Olefin Inversion. Protection of the Sulfide Function in the Stereospecific Synthesis of *trans*-Thiacyclooct-4-ene

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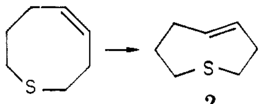
The concerted fragmentation method of Whitham[5a] has been applied to the configurational inversion of *cis*-thiacyclooct-4-ene (1) to give (35% overall yield) *trans*-thiacyclooct-4-ene (2) of >98% configurational purity. The required protection of the S atom has been afforded by methylation, while deprotection was achieved by homogeneous $LiAlH_4$ reduction in THF. Some peculiar NMR properties of the 1-methyl and 1-oxide derivatives of *trans*-thiacyclooctene are reported.

Stereospecific olefin synthesis has received widespread attention in the last two decades, and several methods have been developed for inverting the configuration of a double bond,[1-6] some of which[3-6] are capable of effecting stereospecific transformations even in cases where the product olefin is highly strained (e.g., *cis*- → *trans*-cyclooctene).[3-6] As far as we are aware, however, the cis → trans isomerization of a heterocyclic olefin has never been reported. We were confronted with such a problem in the course of another investigation where isomerically pure *trans*-thiacyclooct-4-ene was required for resolution into optical isomers. As the synthetic route to thiacyclooct-4-ene largely yields the cis isomer,[7] it was decided to synthesize the trans isomer through one of the available stereospecific olefin inversion methods. This paper gives an account of how this goal was achieved.

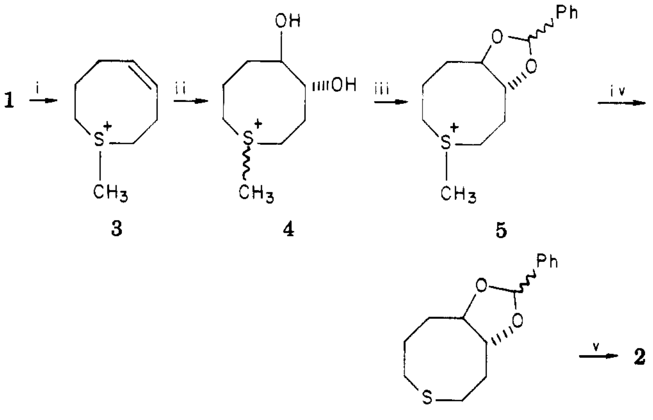
Results and Discussion

To effect the desired transformation, 1 → 2, we adopted the Whitham method[5a] of concerted fragmentation of a dioxolane derivative. This comprises three steps: (i) trans hydroxylation of the starting olefin, (ii) formation of a cyclic acetal of benzaldehyde, and (iii) reaction of the acetal with butyllithium. The procedure, however, cannot be applied as such to a sulfur-containing cyclic olefin. To start with, the first, hydroxylation, step requires conditions under which the sulfide is oxidized to sulfone before any epoxidation of the double bond occurs.[8] Although reduction of sulfone to sulfides may be feasible,[9] it is known to be a very difficult and unproductive process in cyclic systems,[10] and we confirmed this notion by carrying out a number of unsuccessful model reductions of thiocane 1,1-dioxide.



1 2

Scheme I[a]



[a] (i) $CF_3SO_3CH_3$, CH_2Cl_2. (ii) (1) MCPBA, CH_2Cl_2; (2) H^+, H_2O. (iii) PhCHO, $ZnCl_2$, 70 °C. (iv) $LiAlH_4$, THF. (v) BuLi, THF, −10 °C.

An attempt was also made at selective oxidation by the recently reported procedure of Reamonn and O'Sullivan which makes use of hypochlorite under controlled pH conditions.[11] The method, however, failed with our substrate, the only products formed with 1 or 2 equiv of NaClO being *cis*-thiacyclooct-4-ene 1-oxide and 1,1-dioxide, respectively. Clearly the procedure is not a general one, and Reamonn and O'Sullivan's success was likely due to the peculiar structure of their substrate.[11]

Alkylation of sulfide to sulfonium was eventually adopted as it appeared to provide efficient protection: the sulfonium function is resistant to further oxidation, and the nucleophilic character of the sulfur atom is lost, guaranteeing against transannular reactions. It is not completely free of complications with respect to deprotection, however, since those reactions that can cleave the exocyclic S-alkyl bond may also occur at the α ring carbon, causing ring opening. Best results were obtained by using methyl as the protecting group with subsequent deprotection effected by $LiAlH_4$ reduction.

