1.54 g of pale beige powder: IR (KBr) peaks absent at 1176 cm^{-1} for tosyl ester precursor, as well as at 1365 cm^{-1} (*N,N*-dialkylimidazolium nucleus) and 1196, 1123, 1034, 1012 and 569 cm^{-1} (tosylate anion) from quaternization, and 1630 cm^{-1} from elimination side products, peaks present at 3105 (w), 1508 (m), 1284 (m), 1231 (m), 1108 (m), 1076 (m), 905 (m), 663 (s), and 624 (m) cm^{-1} (all attributed to the *N*-alkylimidazole functionality). Anal. Calcd for $(C_{10}H_{10})_{0.01}{\cdot}(C_8H_8)_{0.70}{\cdot}(C_{13}H_{14}N_2)_{0.29}$: N, 6.17. Found: N, 5.87.

[2-(*N*-Methyl-*N*-(*p*-tolylsulfonyl)amino)ethyl]polystyrene (14). A mixture of tosylated polymer 7 [$(C_{10}H_{10})_{0.01}{\cdot}(C_8H_8)_{0.70}{\cdot}(C_{17}H_{18}SO_3)_{0.29}$] (0.3894 g, 0,53 mequiv) with *N*-methyl-*p*-toluenesulfonamide (0.1373 g, 0.74 mmol) and anhydrous potassium carbonate (0.212 g, 1.53 mmol) in 4 mL of dry dimethyl sulfoxide containing 0.5 mL of HMPA was stirred overnight at 60 °C under nitrogen. After cooling, the beige suspension was filtered, and the residue was washed with acetone, H_2O (3×), MEK (1×), CH_2Cl_2 (1×), and CH_3OH (2×) and dried under vacuum overnight, yielding 0.3926 g of pale beige powder: IR (KBr) peaks absent at 1363 and 1176 cm^{-1} from tosyl ester precursor and at 1630 cm^{-1} from elimination byproduct, peaks present at 1344 (s, SO–NC), 1161 (s, SO–NC), 653 (m, Ar SO_2) and 549 cm^{-1} (m, Ar SO_2). Anal. Calcd for $(C_{10}H_{10})_{0.01}{\cdot}(C_8H_8)_{0.70}{\cdot}(C_{18}H_{21}NSO_2)_{0.29}$: N, 1.91; S, 4.53. Found: N, 1.98, S, 4.80.

An alternate procedure with sodium hydride in DMF at 10 °C was somewhat less satisfactory.

[2-(*N*-Methylamino)ethyl]polystyrene (15). Sodium metal (0.094 g, 4.1 mequiv) and naphthalene crystals (0.63 g, 4.9 mequiv) were stirred together in 4 mL of dry dimethoxyethane under nitrogen for 90 min, and then polymer 14 prepared above [$(C_{10}H_{10})_{0.01}{\cdot}(C_8H_8)_{0.70}{\cdot}(C_{18}H_{21}NSO_2)_{0.29}$] (0.378 g, 0.68 mequiv) was added in portions. After being stirred at room temperature for 30 h, the dark brown solution was filtered and the residue washed with H_2O (3×), MEK (1×), CH_2Cl_2 (1×), and CH_3OH (2×) and then dried under vacuum overnight, yielding 0.348 g of pale yellow-green powder: IR (KBr) peaks absent at 1344, 1161, 653, and 549 cm^{-1} for precursor sulfonamide, peaks present at 1155 (w, C–N) and 1116 cm^{-1} (w, C–N). Anal. Calcd for $(C_{10}H_{10})_{0.01}{\cdot}(C_8H_8)_{0.70}{\cdot}(C_{18}H_{21}N)_{0.29}$: N, 3.36. Found: N, 2.43; S, 1.05.

(2-Aminoethyl)polystyrene (16). $(C_{10}H_{10})_{0.01}{\cdot}(C_8H_8)_{0.70}{\cdot}(C_{17}H_{18}SO_3)_{0.29}$ (0.200 g, 0.36 mequiv), phthalimide (0.062 g, 0.42 mequiv), and anhydrous potassium carbonate (0.0567 g, 0.41 mequiv) were stirred in 2.0 mL of dry DMF at 60 °C under nitrogen for 48 h. The pale yellow-green suspension was filtered and the residue washed with H_2O (3×), MEK (1×), CH_2Cl_2 (1×), and CH_3OH (2×) and then dried under vacuum overnight, yielding 0.198 g of pale beige-yellow powder: IR (KBr) peaks absent at 1363 and 1176 cm^{-1} for tosyl ester precursor and 1630 cm^{-1} for elimination side product, peaks present at 1774 (w, C=O), 1716 (s, C=O), 719 cm^{-1} (m, Ar C=O). Anal. Calcd for $(C_{10}H_{10})_{0.01}{\cdot}(C_8H_8)_{0.70}{\cdot}(C_{18}H_{15}NO_2)_{0.29}$: N, 2.63. Found: N, 2.54.

