a light yellow foam. Purification by gradient elution chromatography on silica gel using ethyl acetate/hexane as eluants gave the pure compounds. The physical constants and spectroscopic data of compounds (12a–d) are summarized in Table III.

Methyl 6β-(Phenylacetamido)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2α-carboxylate 1α-S-Oxide (7a). Zn (2.0 g) was added to a solution of **12a** (1.0 g) in THF (15 mL), followed by 1 M aqueous ammonium acetate (5 mL) under stirring at room temperature. After 2 h stirring at this temperature, the reaction mixture was filtered through Celite, and the filtrate was washed with water, diluted HCl, and brine solution successively.

The organic phase was dried over Na_2SO_4 and concentrated, and the residue was chromatographed over silica gel by using ethyl acetate/dichlomethane (35:65) as eluant. The title compound was obtained as a white foam. Similarly, compounds **7c** and **7d** were prepared. The data for compounds (**7a**, **7c**, and **7d**) are summarized in Table III.

Stereoselective Synthesis, Structural Studies, and Hydrolysis of Tricyclic Alkoxysulfonium Salts

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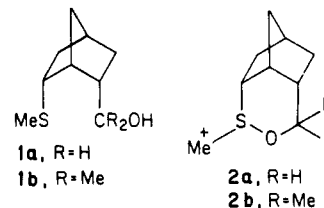
The crystal and molecular structure of endo tertiary alcohol **1b** determined by X-ray crystallographic techniques is reported. The molecule crystallizes in the space group $P2_1/n$ with a = 14.628 (7) Å, b = 5.648 (1) Å, c = 14.973 (8) Å, β = 113.78 (4)°, Z = 4. This structure features an unsymmetrical contra twist of the norbornyl skeleton and an intramolecular hydrogen bond between the sulfur atom and hydroxyl group with a very short distance of 3.119 Å. IR spectroscopic studies provide evidence for this intramolecular hydrogen bond in dilute solutions of endo tertiary alcohol **1b** but not in endo primary alcohol **1a**. Treatment of endo primary alcohol **1a** and endo tertiary alcohol **1b** with *tert*-butyl hypochlorite followed by mercury(II) chloride provides the corresponding alkoxysulfonium salts **2a** and **2b**, respectively. The crystal and molecular structures of these salts were determined by single-crystal X-ray studies. These salts crystallize in the space groups $P2_1/c$ and $P\bar{1}$, respectively, with a = 10.152 (3) Å, b = 11.857 (4) Å, c = 12.087 (3) Å, β = 97.98 (2)°, Z = 4, and a = 8.416 (3) Å, b = 9.678 (3) Å, c = 10.688 (4) Å, β = 87.72 (3)°, Z = 2, respectively. Both structures feature short S–O bond lengths of 1.58 (1) Å and 1.587 (4) Å, respectively, and large S–O–C (8) bond angles of 121.2 (9)° and 124.0 (3)°, respectively. Base hydrolysis of these salts produces the corresponding sulfoxides **11a** and **11b** by nucleophilic attack by hydroxide ion on sulfur.

Introduction

Alkoxysulfonium salts, $(RR^1SOR^2)^+ X^-$, are intermediates in several important reactions. Oxidation of alcohols,[1] halides, and p-toluenesulfonates[2] to aldehydes and ketones with dimethyl sulfoxide and related reactions[3] proceed via alkoxysulfonium salts. Neighboring-group participation by sulfoxide groups in the solvolysis of halides and sulfonates[4] and protonation of medium-sized ring keto sulfoxides[5] results in the formation of alkoxysulfonium salts.

Our[6] and others'[7] studies on the oxidation of sulfides with suitably disposed alcohol moieties reveal the generation of alkoxysulfonium salts. Such neighboring-group participation has important consequences such as the unusually low potential for oxidation of endo primary alcohol **1a**.[8] In addition, pulse radiolysis studies[9] on endo tertiary

1a, R=H
1b, R=Me

2a, R=H
2b, R=Me

alcohol **1b** show stabilization of the corresponding one-electron oxidation products which is ascribed to neighboring-group participation by the alcohol moiety.

Despite the importance of alkoxysulfonium salts only one detailed structure study had been communicated[10] prior to our initial report.[6] This paper presents the full details on the preparation and X-ray crystal structure study of alkoxysulfonium salt **2a** and similar studies on

(1) Moffat, J. G. In "Oxidation"; Augustine, R. L., Trecker, D. J., Eds; Dekker: New York, 1971; pp 1–64. Albright, J. D. *J. Org. Chem.* **1974**, *39*, 1977.

(2) Kornblum, N.; Jones, W. J.; Anderson, G. J. *J. Am. Chem. Soc.* **1959**, *81*, 4113. Ganem, B.; Boeckman, R. K., Jr., *Tetrahedron Lett.* **1974**, 917.

(3) Corey, E. J.; Kim, C. U. *J. Am. Chem. Soc.* **1972**, *94*, 7586. Corey, E. J.; Kim, C. U; Takeda, M. *Tetrahedron Lett.* **1972**, 4339. Corey, E. J.; Kim, C. U. *Ibid.* **1973**, 919. Corey, E. J.; Kim, C. U. *Ibid.* **1974**, 287. McCormick, J. P. *Ibid.* **1974**, 1701. Barton, D. H. R.; Forbes, C. P. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1614.

(4) Hogeveen, H.; Maccagnani, G.; Montanari, F. *Boll. Sci. Fac. Chim. Ind. Bologna* **1963**, *21*, 257; *Chem. Abstr.* **1964**, *60*, 10511e. Ghersetti, S.; Hogeveen, H.; Maccagnani, G.; Montanari, F.; Taddel, F. *J. Chem. Soc.*, **1963**, 3718. Montanari, F.; Daniel, R.; Hogeveen, H.; Maccagnani, G. *Tetrahedron Lett.* **1964**, 2685. Jones, D. N.; Saeed, M. A. *Proc. Chem. Soc. (London)* **1964**, 81. Martin, J. C.; Uebel, J. J. *J. Am. Chem. Soc.* **1964**, *86*, 2939. Buck, K. W.; Foster, A. B.; Perry, A. R.; Webber, J. M. *J. Chem. Soc., Chem. Commun.* **1965**, 433. Cinquini, M.; Colonna, S.; Montanari, F. *Tetrahedron Lett.* **1966**, 3181. Hogeveen, H.; Maccagnani, G.; Montanari, F. *J. Chem. Soc. C* **1966**, 1585. Cinquini, M.; Colonna, S.; Montanari, F. *Ibid.* **1967**, 1213. Foster, A. B.; Hasan, Q. H.; Hawkins, D. R.; Webber, J. M. *J. Chem. Soc., Chem. Commun.* **1968**, 1084. Jones, D. N.; Green, M. J.: Saeed, M. A.; Whitehouse, R. D. *J. Chem. Soc. C* **1968**, 1362.