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(1) For a review, see: Reucroft, J.; Sammes, P. G. *Q. Rev., Chem. Soc.* **1971**, *25*, 135.

(2) (a) Aratani, T.; Nakanisi, Y.; Nozaki, H. *Tetrahedron* **1970**, *26*, 4339. (b) Vedejs, E.; Fuchs, P. L. *J. Am. Chem. Soc.* **1973**, *95*, 822. (c) Clive, D. L. J.; Denyer, C. V. *J. Chem. Soc., Chem. Commun.* **1973**, 253. (d) Dowd, P.; Kang, K. *Ibid.* **1974**, 384. (e) Dervan, P. B.; Shippey, M. A. *J. Am. Chem. Soc.* **1976**, *98*, 1265. (f) Van Ende, D.; Krief, A. *Tetrahedron Lett.* **1975**, 2709. (g) Remion, J.; Dumont, W.; Krief, A. *Ibid.* **1976**, 1385. (h) Sonnett, P. E.; Oliver, J. E. *J. Org. Chem.* **1976**, *41*, 3279. (i) Marshall, J. A.; Lewellyn, M. E. *Ibid.* **1977**, *42*, 1311. (j) Hanessian, S.; Bargiotti, A.; La Rue, M. *Tetrahedron Lett.* **1978**, 737. (k) Mulzer, J.; Pointner, A.; Chucholowsky, A.; Brüntrup, G. *J. Chem. Soc., Chem. Commun.* **1979**, 52.

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(5) (a) Hines, J. N.; Peagram, M. J.; Thomas, E. J.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2332. (b) Jones, M.; Temple, P.; Thomas, E. J.; Whitham, G. H. *Ibid.* **1974**, 433.

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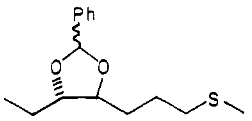
The reaction sequence resulting from this protection–deprotection procedure is shown in Scheme I.

The epoxidation of the sulfonium salt **3** was found to be remarkably slow compared to ordinary olefins (e.g., cyclooctene[12]), most likely as a consequence of a field effect of the transannular positive sulfur atom. Aside from this, epoxidation and hydrolysis gave quantitatively the diol sulfonium salt **4**. The latter yielded the cyclic acetal **5** by reaction with excess (neat) benzaldehyde. Very substantial proportions of acid catalyst ($ZnCl_2$) were found to be necessary for acetalization, presumably because the catalyst functioned also as dehydrating agent. The acetal **5** was demethylated by reduction with $LiAlH_4$. Since literature reports on the $LiAlH_4$ reduction of sulfonium salts fail to mention yields,[13] it was rather surprising to find that the reduction proceeded smoothly, giving **6** in high yield. This success is probably due to the fact that, with triflate as counterion, the reduction could be carried out homogeneously in THF. In spite of the satisfactory yield, however, the reaction is complicated by some simultaneous ring opening which produces a methyl sulfide, probably **7**. This must be separated from **6** before performing the final cycloelimination step; otherwise **2** would be obtained contaminated by the acyclic olefin formed from **7**, *trans*-hept-4-en-1-yl methyl sulfide, **8**. Although such separation could be achieved straightforwardly, the overall isolated yield of **6** was reduced to 55%.



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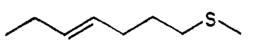

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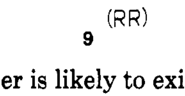
Because of solubility problems, the final, cycloelimination, step could not be carried out under the conditions optimized by Whitham for *trans*-cyclooctene.[5a] In fact the dioxolane **6** is but slightly soluble in petroleum ether, and the reaction had to be carried out in THF. Fortunately, however, and unlike the *trans*-cyclooctene case,[5a] no product of butyllithium addition to the strained olefin appeared to be formed.

