols **4a, b** (warming to room temperature is necessary) to method B. An overall yield of 50%, based on starting vinyl sulfides **1**, was routinely obtained.

Further oxidation with MnO_2[15] in CH_2Cl_2 at 25°C of these "[1:3] adducts" afforded the corresponding keto epoxysulfoxides **10a, b** in near quantitative yield. Support for the proposed structures was also provided by ASIS measurements. It should be noted that no stereochemical change at the sulfinyl center occurs during this reaction and the more populated conformer for **10b** exists probably with R=H, axially oriented.[16]



10 **a** R=Me
b R=H

In conclusion, epoxidation of allylic alcohols **4a, b** on the one hand and, on the other hand, oxidation of the thioether moiety in the non isolated hydroxy-epoxysulfides intermediates X_1 trans with ozone result in forming isomerically pure hydroxy-epoxysulfoxides **8a, b**. This latest specificity was attributed to hydrogen bonding between sulfoxide and hydroxyl groups. It was ascertained that the hydroxyl group, positioned in such a close proximity, drives efficiently and selectively the ozone molecule to the sulfur lone-pair pointing toward the hydroxyl site.

Further work will focus on the ozone-promoted oxidations of more functionalized thioenol ethers in C_6-series, where hydroxyl or carboxylic acid groups at a convenient distance may be present.

EXPERIMENTAL

General. Melting points were determined on a Reichert microscope and are uncorrected. IR spectra were run on a Perkin Elmer Spectrophotometer in CCl_4 solution, unless otherwise stated. ^1H NMR spectra were recorded with a Varian A 60 D Spectrometer in $CDCl_3$ relative to Me_4Si as internal standard. For each signal, chemical shifts (ppm), multiplicity, intensity, and coupling constant (Hz) are reported in that order by using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C NMR spectra were taken on a Bruker Spectrospin WP 60 apparatus operating at 15.08 MHz and measured in $CDCl_3$ solution relative to Me_4Si. Microanalyses were performed by the Center of analyses of the CNRS, 69390, Vernaison. Preparative separations were performed by using a Jobin Yvon Chromatospac Prep. Liquid Chromatograph packed with 15 μm Merck silica gel 60F and equipped with a Knauer Differential Refractometer as detector and a Gilson T220 collector, or by using chromatography columns packed with 0.063–0.200 mesh Merck silica gel. G C analyses were carried out on a 3 m × ⅛ in. column packed with 5% SEDC550 on chromosorb GAW 60/80 in a Girdel 3000 series chromatograph. The ozone source was a laboratory Trailigaz-Welsbach T 23 type ozone generator using dry oxygen as the feed gas.

Materials. Dichloromethane was distilled from phosphorus pentoxide prior to use. Pyridine was distilled from calcium hydride and stored over KOH pellets.

The cycloalkenyl methyl sulfides **1a** and **1b** were prepared and purified according to published procedures.[17,18] The allylic alcohols **4a** and **4b** used in this study were prepared by reaction of the corresponding vinylsulfides with one molar equiv of ozone, as already described.[2]

General Procedure for Ozonation. The general procedure has been described in detail earlier.[2] Depending of the molar ratio ozone/substrate three methods have been applied here.

Method A (1 mol O_3): Allylic alcohol **4a** (2 g, 10 mmol) was dissolved in dry dichloromethane (50 ml) containing pyridine (1 ml, 10 mmol) and ozonized with a stoichiometric amount of ozone at −70°C according to the general procedure. The resulting solution was allowed to warm up to room temperature and the solvent then removed by rotary evaporation. The residual mixture was taken up in 20 ml of petroleum ether and the solution further triturated to deposit crude solids. The precipitated solids were filtered off on a small conical glass-fritted funnel and washed with petroleum ether. The white powder isolated (320 mg) was shown by ^1H NMR spectral analysis to be a mixture of **8a** and **9a** in a 3/2 ratio. Pure samples of each compound were finally obtained by fractional recrystallizations from ethyl acetate (**8a**) and petroleum ether or pentane (**9a**). On the other hand, the filtrate was concentrated to a yellow oil which was purified by preparative chromatography on a Jobin Yvon Chromatospac apparatus using 200 g of silica gel as the stationary phase, eluting with 92:8 cyclohexane-ethyl acetate (4 l). The faster running component was identified as **5a** (205 mg). The second fraction was shown to contain an inseparable mixture of isomers **6a** and **7a** (1.09 g).