Part of the product (0.139 g, 0.26 mequiv) and 40% hydrazine/H_2O (0.10 mL, 1.3 mequiv) were stirred with 2 mL of ethanol at reflux for 5 h, then the white suspension was filtered, and the residue was washed with acetone (1×), H_2O (3×), 5% NaOH/EtOH (1×), H_2O (3×), EtOH (1×), MEK (1×), CH_2Cl (1×), and CH_3OH (2×) and dried under vacuum overnight, yielding 0.109 of white powder: IR (KBr) peaks absent at 1774, 1716, 719 cm^{-1} (as present above), peaks present at 3410 (m, NH_2) and 1098 (m, C–N) cm^{-1}. Anal. Calcd for $(C_{10}H_{10})_{0.01}{\cdot}(C_8H_8)_{0.70}{\cdot}(C_{10}H_{13}N_2)_{0.29}$: N, 3.48. Found: N, 2.61.

[2-(Butylthio)ethyl]polystyrene (17). Tosylated polymer 7 with DF = 0.31 [$(C_{10}H_{10})_{0.01}{\cdot}(C_8H_8)_{0.68}{\cdot}(C_{17}H_{18}SO_3)_{0.31}$] (0.50 g, 0.94 mequiv), butanethiol (0.22 mL, 2.1 mequiv), hexadecyltributylphosphonium bromide (0.077 g, 0.15 mequiv) and anhydrous potassium carbonate (0.33 g, 2.4 mequiv) were stirred rapidly in 4.5 mL of refluxing toluene under nitrogen for 50 h, then the white suspension was filtered, and the residue was washed with H_2O (3×), MEK (1×), CH_2Cl_2 (1×), and CH_3OH (2X) and dried under vacuum overnight, yielding 0.44 g of white powder: IR (KBr) peaks absent at 1363 and 1176 cm^{-1} for tosyl ester precursor and 1630 cm^{-1} for elimination side product, peak present at 2853 cm^{-1} (m, CH_2). Anal. Calcd for $(C_{10}H_{10})_{0.01}{\cdot}(C_8H_8)_{0.68}{\cdot}(C_{14}H_{20}S)_{0.31}$: S, 7.08. Found: S, 5.76.

[2-(Diphenylphosphino)ethyl]polystyrene (18). A 25 wt % dispersion of lithium metal in mineral oil (0.10 g, 3.6 mequiv) was suspended in 5 mL of dry THF under argon; chlorodiphenylphosphine (0.30 mL, 1.7 mequiv) was added slowly, and the whole was stirred at room temperature for 3 h. The resulting red solution was then decanted through a double-ended needle onto tosylated polymer 7 (0.50 g, 0.94 mequiv), together with 0.5 mL of dry Me_2SO, and the mixture was stirred under argon at 25 °C for 24 h and then at 50 °C for 24 h. The red suspension was then filtered, and the residue was washed with acetone (1×), H_2O (3×), MEK (1×), benzene (1×), and CH_3OH (3×) and dried under vacuum overnight, yielding 0.51 g of pale beige powder: IR (KBr) peaks absent at 1363 and 1176 cm^{-1} for tosyl ester precursor, peaks present at 1435 (m, P–Ar), 1481 (w, P–Ar), and 999 cm^{-1} (w, P–Ar). Anal. Calcd for $(C_{10}H_{10})_{0.01}{\cdot}(C_8H_8)_{0.68}{\cdot}(C_{22}H_{21}P)_{0.31}$: P, 5.65. Found: P, 5.24.

Acknowledgment. Financial support of this research by the Natural Sciences and Engineering Council of Canada in the form of a postgraduate scholarship and an operating grant is gratefully acknowledged.

On the Stereochemistry and Mechanism of the Ozonation of Some Six-Membered Ring Vinyl Sulfides

Daniel Barillier and Michel Vazeux*

Laboratoire des Composés Thioorganiques, UA 480, Université de Caen, 14032 Caen Cedex, France

Received October 2, 1985

Allylic alcohols 3 and α,β-epoxy sulfoxides 6/7 were the partial cleavage products isolated from the ozonation of six-membered-ring vinyl sulfides 1 with respectively stoichiometric and double amounts of ozone. They were characterized by spectroscopic methods, including measurements of aromatic solvent induced shifts (ASIS). From careful examination of the resulting data, the stereochemistry of the ozone addition to vinyl sulfides seemed to derive from an initial, axial carbon–oxygen bond formation at the β-carbon. The intermediary epoxy sulfide 2 was correlated to a mechanism based on stereoelectronic control upon the fragmentation of a primary ozonide adduct, viz., the five-membered-ring 1,2,3-trioxolane IV.

