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Synthesis of Methanethial S-Oxide (Sulfine) and Alkanethial S,S-Dioxides by Fluorodesilylation. Stereochemistry of Their Cyclopentadiene Diels-Alder Adducts[1]

Eric Block* and Alan Wall

Department of Chemistry, State University of New York at Albany, Albany, New York 12222

Abstract: Fluorodesilylation of trimethylsilylmethanesulfinyl chloride **4** in the presence of cyclopentadiene gives 2-thiabicyclo[2.2.1]hept-5-ene endo-2-oxide, **5**; in a like manner 1-trimethylsilylalkanesulfonic anhydrides afford endo- and exo-3-alkyl-2-thiabicyclo[2.2.1]hept-5-ene 2,2-dioxides, with the endo isomer predominating. Sulfine and alkyl sulfenes are invoked.

While a variety of procedures are available for the synthesis of substituted sulfines in solution,[2] the parent sulfine, methanethial S-oxide, **1**, has thus far been prepared only in the gaseous state.[3,4] Recently we reported a useful new approach to the generation of sulfene, **2**, via fluorodesilylation of trimethylsilylmethanesulfonyl chloride (**3**, Scheme 1).[5] We now report that application of this procedure to trimethylsilylmethanesulfinyl chloride (**4**, Scheme 1) in the presence of cyclopentadiene affords the sulfine-cyclopentadiene adduct **5**, providing the first unequivocal evidence for formation of sulfine in solution. We also report that fluorodesilylation of 1-trimethylsilylethanesulfonic anhydride and 1-trimethylsilylpropanesulfonic anhydride (**12a** and **12b**, respectively) in the presence of cyclopentadiene give adducts **13a/14a** and **13b/14b**, whose stereochemical composition was determined by chromatographic, spectroscopic and X-ray crystallographic methods. This work provides the first evidence on the endo/exo preferences of sulfenes in the Diels-Alder reaction.

Treatment of a solution of trimethylsilylmethanesulfinyl chloride,[1b] **4**, in anhydrous CH_3CN with CsF at -20° C in the presence of excess cyclopentadiene gave 2-thiabicyclo[2.2.1]-hept-5-ene endo-2-oxide,[6] **5** (90% yield), together with ca. 10% of 2-thiabicyclo[2.2.1]hept-5-ene exo-2-oxide, **6**. This mixture could be oxidized to 2-thiabicyclo[2.2.1]hept-5-ene 2,2-dioxide,[5] **7**, which upon reduction to 2-thiabicyclo[2.2.1]hept-5-ene,[7] **8**, and reoxidation with MCPBA gave **6**.[6,8] C-13 NMR data for **5**-**8** is given in Table 1. While exo-sulfoxide **6** is stable at room temperature, endo-sulfoxide **5** rearranges below room temperature to 2-oxa-3-thiabicyclo[3.3.0]oct-7-ene, **9**, as described elsewhere.[9] Stereochemical assignments for sulfoxides **5** and **6** are consistent with cyclopentadiene trapping studies on higher alkanethial S-oxides, with the known preference of 2-thiabicyclo[2.2.1]heptane to undergo oxidation with MCPBA to the exo-sulfoxide[8], as well as with the thermal instability of isomer **5**, reflecting the availability of a [2,3]-sigmatropic rearrangment pathway.[10] When two equivalents of **4** was treated with one equivalent of CsF, α-chloromethyl trimethylsilylmethanethiosulfonate[6] (**16**, eq 1) was isolated in good yield, reflecting trapping of sulfine by unreacted **4** by a mechanism previously proposed by us.[1b]

$$\underset{\mathbf{4}}{Me_3SiCH_2S(O)Cl} \quad + \quad CH_2{=}SO \xrightarrow{\qquad\qquad\qquad} \underset{\mathbf{16}}{Me_3SiCH_2SO_2SCH_2Cl} \qquad (1)$$