4,4,6,6-Tetramethyl-2-methylthiocyclohex-2-en-1-one **5a**: colorless oil; IR 1680 cm^{-4} ($\nu C{=}O$); ^1H NMR δ 1.20 (br s, 12H), 1.80 (s, 2H), 2.16 (s, 3H), and 6.06 (s, 1H); ^{13}C NMR δ 14.1, 27.2, 31.2, 31.6, 33.9, 41.6, 48.9, 133.5, 146.7 and 200.9.

Anal. Calc. for $C_{11}H_{18}OS$: C, 66.61; H, 9.15; S, 16.17. Found: C, 66.36; H, 9.29; S 16.15.

4,4,6,6-Tetramethyl-3-hydroxy-2-methylthiocyclohexanone: colorless oil, mixture of stereoisomers **6a** and **7a**; **6a**: IR 1710 cm^{-4} ($\nu C{=}O$); ^1H NMR δ 0.80 to 1.40 (m, 12H), 1.55 (s, 2H), 2.12 (s, 3H), 2.70 (br s, 1H, disappears in D_2O), 3.43 and 3.58 (two d, J = 10 Hz, 2H); ^{13}C NMR δ 13.5, 57.4, 77.0 and 209.4 (other signals are not identified); **7a**: IR 1710 cm^{-1} ($\nu C{=}O$); ^1H NMR δ 0.80 to 1.40 (m, 12H), 1.50 (s, 2H), 2.03 (s, 3H), 2.70 (br s, 1H, disappears in D_2O), 3.84 and 4.22 (two d, J = 2 Hz, 2H); ^{13}C NMR δ 12.9, 58.1, 78.3 and 209.9 (other signals are not identified). Analytical samples of these compounds could not be obtained by GC analysis as they underwent a facile dehydration to give **5a**.

(3,3,5,5-Tetramethyl-6-hydroxycyclohex-1-en)yl sulfoxide **9a**: white needles, mp = 97°C; IR 1055 cm^{-1} ($\nu S{-}O$), 3340 cm^{-1} (νOH); ^1H NMR (mixture of two diastereoisomers) δ 0.85 to 1.25 (m, 12H), 1.33 to 1.64 (m, 2H), 2.60 (br s, 1H, exchanged in D_2O), 2.72 (s, 3H), 4.10 and 4.13 (two s, 1H) and 6.03 and 6.14 (two s, 1H).

Anal. Calc. for $C_{11}H_{20}O_2S$: C, 61.08; H, 9.32; O, 14.8. Found: C, 60.87; H, 9.21; O, 15.18.

An independent sample of the compound was obtained by periodic oxidation[18] of the alcohol **4a** (0.3 g, 1.5 mmol) in a 1:1 mixture of methanol and water (50 ml) at −20°C (overnight, yield = 75%).

Method B (2 mol O_3): Following the general procedure, allylic alcohol **4a** (2 g, 10 mmol) was treated with two molar equivalents of ozone. The crude concentrate was taken up with 20–50 ml of petroleum ether and then was triturated to yield a pale solid. Analytical sample of **8a** or **8b** was obtained by recrystallization from a 1:3 petroleum ether-methanol mixture. No attempts have been made to isolate minor by-products arising from oxydation at sulfur.

2-Hydroxy-3,3,5,5-tetramethyl-7-oxabicyclo[4.1.0]1-heptanyl methyl sulfoxide **8a**: yield = 70%, white needles, mp = 140°C, IR (KBr) 3210 cm^{-1} (νOH); (CCl_4) 1055 cm^{-1} (νSO), 3360 and 3610 cm^{-1} (νOH), no evolution of the absorptivity of the OH bands could be observed when increasing the dilution to 1/10 and 1/50; ^1H NMR ($CDCl_3$) δ 0.85 to 1.35 (m, 14H), 2.83 (s, 3H), 3.32 (s, 1H), 4.00 (s, 1H); (C_6D_6) δ 0.60 to 1.25 (m, 14 H), 2.37 (s, 3H), 3.02 (s, 1H), 4.04 (s, 1H); ^{13}C NMR δ 23.0, 27.6, 28.2, 29.0, 30.4, 35.8, 45.1, 64.2, 72.8 and 76.1.

Anal. Calc. for $C_{11}H_{20}O_3S$: C, 56.87; H, 8.68; S, 13.80. Found: C, 56.65; H, 8.72; S, 14.08.