(5) Leonard, N. J.; Johnson, C. R. *J. Am. Chem. Soc.* **1962**, *84*, 3701. Leonard, N. J.; Rippie, W. L. *J. Org. Chem.* **1963**, *28*, 1957.

(6) Glass, R. S.; Setzer, W. N.; Prabhu, U. D. G.; Wilson, G. S. *Tetrahedron Lett.* **1982**, *23*, 2335.

(7) Kline, J.; Stollar, H. *Tetrahedron* **1974**, *30*, 2541. Hirschon, A. S.; Doi, J. T.; Musker, W. K. *J. Am. Chem. Soc.* **1982**, *104*, 725.

(8) Glass, R. S.; Duchek, J. R.; Klug, J. T.; Wilson G. S. *J. Am. Chem. Soc.* **1977**, *99*, 7349.

(9) Glass, R. S.; Hojjatie, M.; Wilson, G. S.; Mahling, S.; Göbl, M.; Asmus, K.-D. *J. Am. Chem. Soc.* **1984**, *106*, 5382.

(10) Hirschon, A. S.; Beller, J. D.; Olmstead, M. M.; Doi, J. T.; Musker, W. K. *Tetrahedron Lett.* **1981**, *22*, 1195.
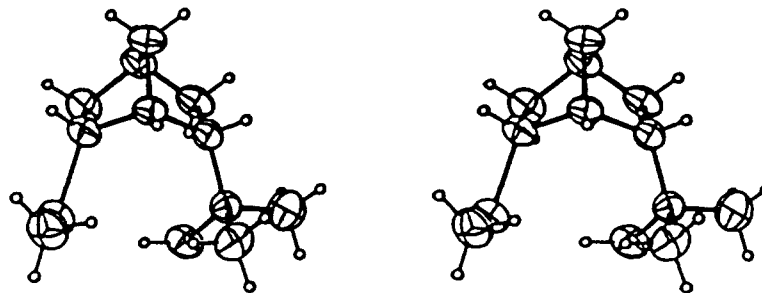
Figure 1. ORTEP[12] stereoview of endo tertiary alcohol **1b**. The hydrogen atoms have been assigned arbitrary thermal parameters. Thermal ellipsoids are drawn to enclose 50% of the probability distribution.

alkoxysulfonium salt **2b**. The preparation and X-ray crystal structure study of endo tertiary alcohol **1b** are also presented. In addition, the diastereoselective oxidations of endo primary alcohol **1a** and endo tertiary alcohol **1b** with *tert*-butyl hypochlorite and the stereospecific hydrolyses of alkoxysulfonium salts **2a** and **2b** are described in detail.

Results and Discussion

Treatment of the known endo ester **3**[11] with methylmagnesium iodide in diethyl ether provided endo tertiary alcohol **1b** in quantitative yield. The epimeric exo tertiary

MeS CO₂Me MeS

3   **4a**, X=C(Me)₂OH
      4b, X=CO₂Me
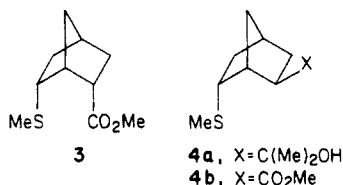
alcohol **4a** was similarly prepared from exo ester **4b**[11] and methyllithium in quantitative yield. The crystal and molecular structure of endo tertiary alcohol **1b** was determined by single-crystal X-ray crystallographic analysis. The crystal data are compiled in Table I, and an ORTEP stereoview[12] of the molecule is shown in Figure 1.

This structural study reveals several interesting features. The norbonyl ring skeleton in endo tertiary alcohol **1b** is significantly distorted from the C_{2v} symmetry of the parent hydrocarbon. There is an unsymmetrical contra twist, $C(+-)$,[13] of the norbornyl skeleton. That is, viewing down the C(1)–C(4) vector, C(3) is located clockwise (+) from C(2) and C(5) is located counterclockwise (–) from C(6). This twisting can also be seen from the C(1)–C(2)–C(3)–C(4) and C(4)–C(5)–C(6)–C(1) torsional angles of +2.6 and –12.7°, respectively. Relief of steric strain in also achieved by substantial opening of the C(2)–C(1)–C(6) bond angle to 117.6 (2)°.[14] In addition, the bonds directed in the endo direction from C(2) and C(6) are not coplanar. Similar distortions of the norbornyl ring were found for 6-*endo*-(methylthio)bicyclo[2.2.1]heptane-2-*endo*-carboxylic acid.[11]

(11) Glass, R. S.; Duchek, J. R.; Prabhu, U. D. G.; Setzer, W. N.; Wilson, G. S. *J. Org. Chem.* **1980**, *45*, 3640.

(12) Johnson, C. K. "ORTEP"; Oak Ridge National Laboratory: Oak Ridge, TN.

(13) Altona, C.; Sundaralingam, M. *J. Am. Chem. Soc.* **1970**, *92*, 1995.

(14) In contrast the C(3)–C(4)–C(5) bond angle is 108.6 (2)°. The C(2)–C(1)–C(6) bond angle for norbornane itself, which is the same as the C(3)–C(4)–C(5) bond angle by symmetry, is 103.5 (15) or 108.6 (18)° as determined by gas-phase electron diffraction methods according to Chiang et al. [Chiang, J. F.; Wilcox, C. F., Jr.; Bauer, S. H. *J. Am. Chem. Soc.* **1968**, *90*, 3149] and Yokozeki et al. [Yokozeki, A.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2356], respectively. Since the propable errors in these data for norbornane are quite large, the values for *exo*-N-(2-norbornyl)benzamide accurately determined by X-ray techniques should be noted. These are 106.6 (3) and 108.8 (4)° for the C(2)–C(1)–C(6) and C(3)–C(4)–C(5) bond angles, respectively, as reported by: Newton, M. G.; Pantaleo, N. S.; Kirbawy, S.; Allinger, N. L. *J. Am. Chem. Soc.* **1978**, *100*, 2176.