Alkylation of **2** with methyl triflate gave a single methyl sulfonium derivative, **9**. Inspection of models shows that only one diastereomer is likely to exist, the *SS,RR*, where the Me group projects outside the ring. Indeed, in the other diastereomer the Me group would have to project inside toward and past C_5 H, in an impossibly congested situation.



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Since the resolution of the sulfonium salt appeared to be a possible way for obtaining optically pure **2**, the $LiAlH_4$ reduction of **9** was attempted. The product appears to consist mainly of the ring-opened sulfide **8** with no trace of **2**. Apparently one of the α ring carbons (C_2) is much more reactive toward hydride attack than the exocyclic methyl carbon, a likely consequence of the unusually large strain of this eight-membered ring.

The comparison of the ^1H and ^{13}C NMR spectra of the sulfonium salt **9** with those of the corresponding sulfide **2** shows the positive charge on the heteroatom has dramatic effects on the shieldings of atoms across the ring. The olefinic proton at δ 5.14 in **2** is shifted to δ 5.9 in **9**. Since the molecule most likely has the twist conformation,[14] the proton concerned must be C_5 H. On the other hand, the olefinic carbon shieldings, 137.3 and 135.1 ppm, also show a downfield shift with respect to the sulfide, 137.5 (C_5) and 130.4 ppm (C_4). In this case, however, the carbon atom most affected appears to be C_4 rather than C_5.

Similar effects are found in the sulfoxide, **10**, a single isomer of which is obtained by oxidation of **2** and which is therefore assumed to have the *RR,SS* configuration. Also, in this case the olefinic proton at C_5 appears to be considerably deshielded (0.60 ppm). However, the olefinic carbon shieldings are not as strongly affected as in the sulfonium cation.

Experimental Section

Proton NMR spectra were recorded at 100 MHz on a Varian XL-100 operating in the CW mode. Proton noise decoupled ^{13}C spectra were recorded at 25.15 MHz with a Varian XL-100 by the FT technique; single-frequency off-resonance spectra were obtained by irradiation at δ -4 in the proton spectrum. Proton and ^{13}C shifts are given in parts per million from Me_4Si in $CDCl_3$ solvent; for the ^{13}C spectra in D_2O, dioxane (δ 67.18) was used as internal standard. GLC analyses were carried out with a Hewlett-Packard 5700 instrument equipped with a flame-ionization detector ($^1/_8$ in. × 3 m column, 10% XE 60 on Chromosorb W). Preparative GLC separations were carried out with a Varian Aerograph 712 instrument ($^3/_8$ in. × 3 m column, 10% XE 60 on Chromosorb W, 60–80 mesh, at 100 °C).

Solvents and reagents were obtained dry as follows. Methylene chloride was distilled from calcium hydride, ethyl ether from $LiAlH_4$, and pyridine from KOH. Tetrahydrofuran, dried over sodium and distilled, was redistilled from $LiAlH_4$ immediately before use.

1-Methyl-*cis*-Δ^4-thiocanium Trifluoromethanesulfonate (Triflate) or Hexafluorophosphate, 3. To a solution of methyl triflate (18 g, 0.11 mol, in 100 mL of CH_2Cl_2) cooled at 0 °C was added *cis*-thiacyclooct-4-ene (12.8 g, 0.10 mol) dropwise over 30 min with stirring. The mixture was then warmed to 10 °C and stirred for 3 h. Removal of the solvent under reduced pressure left a white crystalline solid: 29.0 g (99.3%); mp 83–85 °C. An analytically pure sample was obtained by recrystallization ($EtOH/Et_2O$); mp 85–86 °C. The hexafluorophosphate salt was obtained from the triflate by methathesis with NH_4PF_6: mp 96–97 °C after recrystallization (EtOH); ^1H NMR (acetone-d_6) δ 5.86 (m, 2 H, olefinic protons), 3.90 and 3.64 (m, 2 H each, α ring protons), 3.04 (s, 3 H, SCH_3), 2.84, 2.40, and 2.2 (3 m, 2 H each, β and γ protons); in D_2O the spectrum (triflate salt) is essentially identical except that the SCH_3 singlet is shifted upfield by 0.2 ppm; ^{13}C NMR (D_2O) 132.6 and 128.4 (C_5 and C_4, interchangeable), 46.9 and 43.7 (C_2 and C_8, interchangeable), 25.9 (SCH_3), 25.6, 24.9, and 21.9 (C_3, C_6, and C_7, interchangeable).

