Table II. Selected Key Bond Angles for 6c[a]

bond	angle, deg	bond	angle, deg
C2-I-C3	92.6 (4)	Si1-C1-C2	177 (1)
I-C2-C1	177 (1)	Si2-C4-C3	177 (1)
I-C3-C4	177 (1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

donium atom,[2,4] with two different arrangements for the alkynyl groups in **6**; axial and equatorial. From the fact that in most alkynyl(phenyl)iodonium salts, where the acetylenic group is known[4] to be in the axial position, the IR stretching of the C≡C is generally above 2150 cm^{-1}, we assign the higher C≡C frequencies in **6** to the axial alkyne unit and the lower one to the equatorial one. Hence, on the IR time scale the axial and equatorial alkynyl groups are differentiated. However, the ^{13}C NMR as well as ^1H NMR spectra of iodonium salts **6a-c** in $CDCl_3$ in the temperature range from 25 to -80 °C display only single resonances for each of the different carbons and protons due to degenerate isomerization, presumably by rapid pseudorotation around the iodine atom.[10]

The structure of the disubstituted iodonium triflate **6c** was unambiguously established by a single-crystal X-ray analysis.[11] Selected bond distances and bond angles are summarized in Tables I and II, and the ORTEP representation is shown in Figure 1. The structural data reveal two normal C-C triple bonds with the usual bond lengths and angles, with C_{sp}-I distances of 2.02 Å, typical for iodonium salts,[2,4] and a C-I-C angle close to 90°, as expected for iodonium salts with a pseudo-trigonal-bipyramidal geometry and consistent with the 10-I-3 nature in the Martin-Arduengo formalism.[12] The distance between the iodine atom and the nearest oxygen of the triflate anion is 2.7 Å, which supports the ionic nature of compound **6c**; the C2-I-O and C3-I-O angles are approximately 90° and 180°, respectively. Furthermore, the ORTEP diagram (Figure 1) clearly illustrates how the bulky triisopropylsilyl groups shield the triple bond thereby making it less susceptible to attack by external reagents and thus stabilizing the molecule. This principle for the stabilization of very reactive acetylenes with bulky substituents may be applied in the future to the synthesis of such unusual, hitherto unknown compounds as acetylenic derivatives of heavy noble gases, alkynyl triflate esters, diazonium salts, and other acetylenic derivatives with highly reactive leaving groups.

In conclusion, we have reported the first synthesis of novel dialkynyliodonium triflates **6**. Only those compounds with bulky substituents on the β-position of the acetylene are stable at room temperature. A single-crystal X-ray structure confirms the pseudo-trigonal-bipyramidal, or T-shaped, geometry of these species with *two* different alkynyl ligands, one axial and one equatorial, around the central iodine in the solid state. Likewise, two different C≡C absorptions are observed in the IR spectrum due to the different axial and equatorial alkynyl groups. However, the NMR spectra (both ^1H and ^{13}C) indicate rapid interconversion of the axial and equatorial alkynyl ligands even at -80 °C.

Acknowledgment. This work was supported by the NCI of NIH (2ROCA16903).

Supplementary Material Available: Tables of X-ray crystal and structural data for compound **6c** (9 pages); tables of observed and calculated structure factors for **6c** (12 pages). Ordering information is given on any current masthead page.

(10) Ochiai, M.; Takaoka, Y.; Masaki, Y.; Nagao, Y.; Shiro, M. *J. Am. Chem. Soc.* **1990**, *112*, 5677.

(11) Crystal data for **6c**: $C_{23}H_{42}F_3IO_3SSi_2$, triclinic, $P\bar{1}$, a = 12.230 (4) Å, b = 11.889 (3) Å, c = 13.126 (4) Å, α = 110.94 (2)°, β = 112.82 (2)°, γ = 74.89 (2)°, Z = 2, D_{calcd} = 1.304 g/cm^3; with 5991 reflections measured. The structure was solved with direct methods (MULTAN 82) and standard Fourier techniques. Final R factors: R = 0.0641 and R_w = 0.0702.

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Clear Evidence for the Formation of α-Disulfoxides and Other Intermediates in the *m*-CPBA Oxidation of Bridged Bicyclic Thiosulfinates

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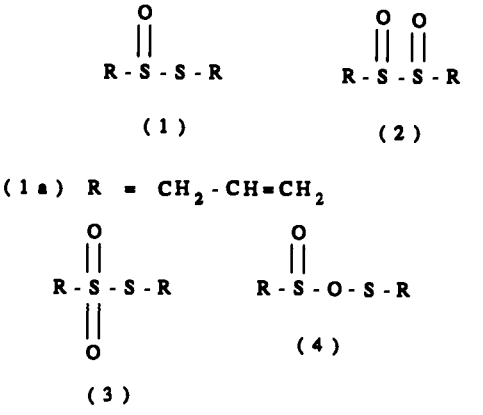
The oxidation of organic disulfides has provided an extremely rich chemistry dating as far back as 1846.[1] Thiosulfinates **1**, the initial oxidized product, are well-known.[2-4] The next step is the most controversial.[5,6] α-Disulfoxides **2** would be expected by HSAB theory;[7] however to date, only thiosulfonates **3** have been isolated.[8-11]