Table I. Crystal Data[a] **for Endo Tertiary Alcohol 1b, Alkoxysulfonium Salt 2a, and Alkoxysulfonium Salt 2b**

data	1b	2a	2b
mol formula	$C_{11}H_{20}OS$	$C_9H_{15}OSHgCl_3$	$C_{11}H_{17}OS$-$HgCl_3$
mol wt	200.336	478.22	506.285
space group	$P2_1/n$[b]	$P2_1/c$ (no. 14)[d]	$P1$
a, Å	14.628 (7)	10.152 (3)	8.416 (3)
b, Å	5.648 (1)	11.857 (4)	9.678 (3)
c, Å	14.973 (8)	12.087 (3)	10.688 (4)
β, deg	113.78 (4)	97.98 (2)	87.72 (3)
Z	4	4	2
d_{obsd}, g cm⁻³	0.210[c]	2.213[e]	2.213[f]
d_{calcd}, g cm⁻³	1.175	2.204	2.187
cryst color, shape	colorless, rectangular plates	colorless, plate	colorless, prismatic plates
cryst dimen, mm	0.3 × 0.3 × 0.5	0.3 × 0.3 × 0.1	0.17 × 0.17 × 0.17
no. of unique data	1993	2683	2722
no. of data used in the calculations	1105	1954	2139
abs coef ($\mu\lambda$), cm⁻¹	2.38	115.5	106.5

[a] The standard deviation of the least significant figure is given in parenthesis. [b] The space group was unambigously determined from systematic absences: $0k0$, $k = 2n + 1$; $h0l$, $n + l = 2n + 1$. [c] The density was determined using a solution of hexane and carbon tetrachloride. [d] The space group was unambiguously determined by the systematic absences: $h0l$, $l \neq 2n$; $0k0$; $k \neq 2n$. [e] The density was determined by the flotation method using a solution of bromoform and carbon tetrachloride. [f] The density was determined by the flotation method using a solution of dichloromethane and hexane.

The conformation about the C(2)–C(8) bond is of particular concern owing to our interest in interactions between the sulfur and oxygen atoms. The conformation found about this bond in the solid state is that expected on the basis of steric effects. The sterically less bulky hydroxyl group is gauche to C(1) and C(3) and directed toward the sulfur atom. Whereas, the methyl groups appended to C(8) are directed away from the sulfur atom and gauche to H(2) and C(1) or C(3). This conformation of endo tertiary alcohol **1b** results in a hydrogen bond between the hydroxyl group and the sulfur atom.[15] The structural evidence for this hydrogen bond is the very short S⋯O distance of 3.119 Å[16] whereas the sum of the van der Waals radii for a sulfur and oxygen atom is 3.25 Å.[17] Furthermore, the C(8)–O–S angle is 100.4°. Steric effects

(15) (a) Srinivasan, R.; Chacko, K. K. In "Conformations of Biopolymers"; Ramachandran, G. N., Ed.; Academic: New York, 1967; Vol. 2, pp 607–615. (b) Aaron, H. S. In "Topics in Stereochemistry", Allinger, N. L., Eliel, E. L. Ed., Interscience: New York; Vol. 11, pp 31–33.

(16) The previously reported S⋯O distances for O–H⋯S hydrogen bonds are 3.21–3.37 Å[15a], 3.180 (7), and 3.199 (6) Å (Kerr, K. A.; VanRoey, P. M. A. O. *Acta Crystallogr.* **1979**, *B35*, 2727 and 3.155 (4) and 3.192 (4) Å (Sarkar, P. B.; Sen Gupta, S. P. *Cryst. Struct. Commun.* **1980**, *9*, 925).

(17) Pauling, L. "The Nature of the Chemical Bond", 3rd ed; Cornell University Press: Ithaca, NY, 1960; p 260.

are believed to be predominantly responsible for the conformation about the C(2)–C(8) bond. In contrast to endo tertiary alcohol **1b**, steric effects in endo primary alcohol **1a** would result in the hydroxyl group at C(8) being directed away from the sulfur atom. Experimental evidence for the conformation about the C(2)–C(8) bond in endo primary alcohol **1a** in solution,[18] as well as for endo tertiary alcohol **1b** in solution, was secured by IR spectroscopic studies. A 10^{-2} M solution of endo primary alcohol **1a** in carbon tetrachloride showed absorption at 3636 cm^{-1} due to the free OH stretching vibration and at 3497 cm^{-1} due to the intermolecularly hydrogen bonded OH stretching vibration. A 10^{-3} M solution of this alcohol showed significant absorption only at 3637 cm^{-1}. Solutions of endo tertiary alcohol **1b** in carbon tetrachloride from 10^{-2} M to 10^{-4} M showed absorption due to intramolecularly hydrogen bonded OH stretching vibration at 3418 cm^{-1}. No free OH stretching vibration could be detected.

Treatment of endo primary alcohol **1a** with an excess of *tert*-butyl hypochlorite followed by 1 equiv of mercury(II) chloride[19] gave alkoxysulfonium salt **2a**.[6] Only one diastereomer of this salt was obtained as shown by ^{1}H NMR spectroscopic analysis. The structure of this salt was unequivocally established by a single-crystal X-ray crystallographic structure study. The crystal data are listed in Table I and ORTEP stereoview[12] of the cation has been published previously.[6] This study revealed that the relative configuration is that depicted in structure **6a**. The

6a, R = H
6b, R = Me
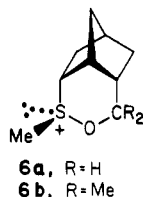
carbon–carbon and carbon–sulfur bond lengths are within the expected values. The sulfur–oxygen bond length of 1.58 (1) Å is longer than the 1.49 ± 0.2 Å found for that in sulfoxides[20] but shorter than 1.70 Å which is the sum of the covalent radii of sulfur and oxygen.[21,22] In addition, the S–O–C (8) bond angle of 121.2 (9)° is surprisingly large. These results are consistent with an sp^2 hybridized oxygen atom and p–d π bonding between S and O resulting in bond shortening.[23] However, there is considerable controversy on the role of p–d π bonding in S$^+$–X bonds in which X has an unshared pair of electrons. Oae[24] and Oae
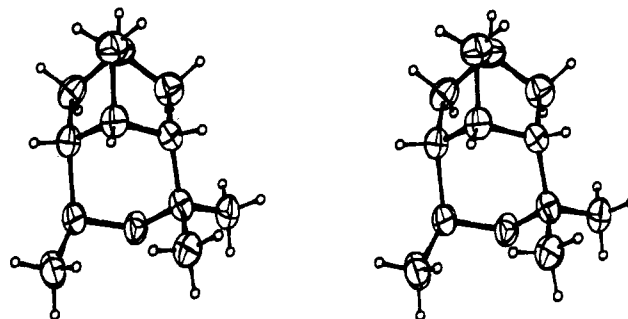