Extensive interest has been shown in the ozone–olefins reactions, a topic which has been recently reviewed by Bailey.[1] Among the main reaction pathways in solution, ozonolysis is well-recognized as a versatile method for

Scheme I. Ozonation of Six-Membered-Ring Vinyl Sulfides 1

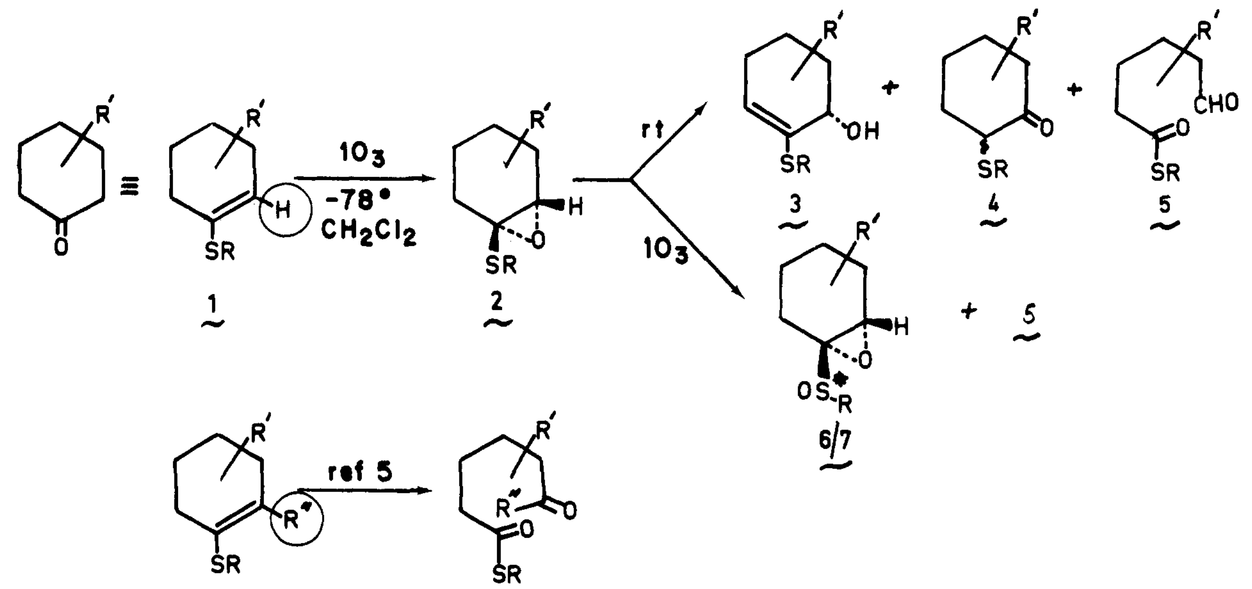
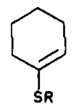
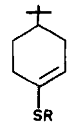
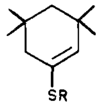
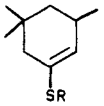


Table I. Allylic Alcohols 3 and α,β-Epoxy Sulfoxides 6/7 Prepared from Vinyl Sulfides[a] 1 with Ozone

			yields[a]				
			1:1 adducts[b]			1:2 adducts[b]	
vinyl sulfides 1	R	compd	allylic alchl 3	ketone 4	oznlysis prod. 5	epoxydes 6/7 (1:1)	5
	Me	1a	5	55	2-3 (ref 5)		
	Et	1b	4	50	5		
	IsoPr	1c	6	50	5		
	Me	1d[c,d]	55 (*E*)	15 (*E*/*Z*:4/1)	5	50	20
	Et	1e[c]	25 (*E*)	45 (*E*/*Z*:9/1)	10	60	10
	Ph	1f		10 (*E*/*Z*:5/1)	45		
	Me	1g[d]	85 (ref 5)			80	
	Ph	1h[c]	60	20	2-3	75	5
	Me	1i[d]	85 (*Z*)		5	80	5

[a] Yields refer to products isolated from silica gel chromatography, unless otherwise stated. All new compounds were fully characterized spectroscopically and, when sufficiently stable, analytically. [b] 1 mol equiv of ozone was used with oxygen as a carrier to produce 1:1 adducts 3 and 4 while for the 1:2 adducts 6/7, 2 mol equiv were employed. [c] Yields were of purified material from chromatography on neutral alumina. [d] With these vinyl sulfides, it was shown that there was little or no temperature effects (−78 to 0 °C, see Experimental Section).

oxidative cleavage of the double bond,[1,2] and the epoxidation route or ozonation, leading to partial cleavage products, is well-known for hindered alkenes and cycloalkenes.[3] Besides simple hydrocarbon alkenes, unsaturated compounds substituted by halogen atoms[4] have received much attention. However, generalization to a broader range of olefins, including thioenol ethers[5] and related systems,[6] remains limited.

---

[1] For a recent comprehensive review of this topic, see: Bailey, P. S. *Ozonation in Organic Chemistry*; Academic: New York, 1978; Vol. I, and 1982; Vol. II.