In an effort to prepare homologues of **4**, 1-trimethylsilylethanethiol[6] and 1-trimethylsilylpropanethiol[6] (**10a** and **10b**, respectively) were each prepared in 30% overall yield (eq 2). Whereas a variety of approaches to the respective sulfinyl chlorides proved unsuccessful with most reactions (e.g. chlorination of the disulfides, sulfinic acids or thioacetates) leading to C-Si bond cleavage, treatment of the sulfonic acids with PCl_5 led either to the respective sulfonyl chlorides[6] **11** (inverse addition: sulfonic acid added to PCl_5) or sulfonic anhydrides[6] **12** (direct addition: PCl_5 added to sulfonic acids). The sulfonic anhydrides **12** proved to be excellent sulfene precursors upon CsF-induced fluorodesilylation, giving cyclopentadiene adducts in a high state of purity.[11] Exo and endo adducts formed in each case (2:3 from **12a**, 1:3 from **12b**) were separable by capillary GC as well as by HPLC. The major cyclopentadiene adduct from **12b**, **14b**,[6] was established as having an endo ethyl group by an X-ray crystallographic structural determination of the corresponding epoxy-derivative, **15b**.[10] The minor (exo) cyclopentadiene adducts **13a,b** from **12a,b** could be prepared in pure form by sequential treatment of 2-thiabicyclo[2.2.1]-hept-5-ene 2,2-dioxide, **7**, with *n*-butyllithium followed by methyl or ethyl iodide, respectively.

While π-effects involving the sulfinyl group and the developing carbon-carbon double bond can be invoked to explain in part the preference of methanethial S-oxide 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 effects involving the alkyl groups.[12]

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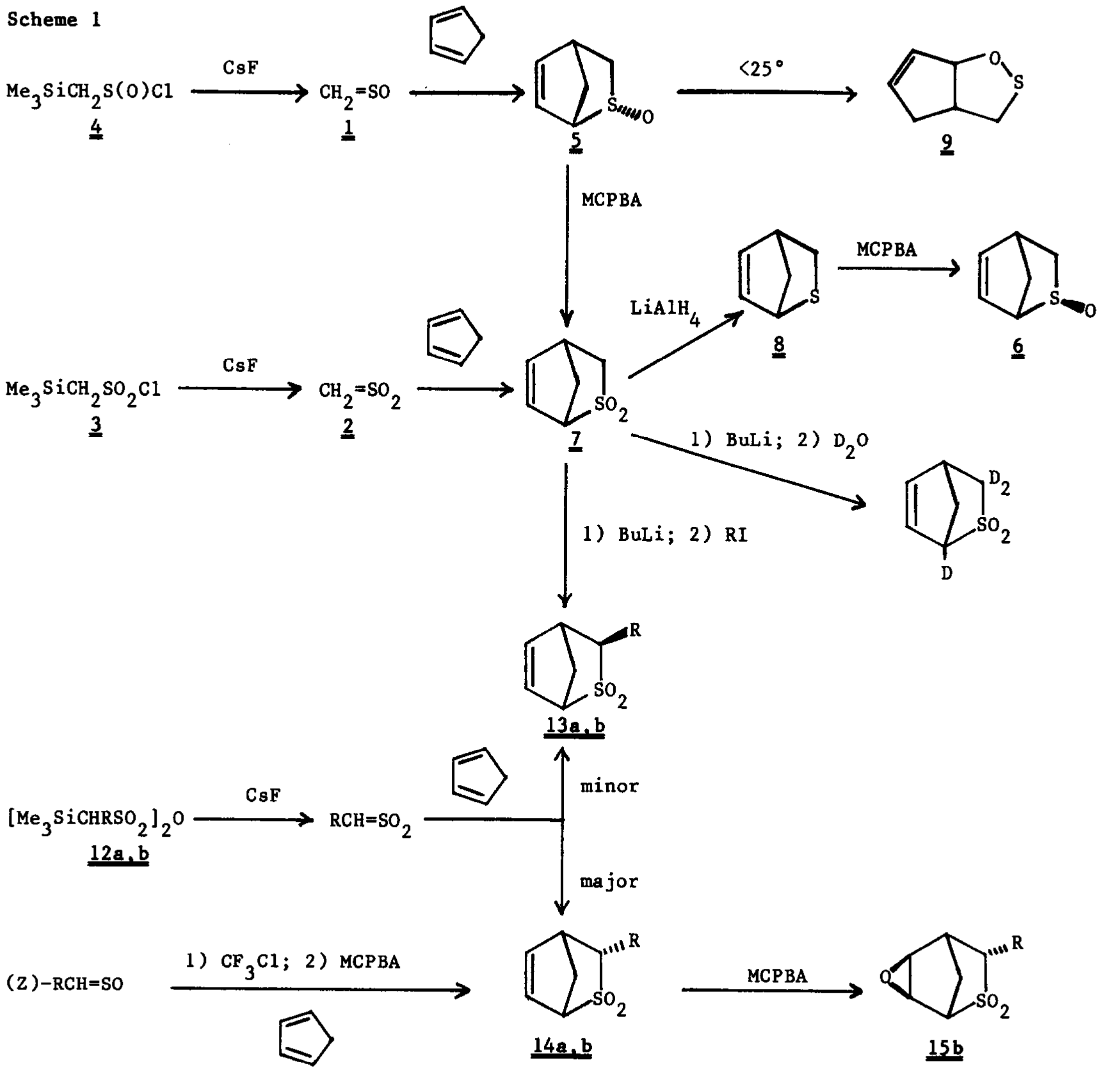
$$\mathrm{Me_3SiCH_2Cl} \xrightarrow{\text{1) }\underline{\text{sec}}\text{-BuLi; 2) RI}} \mathrm{Me_3SiCHRCl} \xrightarrow{\text{1)}\mathrm{(NH_2)_2C{=}S}\text{; 2) }\mathrm{OH^-}\text{; }\mathrm{H_3O^+}} \underset{\underline{\mathbf{10a,b}}}{\mathrm{Me_3SiCHRSH}} \xrightarrow{\text{3MCPBA}}$$