Figure 2. ORTEP[12] stereoview of alkoxysulfonium salt **2b**. The hydrogen atoms have been assigned arbitrary thermal parameters. Thermal ellipsoids are drawn to enclose 50% of the probability distribution.

and Furukawa[25] have reviewed the evidence concerning the nature of the S–O and S–N bonds in sulfoxides and sulfilimines respectively. They suggest that these bonds are best considered to be coordinate covalent, that is, S$^+$–X$^-$. The S–N bond length observed for the azasulfonium moiety: S$^+$–N in dehydromethionine is significantly shorter than the sum of the covalent radii of S and N.[26] Nevertheless, the nitrogen atom is sp^3-hybridized[27] thereby precluding p–d π bonding as the cause of S–N bond shortening. Also theoretical calculations have been used to investigate whether the stabilization of the negative charge on the carbon atom in sulfonium ylides, C$^-$–S$^+$, by the sulfur atom is due to polarization or p–d π conjugation.[28]

The C–S–O bond angles in **6a** are comparable to these found in sulfoxides (ca. 105°) but the C–S–C bond angle in salt **6a** of 104.4 (7)° is larger than those for either dialkyl sulfides or sulfoxides (ca. 99°). All other bond angles are in the expected ranges. The norbornyl ring in salt **6a** is relatively undistorted as illustrated by the C(1)–C(2)–C(3)–C(4) and C(4)–C(5)–C(6)–C(1) torsion angles of 3 and 0°, respectively. The six-membered ring comprised of S, O, C(8), C(2), C(1), and C(6) is in a distorted chair conformation with the following torsion angles: S–O–C(8)–C(2) –55, O–C(8)–C(2)–C(1) –57, C(8)–C(2)–C(1)–C(6) 61, C(2)–C(1)–C(6)–S 54, C(1)–C(6)–S–O 48, C(6)–S–O–C(8) –52. The trichloromercurate anion of salt **6a** adopts a discrete, chlorine-bridged dimeric structure with the mercury atoms adopting distorted tetrahedral geometries.[29]

Treatment of endo primary alcohol **1b** sequentially with excess *tert*-butyl hypochlorite and 1 equiv of mercury(II) chloride[19] gave a 4:1 mixture of diastereomeric alkoxysulfonium salts **2b**. The major product was isolated pure

(18) Carlson, K. D.; Weisleder, D.; Daxenbichler, M. E. *J. Am. Chem. Soc.* **1970**, *92*, 6232. Reference 14b, pp 1–51. Kingsbury, C. A.; Day, V. W.; Day, R. O. *J. Org. Chem.* **1980**, *45*, 5255.

(19) Johnson, C. R.; Jones, M. P. *J. Org. Chem.* **1967**, *32*, 2014.

(20) Laur, P. H. In "Sulfur in Organic and Inorganic Chemistry", Senning, A., Ed. Dekker: New York, 1972; Vol. 3.

(21) Reference 17, p 224.

(22) A shortened S–O bond length and C–O–S bond angle of 110 (1)° were also reported for the only other alkoxysulfonium salt whose crystal structure has been determined.[10] However, the authors expressed some doubt concerning the determination of these parameters. See ref 10, footnote 16.

(23) Recently the molecular structure of [(Me$_2$N)$_3$POP(NMe$_2$)$_3$]$^{2+}$ (CF$_3$SO$_3^-$)$_2$ determined by X-ray crystallographic methods was reported: Aaberg, A.; Gramstad, T.; Husebye, S. *Acta Chem. Scand. A* **1980**, *34*, 717. The P–O–P moiety was linear with shortened P–O bonds. These structural results were interpreted as indicating sp hybridization for the oxygen atom and p–d π-bonding between the two filled p orbitals on the oxygen atom and an empty d orbital on each of the phosphorus atoms. However, the probable importance of steric effects between the substituents on different phosphorus atoms in favoring a linear P–O–P arrangement was also recognized. For theoretical studies on the related dication ethers and the hydroxycyclopropenium cation, see: Apeloig, Y.; Arad, D. *J. Am. Chem. Soc.* **1981**, *103*, 4258.

(24) Oae, S. In "Organic Chemistry of Sulfur", Oae, S. Ed.; Plenum: New York, 1977; pp 393–394.

(25) Oae, S.; Furukawa, N. "Sulfilimines and Related Derivatives", American Chemical Society: Washington, D.C., 1983; pp 51–56.

(26) Glass, R. S.; Duchek, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 965. See also: Hirschon, A. S.; Olmstead, M. M.; Doi, J. T.; Musker, W. K. *Tetrahedron Lett.* **1982**, *23*, 317.

(27) In comparing the geometries of the S-X moiety in dehydromethionine and alkoxysulfonium salt **2a**, it should be noted that in dehydromethionine this moiety is incorporated into a five-membered ring whereas that in alkoxysulfonium salt **2a** is in a six-membered ring. There may be considerably more angle strain in the five-membered ring than the six-membered ring on changing the hybridization of X from sp^3 to sp^2.

(28) Streitwieser, A., Jr.; Williams, J. E., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 191. Bernardi, F.; Csizmadia, I. G.; Mangini, A.; Schlegel, M. B.; Whangbo, M.-H.; Wolfe, S. *Ibid.* **1975**, *97*, 2209. Kral, V.; Arnold, Z.; Havlas, Z. *Collect. Czech. Chem. Commun.* **1981**, *46*, 883. Mitchell, D. J.; Wolfe, S.; Schlegel, H. B. *Can. J. Chem.* **1981**, *59*, 3280. Wolfe, S.; Stolow, A.; LaJohn, L. A. *Tetrahedron Lett.* **1983**, *24*, 4071. Schleyer, P. V. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467.