[2] For recent applications, see: Gupta, D.; Soman, R.; Dev, S. *Tetrahedron* **1982**, *38*, 3013. Whitesell, J. K.; Fisher, M.; Da Silva Jardine, P. *J. Org. Chem.* **1983**, *48*, 1556. Cella, J. A. *Synth. Commun.* **1983**, *13*, 93. Wu, H.; Nakamura, H.; Kobayashi, J.; Ohizumi, Y. *Tetrahedron Lett.* **1984**, *25*, 3719. Wasserman, H. H.; Han, W. T. *Tetrahedron Lett.* **1984**, *25*, 3743 and 3747. Kitahara, T.; Matsuoka, T.; Katayama, M.; Marumo, S.; Mori, K. *Tetrahedron Lett.* **1984**, *25*, 4685. McCullough, K. J.; Nojima, M.; Miura, M.; Fujisaka, T.; Kusabayashi, S. *J. Chem. Soc., Chem. Commun.* **1984**, 35. Wuts, P. G. M.; Bigelow, S. S. *J. Chem. Soc., Chem. Commun.* **1984**, 736. Baraldi, P. G.; Polini, G. P.; Simoni, D.; Barco, A.; Benetti, S. *Tetrahedron* **1984**, *40*, 761. Cardinale, G.; Grimmelikhuysen, J. C.; Laan, J. A. M.; Ward, J. P. *Tetrahedron* **1984**, *40*, 1881. Shuda, P. F.; Heimann, M. R.*Tetrahedron* **1984**, *40*, 2365. Abe, K.; Okumura, H.; Tsugoshi, T.; Nakamura, N. *Synthesis* **1984**, 603. Habib, R. M.; Chiang, C. Y.; Bailey, P. S. *J. Org. Chem.* **1984**, *49*, 2780. Mena, P. L.; Pilet, O.; Djerassi, C. *J. Org. Chem.* **1984**, *49*, 3260. Miura, M.; Nojima, M.; Kusabayashi, S.; McCullough, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 2932.

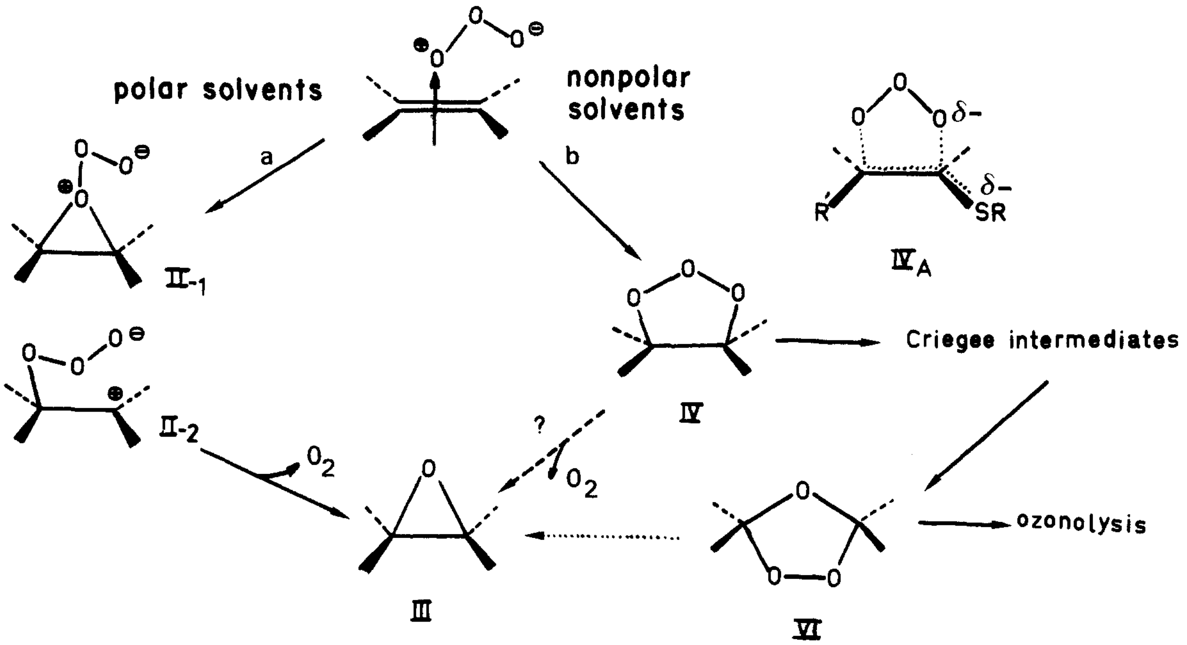
[3] Allinger, N. L.; Eliel, E. L. *Topics in Stereochemistry*; 1973; Vol. 7, p 180. Hochstetler, A. R. *J. Org. Chem.* **1975**, *40*, 1536. Keul, H. *Chem. Ber.* **1975**, *108*, 1207.

[4] Gillies, C. W. *J. Am. Chem. Soc.* **1975**, *97*, 1276; **1977**, *99*, 7239. Agopovitch, J. W.; Gillies, C. W. *J. Am. Chem. Soc.* **1980**, *102*, 7572. Gensler, W. J.; Chan, S.; Ruchirawat, S. *J. Org. Chem.* **1981**, *46*, 1750. Gillies, C. W.; Kuczkowski, R. L. *Isr. J. Chem.* **1983**, *23*, 446.

[5] Barillier, D.; Strobel, M. P.; Morin, L.; Paquer, D. *Nouv. J. Chim.* **1982**, *6*, 201.