Anal. Calcd for $C_9H_{15}S_2O_3F_3$: C, 36.98; H, 5.17. Found: C, 36.89; H, 5.21.

1-Methyl-*trans*-4,5-dihydroxythiocanium Triflate, 4. A solution of **3** triflate (14.6 g, 0.05 mol) and MCPBA (85%, 13 g, 0.06 mol) in 90 mL of CH_2Cl_2 was refluxed for 8 h. *m*-Chlorobenzoic acid was filtered off, and the excess peracid in the filtrate was destroyed (KI test) by shaking with aqueous 10% $NaHSO_3$. The resulting aqueous and organic layers, unseparated, were

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[14] The ^{13}C spectra of diastereomeric 2-methyl-*trans*-thiacyclooct-4-enes are consistent with the twist conformation.[15] Moreover, force-field calculations carried out in this laboratory[16] indicate that **2** is more stable in the twist than in the chair conformation by ca. 5.0 kcal mol^{-1}. It is thus likely that **9** will also adopt the twist conformation.

[15] Ceré, V.; Pollicino, S.; Sandri, E.; Fava, A. *J. Am. Chem. Soc.* **1978**, *100*, 1516.

[16] Guerra, M., submitted for publication.

evaporated at reduced pressure to remove the organic solvent. The aqueous residue, containing a mixture of the title compound and the corresponding cis epoxide, was diluted with water to 60 mL to dissolve the sulfonium salt, filtered to remove the organic acid, and further diluted to 100 mL, and 70% $HClO_4$ was added (5.3 mL). After 3 h at reflux, the solution was neutralized with 20% aqueous KOH and filtered ($KClO_4$). The filtrate was evaporated at reduced pressure and the oily residue taken up with absolute EtOH and filtered. Evaporation of the solvent in vacuo gave a colorless viscous oil (16 g, 98.8%). NMR analysis showed the presence of two isomers in a ~1.2:1 ratio: ^1H NMR (acetone-d_6) δ 4.15 (br s, 2 H, OH), 3.75 (m, 6 H, C_2 H_2, C_8 H_2, C_4 H, and C_5 H), 3.09 (major) and 3.04 (minor) (2 s, 3 H overall, SCH_3), 2.25 (m, 6 H, C_3 H_2, C_6 H_2, C_7 H_2); ^{13}C NMR (D_2O) altogether 16 lines are present which by their intensity can be assigned to the major and (in parentheses) minor isomers, 74.5 and 73.8 (73.0 and 72.0) C_4 and C_5, interchangeable, 42.4 (43.4) C_8, 40.7 (39.1) C_2, 30.4 (29.8) C_6, 28.9 (27.6) C_3, 26.8 (26.2) CH_3, 21.0 (20.0) C_7.

1-Methyl-*trans*-4,5-dihydroxy-*O*-benzylidenethiocanium Triflate, 5. Crude triflate 4 (10.0 g, 0.031 mol) and dry $ZnCl_2$ (4.2 g, 0.031 mol) were mixed with freshly distilled benzaldehyde (60 mL) and stirred for 3.5 h at 70 °C under a nitrogen atmosphere. After cooling at 0 °C the solution was poured into 600 mL of Et_2O under vigorous stirring. The sulfonium salt separated out as an oily layer which was removed, dissolved in water, and extracted with ether. The aqueous solution was evaporated, and the residue was dried in vacuo at 70 °C to give a highly hygroscopic glassy solid (12.5 g, 99%) whose NMR shows the presence of at least three (two major and one minor) of the four possible isomers, as evinced by the presence of three singlets at δ 5.94, 5.89, and 5.86 (overall 1 H) due to the acetal proton. Similarly, three singlets (3 H overall) were present at δ 3.16, 3.07, and 3.04 due to SCH_3 groups. Other absorptions were as follows: δ 7.5 (m, 5 H, Ph group), 4.2 (m, 2 H, C_4 H and C_5 H), 3.8 (m, 4 H, α ring protons), 2.7 and 2.4 (2 m, 8 H overall, β- and γ-H's).