(29) Such tetrahedral geometries for mercuric chloride complexes have been observed before: Cheung, K. K.; Sim, G. A. *J. Chem. Soc.* **1965**, 5988. Glasser, L. S. D.; Ingram, L.; King, M. G.; McQuillan, G. P. *J. Chem. Soc. A* **1969**, 2501.

by fractional recrystallization. Single-crystal X-ray analysis provided its detailed crystal and molecular structure. The crystal data are listed in Table I and an ORTEP stereoview[12] of the salt is presented in Figure 2. As can be seen from the stereoview, the relative configuration of the cation is that depicted in structure **6b**. The structure of alkoxysulfonium salts **6b** is similar to that already discussed for alkoxysulfonium salt **6a**.[30] Of particular interest is the S–O bond length of 1.587 (4) Å and S–O–C (8) bond angle of 124.0 (3)° in alkoxysulfonium salt **6b**. In addition, the C(1)–C(2)–C(3)–C(4) and C(4)–C(5)–C(6)–C(1) torsion angles of the norbornyl ring of 4.6 and –1.1°, respectively, and the distorted chair conformation of the S, O, C(8), C(2), C(1), and C(6) ring with the following torsion angles: S–O–C(8)–C(2) –47.7, C(1)–C(2)–C(8)–0 57.6, C(6)–C-(1)–C(2)–C(8) –63.1, S–C(6)–C(1)–C(2) 50.9, O–S–C(6)–C-(1) –38.1, C(6)–S–O–C(8) 37.7. The trichloromercurate ion of salt **6b** is also a discrete, chlorine bridged dimeric structure with distorted tetrahedral geometries about the mercury atoms.

The high stereoselectivity of the formation of alkoxysulfonium salt **2a** and lesser, but nonetheless, stereoselective formation of alkoxysulfonium salt **2b** are worthy of note. Owing to the considerable current interest in asymmetric induction in the oxidation of sulfides, the basis for the stereoselectivity in the formation of alkoxysulfonium salts **2a** and **2b** is discussed in detail in another paper.

Base hydrolysis of pure alkoxysulonium salts **2a** and **2b** gave the corresponding sulfoxides **11a** and **11b**, respec-

11a, R=H
11b, R=Me

12a, R=H
12b, R=Me
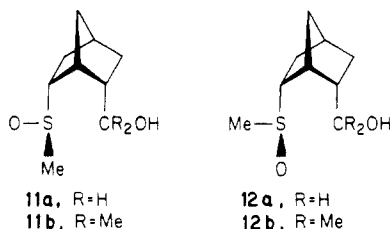
tively. Only one diastereomeric sulfoxide was formed in each case as determined by ^{1}H NMR spectroscopic analysis. Sulfoxides **11a** and **11b** were isolated in pure form in 68 and 87% yield, respectively. Hydrolysis of the mixture of alkoxysulfonium salts obtained by treatment of endo tertiary alcohol **1b** sequentially with *tert*-butyl hypochlorite and mercury(II) chloride gave a mixture of diastereomeric sulfoxides **11b** and **12b**. ^{1}H NMR spectroscopic analysis of this mixture revealed **11b** and **12b** in a 4:1 ratio. This mixture was separated by HPLC to afford each diastereomeric sulfoxide pure. The ratio by weight of isolated **11b** to **12b** was 3.5:1 with 90% of the crude mixture accounted for. The mechanism for these hydrolyses is believed to be that suggested previously for base hydrolyses of most other alkoxysulfonium salts,[31,32] that is, nucleophilic attack by hydroxide ion on the sulfonium sulfur atom with inversion of configuration at sulfur. The evidence is stereochemical studies in one case and [18]O labeling results in the other.

Single-crystal X-ray structural studies unequivocally showed that the major diastereomer produced by oxidation of endo primary alcohol **1a** with *m*-chloroperoxybenzoic acid has the relative configuration shown in structure **12a**.[6] Since this compound is the diastereomer of the sulfoxide produced by hydrolysis of alkoxysulfonium salt **2a**, the relative configuration of the latter must be as shown in structure **11a**. Comparison of the stereochemistry at the sulfur atom of alkoxysulfonium salt **2a** with its hydrolysis product **11a** reveals that the hydrolysis occurred with inversion of configuration at sulfur. Hydrolysis of pure alkoxysulfonium salt **2b** with ^{18}O-labeled aqueous base resulted in [18]O incorporation into the oxygen of the sulfoxide not the alcohol moiety of sulfoxide **11b**. Thus, nucleophilic attack by labeled hydroxide ion occurred at sulfur rather than at carbon. This result is interesting because this is the first time that the mechanism for hydrolysis of a *tert*-alkoxysulfonium salt in aqueous base has been determined.[33] This result is of particular interest when compared with the mechanism for the oxidation of sulfides to sulfoxides with *tert*-butyl hypochlorite in *tert*-butyl alcohol.[31a,34,35] In this oxidation (*tert*-butyloxy)sulfonium salts form and decompose to the corresponding sulfoxide and *tert*-butyl cation.[36] In aqueous base, alkoxysulfonium salt **2b** hydrolyzed solely, as far as experimentally discernible, by hydroxide attack at sulfur not by an S_N1 mechanism.[37]

Experimental Section

(30) The differences are mainly the torsion angles about the S–C(6), S–O, and O–C(8) bonds and small differences (but exceeding 3σ) in the bond angles around S, C(6) and the C(8)–C(2)–C(3) and C(4)–C(5)–C(6) bond angles.

(31) (a) Marino, J. P. In "Topics in Sulfur Chemistry", Senning A., Ed.; Thieme: Stuttgart, 1976; Vol 1, pp 73–74. (b) Oae, S.; Numata, T.; Yoshimura, T. In "The Chemistry of the Sulphonium Group"; Stirling, C. J. M., Ed.; Wiley: Chichester, 1981; Part 2, pp 599–601.

(32) Base hydrolysis of methoxysulfonium salts sterically hindered at sulfur was reported to occur by S_N2 attack by hydroxide ion on the methyl carbon atom: Kishi, M.; Komeno, T. *Int. J. Sulfur Chem. A*, **1972**, 2, 1.

(33) Inversion of configuration at sulfur was assumed in the hydrolysis of a tertiary (benzyloxy)sulfonium salt: Balthazor, T. M.; Martin, J. C. *J. Am. Chem. Soc.* **1975**, 97, 5634. Martin, J. C.; Balthazor, T. M. *Ibid.* **1977**, 99, 152.

(34) Johnson, C. R.; Rigau, J. J. *J. Am. Chem. Soc.* **1969**, 91, 5398.

(35) Walling, C.; Mintz, M. J. *J. Org. Chem.* **1967**, 32, 1286. Skattebol, L.; Boulette, B.; Solomon, S. *Ibid.* **1967**, 32, 3111.