$$\mathrm{Me_3SiCHRSO_3H} \xrightarrow{\mathrm{PCl_5}} \begin{cases} \underset{\underline{\mathbf{11a,b}}}{\mathrm{Me_3SiCHRSO_2Cl}} \\ \underset{\underline{\mathbf{12a,b}}}{\mathrm{[Me_3SiCHRSO_2]_2O}} \end{cases} \qquad (2)$$

<u>a</u>, R=Me; <u>b</u>, R=Et

Scheme 1



<u>a</u>, R=Me; <u>b</u>, R=Et

Table 1. Carbon-13 Chemical Shifts (ppm) of Bicyclic Compounds **5**-**8**[a]

Compound	Carbon 1	Carbon 3	Carbon 4	Carbon 5	Carbon 6	Carbon 7
5	65.3	55.1	43.1	139.9	127.8	44.7
6	67.2	56.2	41.4	145.3	126.6	43.8
7	64.4	47.3	41.0	140.6	129.2	45.1
8	50.5	30.3	44.5	130.8	135.6	49.9

[a] Peak assignments were confirmed by deuterium incorporation at the 1 and 3 positions (*n*-BuLi followed by deuterium oxide) in **7** followed by conversion of deuterated **7** to **6** and **8** and, in the case of **7** and **8**, by two dimensional proton-carbon correlation and APT studies at 300 MHz. We thank Dr. Elizabeth Williams for conducting the latter studies.

References and Notes

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

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6. All new compounds were fully characterized as will be detailed in the full report.

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11. Trimethylsilylmethanesulfonic anhydride[6] has also been found to afford a good yield of **7** upon treatment with CsF in dry acetonitrile.

12. Endo stereochemistry is favored in the Diels-Alder reactions of both 3,3,3-trifluoropropene and propene itself: B. Gaede and T.M. Balthazor, J. Org. Chem., 48, 276 (1983); N.A. Belikova, V.G. Berezkin, and A.F. Plate, Zh. Obshch. Khim., 32, 2942 (1962).

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