***trans*-4,5-Dihydroxy-*O*-benzylidenethiocane, 6.** Crude 5 triflate (11.6 g, 0.028 mol) in 100 mL of THF was added dropwise over 30 min to a stirred suspension of $LiAlH_4$ (1.37 g, 0.036 mol) in THF at 0 °C under nitrogen and the mixture stirred for 4 h at 10–15 °C. After being quenched with 20% aqueous NH_4Cl (80 mL), the mixture was diluted with H_2O (300 mL) and filtered from the inorganic salts. The filtrate was extracted with CH_2Cl_2 (3 × 150 mL) and the combined extracts were dried over $CaSO_4$. Evaporation of the solvent under reduced pressure, followed by short-path distillation, gave 4.3 g (61%) of the title compound: bp 160–161 °C (0.6 mm); mp 45–47 °C. The material was obtained pure by crystallization from *n*-hexane: 3.5 g, 50%; mp 48–49 °C. An additional 5% was obtained from the mother liquor by evaporation of the solvent and column chromatography of the residue (SiO_2, $CHCl_3$ eluant). The material appears to be made up of two isomers in nearly equal amounts as proven by the NMR spectra. Thus in the ^1H NMR spectrum the material has two singlets of about equal intensity (1 H overall, δ 5.83 and 5.80) due to the acetal proton. Other absorptions were as follows: δ 7.40 (m, 5 H, Ph ring), 4.68 and 3.99 (2 m, 2 H overall, C_4 H and C_5 H), 3.1–1.7 (large m, 10 H, remaining α-, β-, and γ-CH_2). The ^{13}C NMR has, besides the aromatic resonances, the following: 101.3 and 100.8 (acetal carbon), 83.2, 82.5, 81.7, and 80.4 (C_4 and C_5); 10 absorptions in the aliphatic region (unassigned) 36.2, 35.9, 33.6, 33.1 (two resonances), 32.9, 28.5, 28.4, 27.3, 26.5.

Anal. Calcd for $C_{14}H_{18}SO_2$: C, 67.17; H, 7.24. Found: C, 67.18; H, 7.21.

The $LiAlH_4$ reduction of 5 appeared to cause some ring opening: the material (0.36 g) first eluted in the chromatographic separation of the residue from the mother liquor of crystallization shows in the ^1H NMR the presence of two closely spaced, equally intense SCH_3 singlets. Neither the ^1H nor the ^{13}C NMR spectra, however, were able to establish whether these isomeric sulfides are the result of S–C_2 fission, *trans*-4,5-*O*-benzylideneheptyl methyl sulfide 7, or the alternative product of S–C_8 fission, *trans*-3,4-*O*-benzylideneheptyl methyl sulfide [^1H NMR ($CDCl_3$) δ 7.38 (m, 5 H, Ph ring), 5.89 and 5.87 (2 s, 1 H overall, PhCH), 3.84 (m, 2 H, C_4 H and C_5 H), 2.66 (m, 2 H, CH_2S), 2.10 and 2.08 (2 s, 3 H overall, SCH_3), 1.90 and 1.56 (2 m, 6 H overall), 0.98 (t, 3 H overall, CH_2CH_3)]. Tentatively, the material may be assigned structure 7 on the basis of the ^{13}C spectrum of the olefin arising from it by cycloelimination (see below).

***trans*-Thiacyclooct-4-ene, 2.** To 2.5 g (0.01 mol) of 6 dissolved in THF (20 mL) stirred and cooled at −35 °C under a nitrogen atmosphere was added 13.75 mL of 1.6 M BuLi (0.022 mol) in hexane dropwise via syringe over 5 min. The temperature was raised to −10 °C, and the mixture was stirred for 30 min at 0 °C. After addition of water, the mixture was extracted with pentane. The organic layer was extracted (3 × 20 mL) with 20% aqueous silver nitrate. Evaporation of the organic layer left a residue (1.35 g) largely consisting of valerophenone.[5] The aqueous silver nitrate solution was slowly added to ice-cold aqueous ammonia (28%, 40 mL) and extracted with pentane. The extract was dried and evaporated and gave 0.84 g (66%) of the title compound which contained less than 2% of the cis isomer (GLC): ^1H NMR δ 5.84 (ddd, J = 15.5, 10.0, 2.0 Hz, 1 H, olefinic proton, probably C_4 H, see below), 5.14 (ddd, J = 15.5, 11.0, 3.5 Hz, 1 H, olefinic proton, probably C_5 H, see below), 2.90 (m, 2 H, α-CH_2), 2.50 (m, 2 H, α-CH_2), 2.00 (m, 6 H, β- and γ-CH_2). Irradiation at δ 2 resolves the low-field part of the spectrum into an AB quartet (J = 15.5 Hz; $\Delta\nu$ = 70 Hz). The ^{13}C spectrum coincides within 0.2 ppm with that of the minor isomer formed in the ring expansion of 2-vinylthiolanium methylide,[7] which had been attributed to *trans*-thiacyclooct-4-ene.