2-Hydroxy-3,5,5-trimethyl-7-oxabicyclo[4.1.0]1-heptanyl methyl sulfoxide **8b**: yield = 70%, translucid needles, mp = 87°C, IR (KBr) 3220 cm^{-1} (νOH); (CCl_4) 1050 cm^{-1} (νSO), 3360 and 3610 cm^{-1} (νOH). As for **8a**, there was no evolution of the absorptivity of the OH bands with dilution to 1/10 and 1/50; ^1H NMR ($CDCl_3$) δ 0.60 to 1.90 (m, 11H), 2.72 (s, 3H), 3.00 (br s, 1H, exchanged in D_2O), 3.32 (s, 1H), 4.65 (d, J = 5Hz, 1H); (C_6D_6) δ 0.5 to 1.50 (m, 11H), 2.40 (s, 3H), 3.05 (s, 1H), 3.60 (br s, 1H), 4.75 (br s, 1H); ^{13}C NMR δ 16.1, 24.0, 27.4, 31.9, 32.0, 34.6, 35.2, 61.0, 70.5 and 74.0

Anal. Calc. for $C_{10}H_{18}O_3S$: C, 55.02; H, 8.31; O, 21.99; S, 14.69. Found: C, 55.26; H, 8.43; O, 21.86; S, 14.63.

Method C (one pot reaction): A solution of 3,3,5,5-tetramethyl-1-methylthiocyclohexene **1a** (2 g, 10.9 mmol) in dry CH_2Cl_2 (50 ml) and pyridine (1 ml, 10 mmol) was ozonized at −70°C with a stoichiometric amount of ozone. The resulting solution was allowed to warm up to room temperature and then reozonized at −70°C with two other equivalents of ozone. The crude reaction mixture was worked up as above to afford 1.15 g of white powder, identified as **8a** (yield = 45%). Similarly, the thioenolether **1b** (1.2 g, 7.1 mmol) gave 0.75 g of **8b** (yield = 50%).

Oxydation of **8** *to the keto epoxysulfoxides* **10**. A mixture of the hydroxy epoxysulfoxide **8a** or **8b** (0.5 g, 2.2 mmol) and activated manganese dioxide[15a] (0.5 g, 6 mmol) in 50 ml of dry acetone was heated to reflux for 2 days. After cooling, the resulting suspension was filtered over a pad of celite (2 g) which was then rinsed twice with acetone. The organic solvent was evaporated to dryness to yield a white crystalline solid which on recrystallization from petroleum ether-ethanol was identified as **10a** or **10b**.

2-Oxo-3,3,5,5-tetramethyl-7-oxabicyclo[4.1.0]1-heptanyl methyl sulfoxide **10a**: yield = 80%, white prisms, mp = 102°C, IR (KBr) 1070 cm^{-1} (νSO), 1690 cm^{-1} (νCO); ^1H NMR ($CDCl_3$) δ 0.98 to 1.40 (m, 12H), 1.43 and 2.01 (two d, J = 14 Hz, 2H), 2.73 (s, 3H) and 3.84 (d, J = 1 Hz, 1H); (C_6D_6) δ 0.50 to 1.07 (m, 12H), 0.82 (masked) and 1.64 (two d, J = 14 Hz, 2H), 2.26 (s, 3H) and 3.79 (br s, 1H); ^{13}C NMR δ 25.1, 28.1, 28.2, 29.4, 32.0, 38.1, 42.2, 46.2, 63.8, 73.3 and 210.0.

Anal. Calc. for $C_{11}H_{18}O_3S$: C, 57.36; H, 7.88; O, 20.84. Found: C, 57.10; H, 7.77; O, 21.06.

2-Oxo-3,5,5-trimethyl-7-oxabicyclo[4.1.0]1-heptanyl methyl sulfoxide **10b**: yield = 75%, translucid needles, mp = 103°C, IR (KBr) 1060 cm^{-1} (νSO), 1698 cm^{-1} (νCO); ^1H NMR ($CDCl_3$) δ 1.16 (d, J = 6 Hz, 3H), 1.19 (s, 3H), 1.26 (s, 3H), 1.30 to 2.60 (m, 3H), 2.64 (s, 3H) and 3.77 (s, 1H); (C_6D_6) δ 0.60 to 2.25 (m, 12H), 2.31 (s, 3H), 3.72 (br s, 1H).

Anal. Calc. for $C_{10}H_{16}O_3S$: C, 53.53; H, 7.46; S, 14.83. Found: C, 53.79; H, 7.51; S, 14.73.

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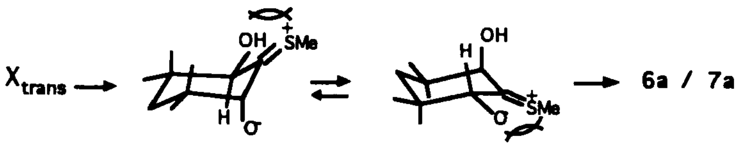

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