Freeman reported the first direct evidence for the existence of α-disulfoxides in a complex mix during the low-temperature (-20 °C) *m*-CPBA oxidation of symmetrical dialkyl thiosulfinates,[12] Freeman's results suggested that the α-disulfoxide **2** was formed and then rearranged to the thiosulfonate, possibly through an *O,S*-sulfenyl sulfinate intermediate **4**. Other experiments reported by Oae[13] and Kice[14] and ourselves[15] have provided further, indirect

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(5) (a) Freeman, F. *Chem. Rev.* **1984**, *64*, 117. (b) Hoyle, J. In *The Chemistry of Sulfinic Esters and Their Derivatives*; Patai, S., Ed.; John Wiley and Sons Ltd.: New York, 1990; Chapter 4.

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(12) (a) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1981**, *103*, 6232. (b) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1982**, *104*, 5766. (c) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1983**, *105*, 4093. (d) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1983**, *105*, 6232. (e) Freeman, F.; Lee, C. *J. Org. Chem.* **1988**, *53*, 1263.

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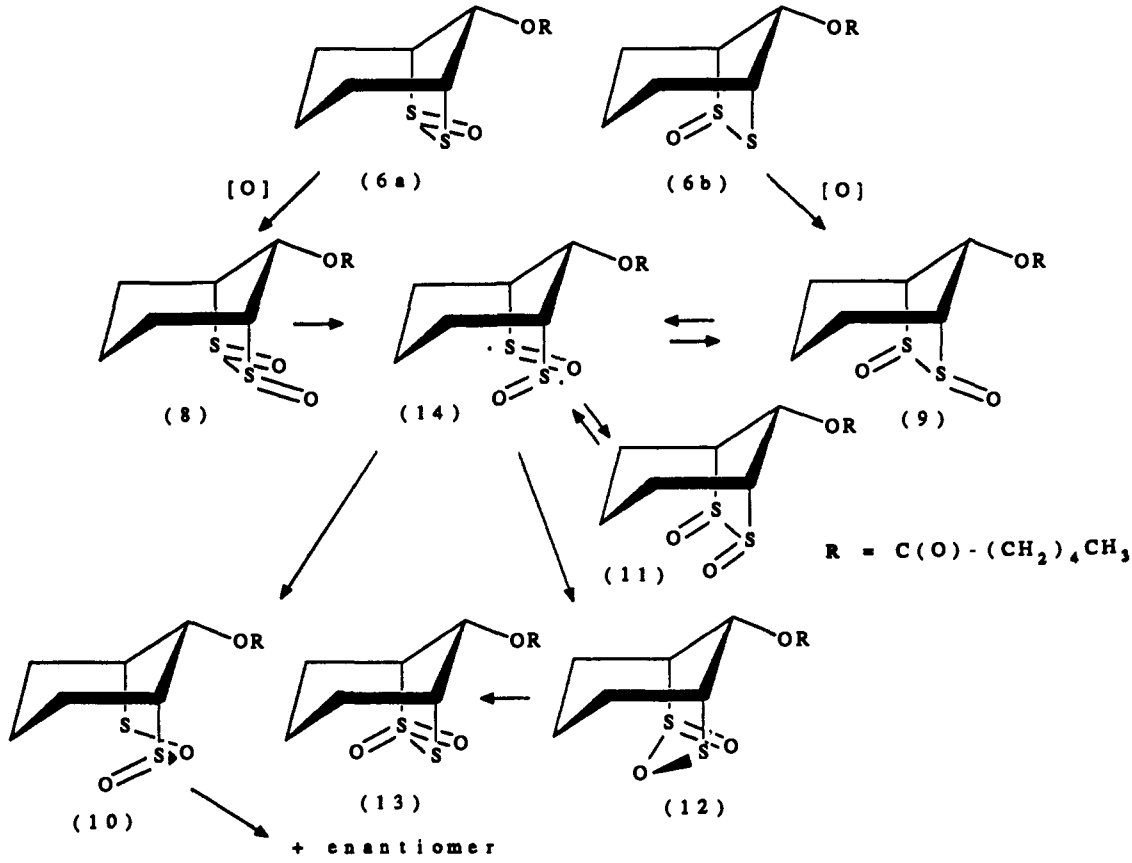
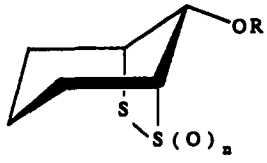
Scheme I



support for the existence of α-disulfoxides.