Anal. Calcd for $C_7H_{12}S$: C, 65.56; H, 9.43. Found: C, 65.51; H, 9.50.

In one experiment, the starting material had been incompletely purified (only short-path distillation) and contained the above-mentioned ring-opened methyl sulfide. The product from this experiment was an ~9:1 mixture of 2 and another olefin which could be separated by preparative GLC. The ^{13}C NMR spectrum of the minor product showed the olefinic carbons to differ by 3.6 ppm, consistent with a linear structure where the double bond is in position 3 rather than 4 (from the terminal Me group). Therefore, the product may be tentatively assigned the *trans*-4-hepten-1-yl methyl sulfide structure, 8, from which structure 7 is deduced for its dioxolane precursor: ^{13}C NMR 131.9 (C_5), 128.3 (C_4), 34.7 and 34.4 (C_1 and C_2, interchangeable), 22.6 (C_6), 13.6 (C_7), 15.5 (SCH_3).

Attempted Selective Oxidation[11] of *cis*-Thiacyclooct-4-ene: *cis*-Thiacyclooct-4-ene 1-Oxide and 1,1-Dioxide. To a dioxane solution of 1 (0.64 g, 0.005 mol in 10 mL) was added a freshly prepared solution of NaOCl (5.6 mL of a 7.35 w/v solution, 0.0065 mol). The mixture was maintained at ~20 °C by intermittent external cooling and was stirred for 30 min. The solution was evaporated to a small volume and the aqueous residue extracted with CH_2Cl_2. Evaporation of the solvent gave an oil (0.63 g, 88%) which appeared to be a sulfoxide (IR $\nu_{S\text{–}O}$ 1020 cm^{-1}), while the ^1H NMR showed the material still had two olefinic protons: ^{13}C NMR 130.1 and 128.7 (C_4 and C_5, interchangeable), 54.0 and 51.9 (C_2 and C_8, interchangeable), 24.8 (C_6), 22.3 (C_3), 18.7 (C_7).

Further oxidation of this material (0.6 g) for 2 h gave the 1,1-dioxide derivative as a white solid (0.61 g, mp 78–81 °C) which was recrystallized from *n*-hexane: mp 82–83 °C; IR ν_{SO_2} 1110 and 1270 cm^{-1}; ^1H NMR δ 5.79 (m, 2 H, olefinic protons), 3.15 (m, 4 H, α-CH_2), 2.45 (m, 4 H, C_3 H_2 and C_6 H_2), 1.86 (m, 2 H, C_7 H_2). Irradiation at δ 2.45 resolved the low-field multiplet into an AB quartet (J = 10.5; $\Delta\nu$ = 19 Hz); ^{13}C NMR 130.7 and 129.0 (C_4 and C_5, interchangeable), 57.9 and 52.9 (C_2 and C_8, interchangeable), 23.2 (C_6), 20.8 and 20.5 (C_3 and C_7, interchangeable).

Anal. Calcd for $C_7H_{12}SO_2$: C, 52.47; H, 7.55. Found: C, 52.90; H, 7.43.

Attempted Reduction of Thiocane 1,1-Dioxide. To a $LiAlH_4$ suspension in ether (1.14 g, 0.03 mol in 50 mL) was added a solution of thiocane 1,1-dioxide[17] (0.81 g, 0.005 mol in 30 mL of Et_2O) and the mixture warmed at reflux. GLC monitoring showed the persistence of the sulfone peak even after 6 h and the appearance of several unidentified peaks. However, the thiocane peak was absent. No better results were obtained by using dioxane as the solvent at reflux for up to 9 h.