(36) The mechanism for oxidation of sulfides by *tert*-butyl hypochlorite in methanol may be different. Addition of *tert*-butyl hypochlorite to thiane in dichloromethane containing ethanol followed by the addition of mercury(II) chloride resulted in the formation of the ethoxy- not *tert*-butoxysulfonium salt.[34] Furthermore, S_N2 displacement by chloride ion on the α-carbon atom of the methoxy group in ethoxysulfonium salts is well-known: Annunziata, R.; Cinquini, M.; Colonna, S. *J. Chem. Soc., Perkin Trans. 1* **1975**, 404. Thus, treatment of sulfides in with *tert*-butyl hypochlorite in methanol may proceed via formation of the corresponding methoxysulfonium chloride followed by S_N2 displacement to produce the corresponding sulfoxide. Indeed treatment of a hindered sulfide with *tert*-butyl hypochloride in a mixture of ^{18}O-labeled methanol and tetrahydrofuran resulted in the formation of ^{18}O-labeled sulfoxide.[32]

(37) The conditions of these reactions differ substantially. In addition, ionization of *tert*-butyloxysulfonium salts to produce two independent species is entropically more advantageous than ionization of alkoxysulfonium salt **2b**.

Preparation of Endo Tertiary Alcohol 1b. A solution of methylmagnesium iodide in ethyl ether was prepared by adding iodomethane (1.35 mL, 21 mmol) to magnesium turnings (0.50 g, 20 mmol) in anhydrous ethyl ether (20 mL). To this solution was added endo ester 3 (1.0 g, 5.0 mmol), synthesized as described previously,[11] dropwise. After completion of the addition the solution was stirred at room temperature for 2 h and then heated at reflux for 2 h. After cooling, the mixture was cautiously added to 1 N aqueous hydrochloric acid solution (25 mL) over crushed ice (ca. 100 g). The mixture was transferred to a separatory funnel and the organic layer separated. The aqueous phase was extracted with ethyl ether (3 × 25 mL) and the combined organic layers were washed successively with water, 10% aqueous sodium bicarbonate solution, and water. The ether phase was dried with anhydrous magnesium sulfate, filtered, and rotary evaporated to a yellow oil which was distilled from bulb to bulb (130 °C/0.9 mm) to give endo tertiary alcohol 1b which crystallized (0.97 g, 97%): mp 35 °C; IR (neat) 3407 (O–H), 1022 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.9–3.25 (ring protons) with s at 1.20 (CH$_3$C), 1.36 (CH$_3$C), and 2.20 (CH$_3$S), 4.2 (br s, OH); MS, m/e 200, 185, 182, 142, 135. Anal. Calcd for C$_{11}$H$_{20}$OS: C, 65.94; H, 10.06; S, 16.00. Found: C, 65.93; H, 10.10; S, 15.99.

Preparation of Exo Tertiary Alcohol 4a. A solution of methyllithium in ethyl ether (1.4 M, 12 mL, 16.8 mmol) was added to exo ester 4b[11] (850 mg, 4.25 mmol) with stirring. After stirring at room temperature for 1 h the mixture was heated at reflux for 2 h. The mixture was allowed to cool to room temperature, and then a saturated aqueous solution of ammonium chloride (25 mL) was added. The organic layer was separated and the aqueous phase was extracted with ethyl ether (3 × 25 mL). The combined organic layers were washed with water, dried with anhydrous magnesium sulfate, filtered, rotary evaporated, and distilled to give exo tertiary alcohol 4a (845 mg, 100%). Further purification was accomplished by GC: IR (neat) 3420 (O–H) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.6–3.25 (ring protons) with s at 1.17 (CH$_3$C), 1.28 (CH$_3$C), 2.10 (CH$_3$S); MS, m/e 200, 185, 182, 142, 135. Anal. Calcd for C$_{11}$H$_{20}$OS: C, 65.94; H, 10.10; S, 16.00. Found: C, 66.16; H, 10.14; S, 15.89.

X-ray Single-Crystal Structure Study of Endo Tertiary Alcohol 1b. Crystals of endo tertiary alcohol 1b suitable for X-ray crystallographic analysis were grown by vapor diffusion of a solution of the compound in cold carbon tetrachloride with hexane. A crystal (0.3 mm × 0.3 mm × 0.5 mm) sealed in a glass capillary was mounted on a Syntex P2$_1$ autodiffractometer. The automatic centering and least-squares routines were carried out on 24 reflections, and the cell constants were determined by least-squares treatment of these reflections are given in Table I. The monoclinic space group was determined from systematic absences to be unambiguously $P2_1/n$. The θ–2θ data collection technique over the range 0° ⩽ 2θ ⩽ 50° was used to collect the data of which those with $F ⩾ 3σ(F)$ were used in the calculations. The data were reduced to F_o and $σ(F_o)$. Polarization and an empirical absorption correction were applied to all reflections. Two standards monitored every 98 reflections indicated no decay.

The structure was solved by direct methods using the SDP program package.[38] The positions of twelve of the thirteen nonhydrogen atoms were obtained from an E-map. The structure was reefined by full-matrix least-squares techniques by using neutral-atom scattering factors with anomalous dispersion terms included for all atoms. This led to isotropic convergence at $R = 0.105$ after nine cycles and anisotropic convergenece at $R = 0.093$. All hydrogen atoms but one were located from electron-density difference maps and were added to the model in geometrically ideal positions. The hydrogen atom thermal parameters were set at 5.0 Å^2. The hydrogen atom parameters were not refined. After three cycles of anisotropic refinement the hydrogen atom on the oxygen atom was added and three additional cycles of anisotropic refinement led to convergence with $R = 0.054$, $R_w = 0.058$, and GOF = 2.08.

Synthesis of Alkoxysulfonium Salt 2a. A solution of endo primary alcohol 1a (146 mg, 0.850 mmol), prepared as described previously,[11] in anhydrous dichloromethane (10 mL) was cooled

to –78 °C in a dry ice/acetone bath, after which *tert*-butyl hypochlorite (0.50 mL, 4.1 mmol) was added to the rapidly stirring reaction mixture.[19] After 45 min mercury(II) chloride (231 mg, 0.850 mmol) was added and the reaction mixture allowed to stir for 1 h. The reaction mixture was allowed to warm slowly to room temperature and stirred at room temperature overnight. The solid precipitate which had formed was filtered, washed with dichloromethane, and recrystallized from nitromethane/diethyl ether to give alkoxysulfonium salt 2a (367 mg, 90% yield) as a colorless crystalline solid: mp 117–118 °C; IR (KBr) 2960, 1450, 1310, 960, 930, 910, 885, 755, 675 cm^{-1}; ^{1}H NMR (CD$_3$CN) δ 3.60 (s, 3 H, –SMe), 1.1–3.0 (m, 10 H, ring H), 4.28 (d, $J = 4$ Hz, 2 H, –OCH$_2$–). Anal. Calcd for C$_9$H$_{15}$OSHgCl$_3$: C, 22.60; H, 3.16; S, 6.70; Cl, 22.24. Found: C, 22.70; H, 3.17; S, 6.67; Cl, 22.19.