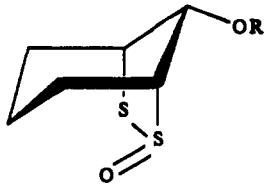
Here we report that the *m*-CPBA oxidation of bridged bicyclic thiosulfinates[16] **6a** and **6b**[17] at low temperatures provides clear evidence for the existence of α-disulfoxides and other key intermediates as well as a detailed picture of the steps involved in the oxidation.



(5) R = $C(O)C_6H_4NO_2$, n = 1

(6a) R = $C(O)(CH_2)_4CH_3$, n = 1

(7) R = H, n = 0



(6b) R = $C(O)(CH_2)_4CH_3$

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(15) Harpp, D. N.; Bodzay, S. J. *Sulfur Lett.* **1988**, *7*, 73. This appears to be the first direct evidence for *O,S*-sulfenyl sulfinates such as **4**.

(16) The crystal structure of **5** was recently reported: Folkins, P. L.; Harpp, D. N.; Vincent, B. R. *J. Org. Chem.* **1991**, *56*, 904.

(17) The synthesis of bridged bicyclic thiosulfinates **6a** and **6b** was performed by the esterification of disulfide alcohol **7**. Careful oxidation with 1 equiv of *m*-CPBA provided a mixture of the exo (**6a**) and endo (**6b**) diastereomers (7.4:1) in 90% overall yield; see the supplementary material for analytical data on **6a** and **6b**.

Table I. Percent Composition of Reaction Mixtures During Oxidation of **6a** and **6b**[a]

temp (°C)	6a (6b)	8	9	10	11	12	13
−30	71 (83)	16	8 (17)	1 (0)	1 (1)	0 (0)	3 (0)
−20	50 (65)	29	15 (31)	2 (0)	1 (4)	0 (0)	3 (0)
−10	32 (28)	41	18 (60)	4 (2)	1 (8)	0 (0)	4 (2)
0	9 (7)	47	22 (69)	13 (5)	2 (13)	3 (4)	4 (3)
+10	1 (1)	28	23 (61)	30 (12)	5 (14)	8 (10)	5 (4)
+25	0 (0)	1	6 (12)	48 (24)	13 (24)	26 (36)	6 (4)

[a] Based on integration of ^{1}H NMR spectra.

The *m*-CPBA oxidation of **6a** and **6b** was followed by ^{13}C and ^{1}H NMR spectroscopy at temperatures ranging from −30 to +25 °C using a similar procedure to Freeman's.[12c] The first intermediate formed in the oxidation of both **6a** and **6b** at −30 °C was *not* thiosulfonate **13**. In the oxidation of **6a**, it was a species (**8**) in which C1 and C4 are chemically equivalent suggesting a structure that is symmetric about the C8–C6 axis. The only reasonble explanation is that oxidation occurred on the sulfenyl sulfur atom of **6a** from the exo face to give symmetric α-disulfoxide **8** (Scheme I). The mutual dipolar repulsion of the adjacent sulfur–oxygen bond must not be strong enough to inhibit the attack of oxygen parallel to it; clearly the endo face must be highly hindered. The chemical shifts were consistent with such a structure.[18]

There were six different species formed during the oxidation of **6a** (Table I), including intermediate **8** and the expected product, **13**. The amount of each compound present at each temperature is based on the integration of the ^{1}H NMR signal for H8.[19] The concentration of **8** increased until 0 °C and was still present in small amounts at +10 °C. In the oxidation of **6b**, all intermediates

(18) NMR data for compounds detected during the oxidation of **6a** and **6b** are given in the supplementary material.

(19) The ^{13}C NMR spectra were completely consistent with the ^{1}H results. The α-disulfoxides were usually present at higher temperatures in the ^{1}H experiments due to the shorter acquisition time for these spectra. In time, the intermediates always rearranged to final product(s).

that were formed in the oxidation of **6a**, except **8**, were detected. The compositions of the reaction mixture at each temperature during the oxidation of **6b** are also given in Table I. The initial intermediate in this reaction (**9**) was an unsymmetrical species (C1 and C4 were not equivalent) and reached a peak concentration of 69% at 0 °C and subsequently continued to disappear.

The identity of **9** was determined from two observations; it was the first compound formed in the oxidation of **6b** and the second detected during the oxidation of **6a**. Also, α-disulfoxide **8** was not formed during the oxidation of **6b**. It is clear that oxidation of **6b** at the sulfenyl sulfur atom and from the expected direction (exo) would give an α-disulfoxide that is not symmetric about the C8–C6 axis, thus C1 and C4 should have different chemical shifts. The chemical shifts for **9**[17] indicated that it was nonsymmetric, thus it can be assigned as the unsymmetrical α-disulfoxide (Scheme I).