1-Methyl-*trans*-Δ^4-thiocanium, 9, triflate and hexafluorophosphate were prepared as described for 3 from *trans*-thiacyclooct-4-ene (0.768 g, 0.006 mol). The triflate salt (1.54 g, 88%) was an uncrystallizable material. The hexafluorophosphate

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(17) Friedman, P.; Allen, P., Jr. *J. Org. Chem.* **1965**, *30*, 780.

salt (1.43 g) was obtained by metathesis with NH_4PF_6 and CH_2Cl_2 extraction as a viscous material which crystallized on standing in vacuo; mp 73–75 °C. This product was recrystallized from ethanol and dried in vacuo: mp 78–79 °C; ^1H NMR (acetone-d_6) δ 5.96 (m, 2 H, olefinic protons), 4.12 (m, 2 H, α-CH_2), 3.50 (m, 2 H, α-CH_2), 2.98 (s, 3 H, SCH_3), 2.84 (m, 2 H, probably C_3 H and C_6 H), 2.42 (m, 4 H, C_7 H_2, C_3 H, C_6 H); ^{13}C NMR (acetone-d_6) 137.3 (C_5), 135.1 (C_4), 58.0 (C_2), 49.2 (C_8), 32.4, 31.9, and 31.3 (C_3, C_6, and C_7 interchangeable), 26.6 (SCH_3).

Anal. Calcd for $C_8H_{15}SPF_6$: C, 33.34; H, 5.24. Found: C, 33.41; H, 5.17.

An attempt was made to see whether the sulfonium salt **9** (0.584 g, 0.002 mol) could be reduced back to the trans sulfide **2**. The reaction was performed as described for **4** and monitored by GLC. No trace of **2** appeared in the chromatogram which consisted of a single peak with a retention time identical with that of the acyclic sulfide formed along with **2** in the cycloelimination of incompletely purified **6**. Workup gave a colorless oil (0.24 g) whose ^{13}C NMR confirmed the presence of *trans*-4-hepten-1-yl methyl sulfide, together with a minor (~10%) unidentified isomer.

***trans*-Thiacyclooct-4-ene 1-oxide** was obtained as an oily material by aqueous periodate oxidation[18] of **2** at 0 °C for 5 h; ν_{SO} 1020 cm^{-1}. The ^1H NMR spectrum has two absorption regions: δ 5.69 (m, 2 H, olefinic protons) and an extremely complex band between δ 3.8 and 1.9 (10 H). Irradiation at δ 3.1 resolved the low-field part of an AB quartet (δ 5.78; J = 15.4 Hz), the high-field part of which (at δ 5.64) was resolved by irradiation at δ 2.5. The ^{13}C NMR spectrum was as follows: 135.3 and 131.1 (C_5 and C_4, interchangeable), 62.1 and 61.7 (C_2 and C_8, interchangeable), 32.1 (C_6), 29.8 (C_3), 27.4 (C_7). The ^{13}C spectrum indicated that the material contained ~15% of *cis*-thiacyclooct-4-ene 1-oxide. Clearly some $E \rightarrow Z$ isomerization takes place during oxidation.

***trans*-Thiacyclooct-4-ene 1,1-Dioxide.** Aqueous periodate oxidation[18] of **2** at 25 °C for 5 h gave after workup a low-melting solid, twice crystallized from *n*-hexane; mp 70–78 °C. The ^{13}C NMR spectrum indicated this material contains the title compound together with *cis*-thiacyclooct-4-ene 1-oxide (~25%) and *trans*-thiacyclooct-4-ene 1-oxide (~15%): ^{13}C NMR 135.6 and 129.5 (C_5 and C_4, interchangeable), 65.0 and 60.2 (C_2 and C_8, interchangeable), 31.8 (C_6), 29.4 (C_3), 25.8 (C_7).