X-ray Single-Crystal Structure Study of Alkoxysulfonium Salt 2a. Clear, colorless crystals of alkoxysulfonium salt 2a were obtained by vapor diffusion of a solution of the compound in nitromethane with diethyl ether. A well-formed crystal was mounted on a Syntex P2$_1$ autodiffractometer equipped with scintillation counter and graphite monochromated Mo K$_α$ radiation. The automatic centering, indexing, and least-squares routines were carried out on 25 reflections to obtain the cell dimensions given in Table I. The space group was determined by systematic absences to be unambiguously $P2_1/c$. The θ–2θ data collection technique over the range 4° ⩽ 2θ ⩽ 50° was used to collect the data of which those with $I ⩾ 3σ(I)$ were considered observed and were used in the calculations. A semiempirical absorption correction using ψ-scan data was applied to the data using a locally modified version of the program TAPER, and a 20% decomposition correction was applied. Lorenz and polarization corrections were applied to all reflections.

The structure was solved by the heavy-atom method. The position of the mercury atom was located from a three-dimensional Patterson map. The remaining atoms were located by subsequent structure factor calculations and difference electron density maps.[39] The structure was refined by full-matrix least-squares techniques using neutral atom scattering factors for all species.[40] The mercury, chlorine, and sulfur atoms were treated as anomalously scattering. Several cycles of isotropic refinement led to convergence at $R = 0.087$. Anisotropic refinement converged at $R = 0.064$. The hydrogen atoms were added to the structure in geometrically ideal positions. The hydrogen atom thermal parameters were set to $B_H = B_N + 1$, where N is the atom to which H is bonded. The hydrogen atom parameters were not refined. Several cycles of anisotropic refinement led to convergence with $R = 0.062$, $R_w = 0.073$, and GOF = 3.02.

Synthesis of Alkoxysulfonium Salt 2b. *tert*-Butyl hypochlorite (1.09 g, 1.16 mL, 10 mmol), prepared according to the method of Teeter and Bell,[41] was rapidly added to a solution of endo tertiary alcohol 1b (400 mg, 2.0 mmol) in anhydrous dichloromethane (15 mL) under an argon atmosphere and cooled in a dry ice–acetone bath.[19] The solution was stirred for 1 h after completion of the addition. Mercury(II) chloride (543 mg, 2.0 mmol) was then added, and the yellow-colored solution was stirred for 1 h at –78 °C. The solution was allowed to warm to room temperature overnight during which time a white precipitate formed. The precipitate was collected by filtration and washed with cold, anhydrous dichloromethane to provide alkoxysulfonium salt 2b (1.0g) in quantitative yield: mp 145 °C; ^{1}H NMR [(C-D$_3$)$_2$SO] δ 1.14 (dd, major isomer, $J = 12$, 6 Hz), 1.24 (dd, minor isomer, $J = 12$, 6 Hz), 1.38 (s, 3 H, CH$_3$C major isomer), 1.40 (s, 0.75 H, CH$_3$C minor isomer), 1.59 (s, 3 H, CH$_3$C, major isomer), 1.62 (s, 0.75 H, CH$_3$C minor isomer), 1.65–2.39 (m, ring protons), 3.01–3.15 (m, ring protons), 3.25 (s, 0.75 H, CH$_3$S, minor isomer), 3.42 (s, 3 H, CH$_3$S, major isomer), 3.56–3.71 (m, ring protons). Recrystallization was accomplished by vapor diffusion of a solution

(38) Frenz, B. A. In "Computing in Crystallography"; Schenk, H.; Olthof-Hazelkamp, R., van Konigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978, pp 64–71.

(39) The major programs used during the solution and refinement of the structure were the Fourier summation program FORDAP (Zalkin, A. Lawrence Livermore Lab., Berkeley, CA); and the structure factor calculation and full-matrix least squares refinement program NUCLS (Ibers, J. A. Northewestern Univ., Evanston, IL), itself a modification of ORFLS (Busing, W. R.; Martin, K. O.; Levy, H. A. Oak Ridge National Lab, Oak Ridge, TN).

(40) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, UK, 1974; Vol. IV, pp 71–98.

(41) Teeter, H. M.; Bell, E. M. *Org. Synth.* 1953, *31*, 20.

of the compound dissolved in nitromethane with dichloromethane: mp 156–157 °C; IR 2962–2850, 1040 cm^{-1}; ^{1}H NMR (CD$_3$CN/ (CD$_3$)$_2$SO, 250 MHz) δ 1.19 (dd, 1 H, J = 12, 6 Hz), 1.39 (s, 3 H, CH$_3$C), 1.60 (s, 3 H, CH$_3$C), 1.63–1.68 (m, 1 H), 1.71 (br s, 2 H), 1.76–1.89 (m, 1 H), 2.17–2.35 (m, 1 H), 2.42 (m, 1 H), 3.12 (br t, 1 H, J = 3.6 Hz), 3.22 (br s, 1 H), 3.41 (s, 3 H, CH$_3$S), 3.67 (td, 1 H, J = 3.5, 12 Hz, H6). Anal. Calcd for C$_{11}$H$_{19}$Cl$_3$HgOS: C, 26.10; H, 3.78; Cl, 21.01. Found: C, 26.03; H, 3.80; Cl, 20.91.

X-ray Single-Crystal Structure Study of Alkoxy-sulfonium Salt 2b. Crystals of alkoxysulfonium salt **2b** suitable for X-ray crystallographic analysis were grown by vapor diffusion of a solution of the compound in dichloromethane with hexane. A crystal (0.17 × 0.17 × 0.17 mm) was mounted on a Syntex P2$_1$ autodiffractometer. The automatic centering and least-squares routines were carried out on 25 reflections and the cell contants determined by least-squares treatment of these reflections are given in Table I. The triclinic space group was determined P$\bar{1}$. The θ–2θ data collection technique over the range 0° $\leqslant$ 2θ $\leqslant$ 50° was used to collect the data of which those with $F \geqslant 3\sigma(F)$ were used in the calculations. The data were reduced to F_o and $\sigma(F_o)$. Polarization and semiempirical absorption corrections using ψ-scan data were applied to all reflections. Two standard reflections monitored after every 98 reflections indicated some decomposition for which correction was made (2.7% decay).