[6] Enol ethers: Corey, E. J.; Katzenellenbogen, J. A.; Gilman, N. W.; Roman, S. A.; Erickson, B. W. *J. Am. Chem. Soc.* **1968**, *90*, 5618. Effenberger, F. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 295. Keul, H.; Choi, H. S.; Kuczkowski, R. L. *J. Org. Chem.* **1985**, 50, 3365. Enamines: Herr, M. E.; Heyl, F. W. *J. Am. Chem. Soc.* **1952**, 74, 3627. Strobel, M. P.; Morin, L.; Paquer, D. *Tetrahedron Lett.* **1980**, 21, 523 and *Nouv. J. Chim.* **1980**, 603. Silylenol ethers: Clark, R. D.; Heathcock, C. H. *Tetrahedron Lett.* **1974**, 2027. Vedejs, E.; Larsen, S. D. *J. Am. Chem. Soc.* **1984**, *106*, 3030.

Scheme II. Classical Routes for Ozonolysis and Ozonation of the Carbon–Carbon Double Bond[31]



Recent investigations by Trost[7] into the chemistry of 1-(phenylthio)alkenes and -cycloalkenes indicate that these compounds may be promising sulfur-derived enolonium equivalents. As such, they have found some use in carbon–heteroatom bond-forming processes. Their ability to achieve α-substitution regioselectively combined with subsequent selective reactions on the vinyl sulfide function[8] or on the newly introduced heteroatom itself make thioenol ethers attractive carbonyl substitutes. Consequently, we have pursued a study aimed at the reactivity of some six-membered-ring vinyl sulfides toward ozone. Herein we report the results on the synthesis and structure of the partial cleavage products **3** and **6**/**7**. On the other hand, our desire to gain insight into the mechanism responsible for this phenomena led us to analyze in some detail the stereochemical requirement[9] for this reaction.

Results

Ozonation of Vinyl Sulfides 1. A series of six-membered-ring alkenyl sulfides **1a–i** has been reacted with ozone, according to Scheme I. Table I gives the results of experiments with these simple molecules. The usual procedure of bubbling gaseous ozone oxygen into a dichloromethane solution of substrate **1** containing pyridine at −78 °C led usually to very good yields of allylic alcohols **3** or α,β-epoxy sulfoxides **6**/**7**. Besides vinyl sulfides derived from symmetrical cyclohexanones, we have also examined the isophorone skeleton. High yield reactivity toward ozonation was expected since previous work by Paquer[5] has shown that substituents on the ring favor this route and, most importantly, before this reaction can be used fully in synthetic organic transformations, its regio- and stereochemistry must be known.

The salient feature in Table I is the extent to which ozonolysis (C═C bond cleavage) competes with ozonation (reaction with ozone in the absence of C═C bond cleavage). The success of the latter route depends on the degree of substitution on the ring but also on the nature of the SR group; the behavior of 4-*tert*-butyl-1-(phenylthio)cyclohexene (**1f**) contrasts markedly with that of its methylthio analogue **1d**. This result has some mechanistic implications (vide infra). On the other hand, while the cycloalkenyl system itself **1a–c** leads essentially to the 2-(alkylthio)cyclohexanone[5] **4a–c**, systems bearing alkyl substituents on the six-membered ring as **1d,e,g,h,i** offer the opportunity to stop the reaction at the allylic alcohol stage. Of particular interest is the fact that allylic alcohols **3d,e,h** when left alone or adsorbed on silica gel smoothly produce the corresponding ketones **4**. This suggests that no ketone was formed directly but rather was generated by rearrangement of the initially formed allylic alcohol.[10] In short, the main chemical changes observed here were either the regioselective introduction of a hydroxyl group with a shifting of the double bond or the transposition[11] of a keto group, as outlined in Scheme I.

Further experiments indicate that there are only minor solvent effects regarding the competition between ozonation and ozonolysis. The fact that use of pentane or diethyl ether as solvent instead of dichloromethane caused little change in the product distribution seems to infer that the reaction might proceed through low polar intermediates. Also significant under our working conditions is that allylic alcohols **3** can be first produced even in the presence of oxydant-sensitive sulfur atom. (See Experimental Section.)

The preparations of epoxy sulfoxides **6**/**7d,e,g,h,i** were easily achieved according to this scheme, and the results are also summarized in Table I. When allowed to react with a stoichiometric amount of ozone (heterogeneous procedure), vinyl sulfides **1d,e,g,h,i** produced the corresponding epoxy sulfides **2** (two of them have been characterized spectroscopically) which may be trapped by adding another equivalent of ozone thus affording two

---

[7] Trost, B. M.; Tanigawa, Y. *J. Am. Chem. Soc.* **1979**, *101*, 4413. Trost, B. M.; Lavoie, A. C. *J. Am. Chem. Soc.* **1983**, *105*, 5075 and references therein.