Registry No. 1, 64945-38-6; **1** sulfoxide, 72050-53-4; **1** 1,1-dioxide, 72075-87-7; **2**, 64945-41-1; **2** sulfoxide, 72074-95-4; **2** 1,1-dioxide, 72050-54-5; **3** hexafluorophosphate, 72050-56-7; **3** triflate, 72050-57-8; **4**, isomer 1, 72050-59-0; **4**, isomer 2, 72074-97-6; **5**, 72050-61-4; **6**, isomer 1, 72050-62-5; **6**, isomer 2, 72074-98-7; **7**, 72050-63-6; **8**, 72050-64-7; **9** hexafluorophosphate, 72075-00-4; **9** triflate, 72120-46-8.

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S-Ethenylsulfoximine Derivatives. Reagents for Ethylenation of Protic Nucleophiles

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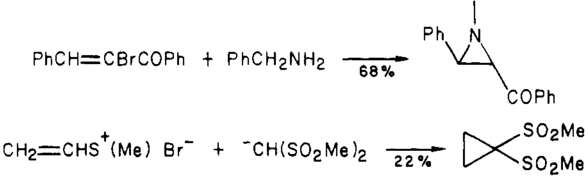
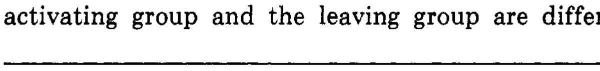
The preparation of *S*-vinyl and *S*-(2-substituted)ethenyl derivatives of sulfoximines is described. Vinyl-, (2-phenylethenyl)-, (2,2-diphenylethenyl)-, (2-methyl-1-propenyl)-, [2-(*p*-tolyl)ethenyl]-, and [2-(2-furanyl)ethenyl](dimethylamino)phenyloxosulfonium fluoborates were found to undergo an addition–elimination reaction sequence with protic nitrogen and carbon nucleophiles, resulting in ethylenation of the nucleophile and *N*,*N*-dimethylbenzenesulfinamide. Primary amines gave aziridines, enamines gave cyclopropyl derivatives of iminium salts or pyrrolidinium salts, anions of active methylene compounds gave dihydrofurans and/or cyclopropanes, and anions of nitroalkanes gave cyclic nitronic esters and/or nitrocyclopropanes. In several cases vinyl salts were generated in situ from β-methoxyoxosulfonium salts. Treatment of (–)-(*S*)-(dimethylamino)phenyl(*trans*-2-phenylethenyl)oxosulfonium fluoborate with methyl cyanoacetate in methanol containing sodium methoxide gave, in 81% yield, (+)-(1*S*,2*R*)-methyl 1-cyano-2-phenylcyclopropanecarboxylate of 25.5% optical purity. The same salt upon treatment with methyl nitroacetate gave, in 95% yield, methyl 4-phenyl-3-isoxazolinecarboxylate 2-oxide with 33% enantiomeric excess. Cyclopropanes were formed upon treatment of *S*-methyl-*S*-(*trans*-2-phenylethenyl)-*N*-(*p*-tolylsulfonyl)sulfoximine with anions of active methylene compounds.

An addition–displacement reaction of nucleophiles of the type ^-NuH or $:NuH_2$ with Michael acceptors such as α-halovinyl ketones has proven to be an interesting approach to aziridines, cyclopropanes, and related compounds[1-3] (e.g., eq 1).[1] In such a reaction the Michael-activating group and the leaving group are different moieties. Vinylsulfonium salts have been found to undergo similar reactions (e.g., eq 2); in these reactions the sulfonium group plays a dual role—activating group for nucleophilic addition and leaving group.[4]

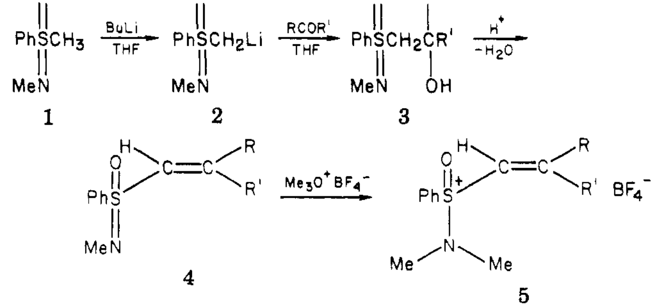


(1)



(2)

Scheme I



a, R = R′ = H; b, R′ = H, R = Ph; c, R = R′ = Ph; d, R = R′ = Me; e, R′ = H, R = *p*-tolyl; f, R′ = H, R = 2-furanyl

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