The structure was solved by the heavy-atom method.[38] The position of the mercury atom was located from a three-dimensional Patterson map. The remaining atoms were located by subsequent structure factor calculations and difference electron density maps. The structure was refined by full-matrix least-squares techniques using neutral atom scattering factors for all species. The mercury, chlorine, and sulfur atoms were treated as anomalously scattering. This led to isotropic convergence at R = 0.074 after six cycles and anisotropic convergence at R = 0.032. The hydrogen atoms were added to the structure in geometrically ideal positions. The hydrogen atom thermal parameters were set at 5.0 Å^2. The hydrogen atom parameters were not refined. Three additional cycles of anisotropic refinement led to convergence with R = 0.030, R_w = 0.033, and GOF = 1.43.

Base Hydrolysis of Alkoxysulfonium Salt 2a. A sample of alkoxysulfonium salt **2a** (203 mg, 0.425 mmol) was treated with 10% aqueous sodium hydroxide solution (10 mL). The reaction mixture was stirred until all of the sulfonium salt had dissolved. The product was extracted from the reaction mixture with dichloromethane. The organic layer was separated and dried over anhydrous magnesium sulfate. The solution was filtered and the dichloromethane removed under reduced pressure. Recrystallization of the product from dichloromethane/pentane gave sulfoxide **11a** as a colorless crystalline solid (54.2 mg, 68% yield): mp 98–99 °C; IR (KBr) 3250 (s, –OH), 2940, 2880, 1430, 1300, 1200, 1060, 1000–1030, 950, 700, 670 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.72 (s, 3 H, –SMe), 0.65–3.0 (m, 11 H, ring H and –OH), 3.69 (m, 2 H, –CH$_2$O–). Anal. Calcd for (C$_9$H$_{16}$SO$_2$)$_2$·H$_2$O: C, 54.79; H, 8.69; S, 16.25. Found: C, 54.81; H, 8.70; S, 16.26.

Base Hydrolysis of Recrystallized Alkoxysulfonium Salt 2b. A sample of recrystallized alkoxysulfonium salt **2b** (320 mg, 0.62 mmol) was stirred in 10% aqueous sodium hydroxide solution (10 mL). The yellow colored cloudy mixture was stirred at room

temperature for 3 h and then extracted with dichloromethane (5 × 25 mL). The combined organic extracts were washed with water, dried with anhydrous magnesium sulfate, filtered, and rotary evaporated to give a white solid (124 mg): mp 130–133 °C. Recrystallization by vapor diffusion of a solution of this material in dichloromethane with hexane provided colorless crystals of sulfoxide **11b** (108 mg, 87% yield): mp 134–135 °C; IR (KBr) 3450 (O–H); 1045 (S→O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.84–3.02 (ring protons) with s at 1.05 (CH$_3$C) and 1.25 (CH$_3$C), 2.50 (s, 3 H, CH$_3$SO), 4.9 (s, 1 H, OH); MS, m/e 217 (P + 1), 216 (P), 201 (P – Me), 199 (P – OH), 153 (P – MeSO), 141, 135, 109, 107, 96, 95, 91, 79, 78, 71, 64 (MeSOH$^+$). Anal. Calcd for C$_{11}$H$_{20}$O$_2$S: C, 61.11; H, 9.25; S, 14.81. Found: C, 61.23; H, 9.35; S, 14.84.

Base Hydrolysis of Crude Alkoxysulfonium Salt 2b. A sample of crude (washed but not recrystallized) alkoxysulfonium salt **2b** (200 mg, 0.39 mmol) was hydrolyzed and worked up as outlined above for the recrystallized material to afford a white solid (75 mg): mp 135 °C dec; ^{1}H NMR (CDCl$_3$) δ 0.824–3.02 (ring protons) with s at 1.06 (CH$_3$C, major isomer), 1.11 (CH$_3$C; minor isomer), 1.25 (CH$_3$C, major isomer), 1.41 (CH$_3$C, minor isomer), 2.48 (CH$_3$SO, minor isomer), 2.54 (CH$_3$SO, major isomer), 4.62 (OH). This mixture (200 mg) was separated by chromatography using a Perkin-Elmer Series 4 HPLC chromatograph equipped with a Lichrosorb column (SI 100, 25 cm × 4.6 mm) and eluting with an acetonitrile, methanol gradient from pure acetonitrile to 1:1 acetonitrile:methanol. the major component **11b** (140 mg) had a retention time of 3.2 min and the identical ^{1}H NMR spectrum and mp as that prepared from the recrystallized alkoxysulfonium salt **2b**. The minor isomer **12b** (40 mg) had a retention time of 4.4 min: ^{1}H NMR (CDCl$_3$) δ 0.80–2.99 (ring protons) with s at 1.11 (CH$_3$C), 1.42 (CH$_3$C) and 2.41 (CH$_3$SO), 4.78 (br, OH), MS, m/e 217 (P + 1), 216 (P), 201 (P – CH$_3$), 153 (P – CH$_3$SO), 141, 135, 109, 95, 93, 79, 71, 67, 63, 59.

Hydrolysis of Alkoxysulfonium Salt 2b in ^{18}O-Labeled Aqueous Base. A sample of aloxysulfonium salt **2b** (20 mg, 0.039 mmol) was hydrolyzed as above but in ^{18}O-labeled water, and then worked up as previously. Recrystallization from methylene chloride–hexanes gave sulfoxide **11b**: mp 140–141 °C; MS, m/e 219, 218, 203, 201, 153, 141, 135, 109, 107, 96, 95, 91, 79, 78, 71, 66.

Supplementary Material Available: Stereoscopic views of endo tertiary alcohol **1b** and alkoxysulfonium salt **2b** and of the packing molecules in the unit cell of endo tertiary alcohol **1b** and alkoxysulfonium salts **2a** and **2b**, tables of final atomic positional and thermal parameters, bond lengths, bond angles, and selected torsion angle data for endo tertiary alcohol **1b** and alkoxysulfonium salts **2a** and **2b**, and listings of structure factor amplitudes for endo tertiary alcohol **1b** and alkoxysulfonium salts **2a** and **2b** (48 pages). Ordering information is given on any current masthead page.