Tetrahedron Letters,Vol.26,No.11,pp 1425-1428,1985
Printed in Great Britain

0040-4039/85 $3.00 + .00

# 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]

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

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]

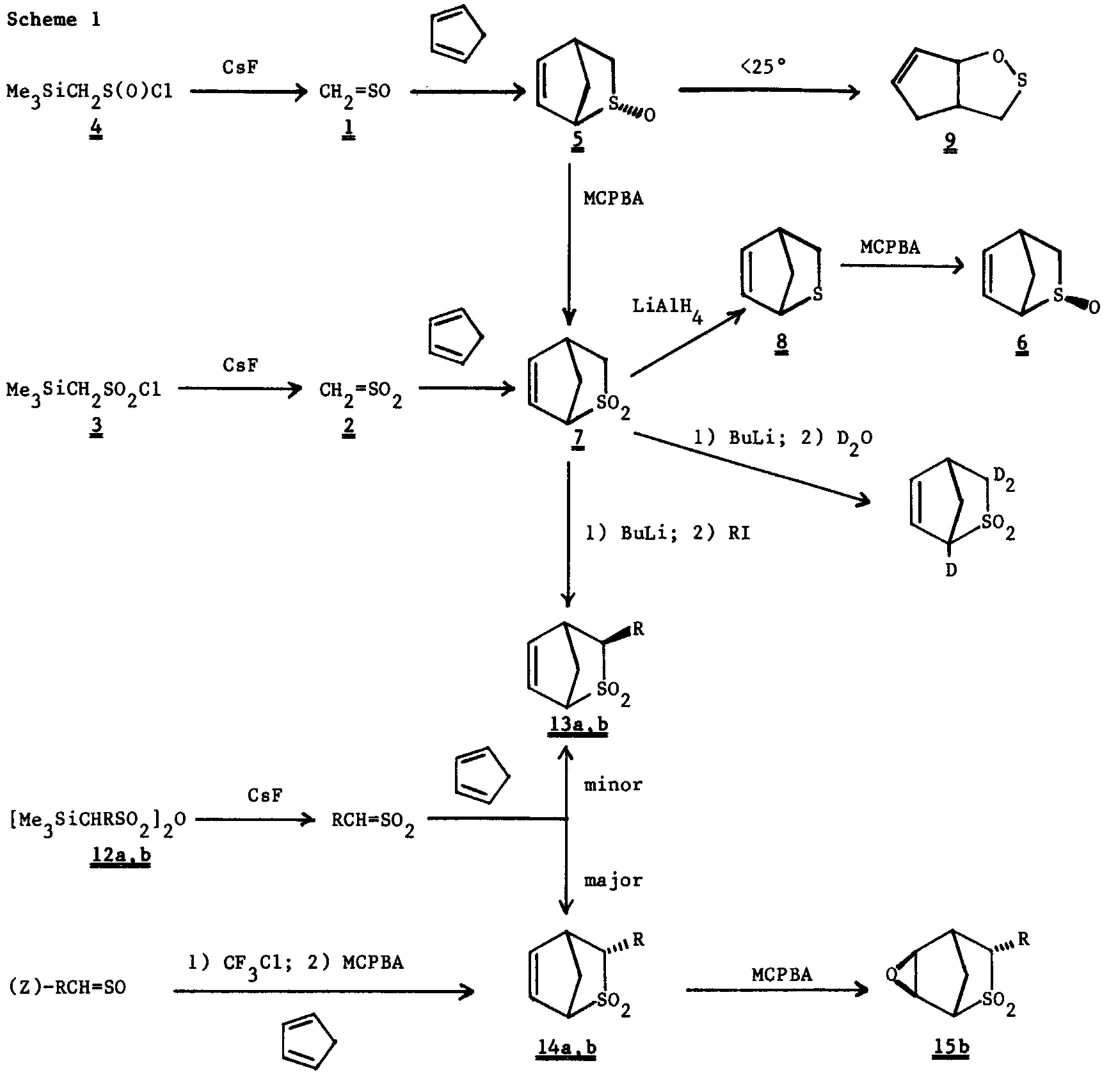
*Acknowledgment*. We gratefully acknowledge support from the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Societe Nationale Elf Aquitaine, and the John Simon Guggenheim Memorial Foundation.

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

$$\begin{tikzcd} & \underset{\mathbf{\underline{11a,b}}}{Me_3SiCHRSO_2Cl} \\ Me_3SiCHRSO_3H \arrow[ur, "PCl_5"] \arrow[dr] & \\ & \underset{\mathbf{\underline{12a,b}}}{[Me_3SiCHRSO_2]_2O} \end{tikzcd} \qquad (2)$$

**a**, R=Me; **b**, R=Et

Scheme 1



**a**, R=Me; **b**, 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.

1. a) The Chemistry of Sulfines. 10; b) part 9: E. Block and A.A. Bazzi, *Tetrahedron Lett.*, *23*, 4569 (1982); c) presented at the 18th Organosilicon Symposium, Schenectady, NY, April 6, 1984.

2. E. Block in *Organic Sulfur Chemistry*, R.Zh. Freidlina and A.E. Skorova, Ed., Pergamon Press, Oxford, 1981, pp 15-34; B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, *101*, 1 (1982).

3. E. Block, R.E. Penn, R.J. Olsen and P.F. Sherwin, *J. Amer. Chem. Soc.*, *98*, 1264 (1976); E. Block, H. Bock, S. Mohmand, P. Rosmus and B. Solouki, *Angew. Chem.*, *15*, 383 (1976).

4. During the course of this work we learned of studies by Freeman implicating sulfine as an intermediate in reactions of methanesulfinyl chloride with nitrogen bases: F. Freeman and M.C. Keindl, *J. Chem. Soc., Chem. Commun.*, 138 (1984). We thank Professor Freeman for informing us of his independent studies in this area.

5. E. Block and M. Aslam, *Tetrahedron Lett.*, *23*, 4203 (1982).

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

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

8. Oxidation of sulfide 8 to sulfoxide has been described although stereochemical assignents were not made: J.E. Keiser, *Ph.D. Thesis*, Wayne State University, 1966. We thank Professor Carl Johnson for bringing this work to our attention.

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

10. E. Block, A. Wall and J. Zubieta, *Abstracts Orgn. 47*, 187th ACS National Meeting, St. Louis, MO, April 8, 1984; E. Block, A. Wall and J. Zubieta, manuscript submitted.

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).

(Received in USA 4 December 1984)