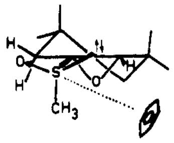
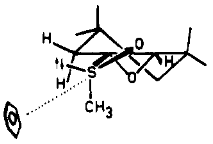
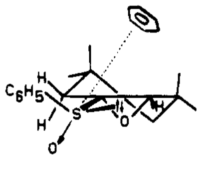
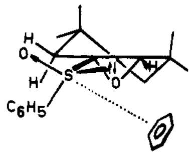
[8] Corey, E. J.; Shulman, J. I. *J. Org. Chem.* **1970**, *35*, 777. Takei, H.; Sugimura, H.; Miura, M.; Okamura, H. *Chem. Lett.* **1980**, 1209. Trost, R. M.; Ornstein, P. L. *J. Org. Chem.* **1982**, *47*, 751. Yamagiwa, S.; Sato, H.; Hoshi, N.; Kosugi, H.; Uda, H. *J. Chem. Soc., Perkin Trans. 1* **1979**, 570.

[9] Earlier work has shown the necessity of a β-hydrogen atom cis to the SR group for the success of ozone–vinyl sulfide epoxidation.

[10] Double bond migration followed by keto–enol tautomerism give isomeric β-keto sulfides **4** here.

[11] Morris, D. G. *Chem. Soc. Rev.* **1982**, *11*, 397. Kane, V. V.; Singh, V.; Martin, A.; Doyle, D. L. *Tetrahedron* **1983**, *39*, 345.

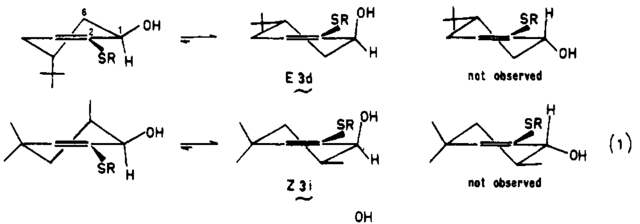
Table II. Proposed Structures and NMR Assignments[a] of Isomeric Epoxy Sulfoxides 6/7g and 6/7h

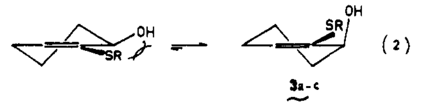
epoxy sulfoxides[b]	compd	solvents	H_{-2}	$\Delta\delta$ ($CDCl_3$-C_6H_6)	H_{-6}
	**6g** (S_S,*S*,*S*)	$CDCl_3$	3.22	0.29	1.58 and 2.32 (ABq)
		C_6H_6	2.93		1.27 and 2.29 (ABq)
	**7g**[c] (R_S,*S*,*S*)	$CDCl_3$	3.37	−0.04	1.58 (s)
		C_6H_6	3.41		1.17 (s)
	**6h** (R_S,*S*,*S*)	$CDCl_3$	3.43	0.20	1.0 and 1.95 (ABq)
		C_6H_6	3.23		0.97 and 2.18 (ABq)
	**7h**[d] (S_S,*S*,*S*)	$CDCl_3$	3.38	0.08	1.24 and 1.75 (ABq)
		C_6H_6	3.30		1.24 and 1.75 (ABq)

[a] Chemical shifts in ppm downfield from internal Me_4Si. [b] The epoxy sulfoxides of each pair **g** or **h** are given in the order of elution on silica gel chromatography. The sequence used in assigning sulfur chirality is O; 1,2-epoxycyclohexyl residue; Me or phenyl and a pair of electrons[21] and is indicated by a subscript S in our notation. The first carbon configuration listed is C_{-1} and the second C_{-2}. Note that (S_S,*S*,*S*) are relative configurations. [c] Other methylsulfinyl epoxides **6/7d,e,i** are given in the Experimental Section and similar shielding effects were observed with benzene as solvent. [d] This choice is tentative and could be reversed.

diastereomeric α,β-epoxy sulfoxides **6/7** in an approximately 1:1 ratio. These polar diastereomers were separated by silica gel chromatography. Interestingly, they were suitable substrates for the investigation of the competition between the spatial arrangement of sulfinyl oxygen vs. the pair of electrons (Table II).

Stereochemistry of Allylic Alcohols 3. The stereochemistry of **3** has been easily established from NMR spectra. Significantly, the ozonation of vinyl sulfides **1** allowed a single isomer to be obtained. Thus, when two protons at C-6 are present, the proton attached to C-1 of **3** shows a small vicinal coupling which precludes any trans-axial relationship and, therefore, indicates the axial nature of the OH group.[12] In the 5-*tert*-butyl derivative **3d**, the width at half-height ($W_{1/2}$ = 7 Hz) for 1-H is consistent with the *E* stereochemistry of the probable preferred conformation **3d**. The coupling constant of 3.4 Hz for the same absorption in **3i** allows us to assign the *Z* sterochemistry to **3i** (eq 1). Such a strong bias for the axial orientation of the hydroxyl group might derive from an $A^{1,2}$ strain[13] as exemplified in eq 2 for **3a–c** ($W_{1/2}$ = 8 Hz). In addition, the structure of these allylic alcohols also seems to correspond to that predicted on the basis of the preferential axial approach of ozone to vinyl sulfides **1**.





From a preparative point of view, ozonation of alkenyl sulfides may represent, at least in C-6 series, distinct advantages with respect to existing procedures for allylic alcohol syntheses: (a) starting materials are easily accessible by various methods,[14-17] (b) high diastereoselectivity can be achieved, (c) overall yields range from 60 to 85%, (d) the characteristics of the reaction may be ultimately used to complement carbonyl transposition strategy.[11] The direct production of alkenyl sulfides without proceeding through carbonyl compounds[17] enhances the usefulness of this reaction.