It is expected that the S–S bond of **6a** and **6b** would be relatively weak due to the strained bicyclic system and the expected repulsion between the two parallel sulfur–oxygen bonds. A concerted-type rearrangement of α-disulfoxide **8** is not likely as the sulfinyl oxygen is not able to reach an empty orbital on the adjacent sulfur atom due to the rigidity of the system. It is expected that homolysis of the S–S bond would occur to give two sulfinyl radicals **14**[20] that can recombine by several possible routes. One of these routes must involve a rotation about one C–S bond and head-to-head recombination to give the unsymmetrical α-disulfoxide **9**. *This was verified by the appearance of* **9** *as the second intermediate in the oxidation of* **6a**.[21]

The final product of the oxidation in both cases was thiosulfonate **13**.[22] The identities of the remaining intermediates, **10**, **11**, and **12**, are deduced by a careful analysis of the possible pathways that intermediates **8** and **9** may follow in order to produce thiosulfonate **13** (Scheme I). It is known from the NMR spectra that **10** and **12** were unsymmetrical species and **11** was symmetric; they were also stable enough to exist at room temperature and above but could not be isolated. Intermediates **10** and **12** are therefore best assigned as the two possible *O,S*-sulfenyl sulfinates and can easily be pictured to form from a head-to-tail recombination of the two sulfinyl radicals,[23] Species **11** logically is assigned as a sulfinic anhydride; however, the disappearance of this species without evidence for a decomposition product argues that **11** is likely the symmetric endo α-disulfoxide (Scheme I). The formation of final product **13** can clearly be pictured to proceed via rearrangement of *O,S*-sulfenyl sulfinates **10** and **12**,[5,13-15]

The electrophilic oxidation of bridged bicyclic thiosulfinates has thus provided the most stable α-disulfoxides to date. In addition, these results give a thorough picture of this important oxidative process.

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Supplementary Material Available: Analytical and NMR data for compounds **6a**, **6b**, and **15** as well as ^{13}C and ^{1}H NMR spectra from low-temperature experiments (5 pages). Ordering information is given on any current masthead page.

(20) Sulfinyl radicals were proposed as intermediates in the disproportionation of aryl arenethiosulfinates (Koch, P.; Ciuffarin, E.; Fava, A. *J. Am. Chem. Soc*, **1970**, *92*, 5971) and in the rearrangement of α-disulfoxides to thiosulfonates in the oxidation of diaryl thiosulfinates (ref 5a and references therein).

(21) α-Disulfoxide **9** could also be formed by a direct attack of the oxidizing agent on the endo side of the sulfur–sulfur bond of **6a**; however, approach from this face has been shown to be unfavorable (ref 16); thus, this mechanism should not account for the formation of a significant amount of **9** from **6a**.

(22) The structure was confirmed by esterification of the unsubstituted bridged bicyclic thiosulfonate (**13**; R = H) and a comparison of the NMR data with that of **13** (R = $C(O)(CH_2)_4CH_3$); see supplementary material for analytical data on **13** (R = H).

(23) A concerted rearrangement of **9** (Scheme I) could also lead to compounds **10** and **12**.

A 32-Membered Fluorinated Multifunctional Heterocycle

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The synthesis and characterization of fluorinated heterocycles have been subjects of intense study in this laboratory[1-3] and others.[4-7] Many of these materials are small rings (seven members or less) containing nitrogen, oxygen, and/or sulfur and are used in applications such as blood substitutes,[7] inert fluids,[1] and antistatic coatings.[8] Small heterocycles containing one or two fluorine atoms or a trifluoromethyl group are common biologically active materials.[4,9,10] In addition, a variety of metalloheterocycles have been synthesized and studied extensively for their potential use in the preparation of conducting polymers.[11-13]

Most recently, a great deal of interest in the synthesis of macroheterocycles (rings containing more than seven members) has been kindled. While the use of crown ethers for metal ion extraction is well-known, current synthetic efforts are directed toward heterocycles which are metal ion specific, e.g., a 16-membered heterocycle containing oxygen and sulfur which is specific for Ag^+,[14] a 15-membered macrocyclic ether containing amide and amine functional groups which reportedly shows selectivity as a chelating agent for Pb^{2+},[15] and a 16-membered heterocycle containing four nitrogen heteroatoms which is specific for nickel.[16] Larger multifunctional heterocycles containing as many as 36 atoms are being designed for selective molecular recognition. These macrocycles demonstrate the ability, for example, to act as biological mimics of ionophore antibiotics,[17] as synthetic analogues of enzyme receptors,[18] and as selective complexing agents for organic picrates.[19] A series of excellent reviews are available covering the synthesis and chemistry of fluorinated and nonfluorinated heterocycles, three of which are referenced here.[20-22]

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