Stereochemistry of Epoxy Sulfoxides 6/7. Tentative structural assignments are based on ^1H NMR spectroscopic results, including aromatic solvent induced shifts.[18] ^1H NMR measurements are collected in Table II together with the proposed structures. Note that the differences observed in the chemical shifts and the splitting pattern of

---

(12) Jackman, L. M.; Sternhell, S. *Applications of NMR Spectroscopy in Organic Chemistry*, 2nd. ed.; Pergamon: Oxford, 1969; pp 280–304.

(13) Johnson, F. *Chem. Rev.* **1968**, *68*, 375. Senda, Y.; Imaizumi, S.; Ochiai, S.; Fujita, K. *Tetrahedron* **1974**, *30*, 539.

(14) Cohen Th.; Bennett, D. A.; Mura, A. J. *J. Org. Chem.* **1976**, *41*, 2506.

(15) Ong, B. S.; Chan, T. H. *Synth. Commun.* **1977**, *7*, 783.

(16) Oida, T.; Tanimoto, S.; Ikehira, H.; Okano, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 959. Cameron, A. G.; Hewson, A. T. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2979. Ager, D. J. *Synthesis* **1984**, 384.

(17) Cohen, Th.; Weisenfeld, R. B. *J. Org. Chem.* **1979**, *44*, 3601. Godleski, S. A.; Villhauer, E. B. *J. Org. Chem.* **1984**, *49*, 2246. Masaki, Y.; Sakuma, K.; Kaji, K. *Chem. Lett.* **1979**, 1235. Trost, B. M.; Vladuchick, W. C.; Bridges, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 3548 and 3554. Petrzilka, M.; Grayson, J. I. *Synthesis* **1981**, 753. Nakayama, J.; Takeue, S.; Hoshino, M. *Tetrahedron Lett.* **1984**, *25*, 2679.

(18) Ronayne, J.; Williams, D. H.; *J. Chem. Soc.* B **1967**, 540 and references therein. Siegl, W. O.; Johnson, C. R. *Tetrahedron* **1971**, *27*, 341. Lett, R.; Marquet, A. *Tetrahedron* **1974**, *30*, 3379. Dean, F. M.; Varma, R. S. *Tetrahedron* **1982**, *38*, 2069. Andersen, K. K.; Caret, R. L.; Karup-Nielsen, I. *J. Am. Chem. Soc.* **1974**, *96*, 8026. Szmant, H. H.; Rigau, J. J. *J. Org. Chem.* **1972**, *37*, 447. Berges, D. A.; Taggart, J. J. *J. Org. Chem.* **1985**, *50*, 413. Iwata, C.; Hattori, K.; Uchida, S.; Imanishi, T. *Tetrahedron Lett.* **1984**, *25*, 2995.

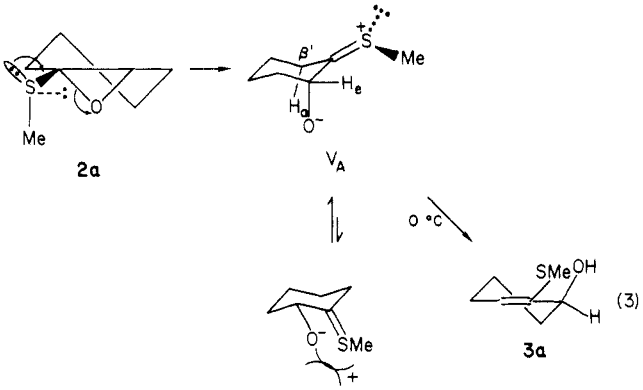
the C-6 methylene protons can be accounted for by the anomeric effect of the S–O bond;[19] the low-field positions of these protons are indicative of their proximity to the S–O bond.

Although the cyclohexane ring may undergo some change in shape with increased substitution, a "half-chair-like" conformation for epoxy sulfoxides **6**/**7** appears to be reasonable.[20] The spectra of methylsulfinyl epoxides **6**/**7g** were in sharp contrast with those of the phenylsulfinyl analogues **6**/**7h**. Thus, the ^{1}H NMR spectrum of both isomeric epoxy sulfoxides **6**/**7h** exhibited for the methylene protons at C-6 an AB quartet due to anisotropy of the sulfinyl oxygen[19] and phenyl group.[22] On the other hand, the spectrum of the first eluted isomer **6g** showed an AB pattern (centered at $\delta = 1.95$ ppm, $\Delta = 0.74$ ppm, $J = 15$ Hz) for the C-6 methylene protons, while the corresponding protons of the more polar isomer **7g** occurred as a singlet ($\delta = 1.58$ ppm).

As outlined in Table II, further support for our assignments was provided by ASIS measurements. In these experiments, the benzene molecule is currently viewed as solvating the positive sulfur end of the sulfoxide dipole,[18] and, therefore, signals of spatially proximate solute protons are more shifted upfield. While the results for methylsulfinyl epoxides **6**/**7g** seem to be in accord with the proposed relative configurations in Table II, some doubt remains about those of epimeric phenylsulfinyl epoxides **6**/**7h**. Consequently, because of the need to verify the earlier conclusions about the detailed structures of these epoxy sulfoxides and to fully define them in the solid state, X-ray crystallographic studies of **6g** and **6h** are under investigation.[23]

Intermediate Epoxy Sulfide 2. The major products isolated in this work may be rationalized as arising from **2**. Earlier NMR experiments[5] identified the epoxy sulfide **2g** by monitoring its conversion to allylic alcohol **3g**. Likewise, the low-temperature (−80 to −10 °C) ^{1}H NMR spectra of **2i** in chloroform solution exhibited a doublet at 3.2 ppm ($J = 2$ Hz) for the proton of the epoxide ring, which then gave way to new signals near 0 °C, corresponding to the allylic alcohol **3i**. The identification of (alkylthio)-substituted epoxides ruled out the possibility of singlet oxygen ene reactions for **1** → **3**,[24] although very low levels of allylic alcohol could have been missed.

Such reactive species have been reported elsewhere[25] and even isolated occasionally.[26] Herein, these epoxy sulfides (which are isomeric with α-alkyl or arylthio carbonyl compounds **4**) display a remarkable regioselective ring opening to allylic alcohols **3** under very mild conditions, contrary to those necessary for poorest activated oxiranes.[27] The question of any intrinsic regiochemical preference within the ring opening of sulfur-substituted epoxides appears to be of synthetic importance since it allows a ready access to nearly pure allylic alcohols with high positional selectivity. As shown in eq 3, the mechanism involved in the process reflects, undoubtedly, a severe control by the sulfur atom.[28] In line with this analysis, minimization of the lone pair–lone pair electron repulsions between O and S in the conformationally flexible 1,2-epoxy-1-(methylthio)cyclohexane system **2a**, makes the conjugative effects of S easier, and the ensuing thionium ion V_A[29] can be further stabilized by β'-proton abstraction. At this stage, for maximum overlap with the sp^2 carbon, the β'-axial proton is suitably located for selective removal.[30] Finally, the overall stereochemistry of the ozonation seems to follow the stereochemistry of ozone cycloaddition to vinyl sulfides (vide infra).



(3)

Discussion

The first point of interest is how to explain the high stereoselectivity of the epoxidation step. More precisely, could the steric course be predicted knowing the reactive initial conformations of the starting vinyl sulfide and factors controlling the approach of the reagent? Usually, the stereochemical outcome of such transformations with ozone has been considered as being related to steric and conformational rather than to electronic effects.

A further point is how to reconcile the structural requirement for epoxidation (this requirement must also explain why vinyl sulfides that bear the cis-β-alkyl group to the sulfur atom were not suitable reaction substrates) with the classical scheme developed by Bailey and Lane[31] for ozone–olefins reactions. Within this scheme, epoxidation and ozonolysis are rationalized in terms of two competing mechanisms (routes a and b). In the first, which is presumably favored in polar media, initial peroxy epoxide II-1 or opened dipolar ion II-2 formation is followed

---

(19) Foster, A. B.; Inch, T. D.; Qadir, M. H.; Webber, J. M. *Chem. Commun.* **1968**, 1086. Barton, D.; Ollis, W. D. *Comprehensive Organic Chemistry*; Edited by Neville-Jones, D., Ed.; Pergamon: 1979; Vol. 3, p 121.

(20) Eliel, E. L. *Stereochemistry of Carbon Compounds*; McGraw-Hill: 1962; p 271.

(21) Cahn, R. S.; Ingold, S. C.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

(22) Popple, J. A. *J. Chem. Phys.* **1956**, *24*, 1111. Gaidis, J. M.; West, R. *J. Chem. Phys.* **1967**, *46*, 1218.

(23) Single crystal X-ray analysis on these systems is being investigated with the collaboration of Dr. Leclaire, A. Laboratoire de Cristallographie et Chimie du Solide, Université de CAEN, France. Initial results obtained with **6g** are in accord with the proposed configurations.

(24) Wasserman, M. H.; Ives, J. L. *Tetrahedron* **1981**, *37*, 1825.

(25) Luchetti, J.; Krief, A. *Synth. Commun.* **1983**, 1153. Reutrakul, V.; Poochaivatananon, P. *Tetrahedron Lett.* **1983**, *24*, 531. Verhé, R.; De Kimpe, N.; De Buyck, L.; Schamp, N. *Synthesis* **1984**, 46. Knapp, S.; Trope, A. F.; Theodore, M. S.; Hirata, N.; Barchi, J. J. *J. Org. Chem.* **1984**, *49*, 608. Israel, R. J.; Murray, R. K., Jr. *J. Org. Chem.* **1985**, *50*, 1573.

(26) Tavares, D. F.; Estep, R. E. *Tetrahedron Lett.* **1973**, 1229. Cohen, Th.; Kuhn, D.; Falck, J. R. *J. Am. Chem. Soc.* **1975**, *97*, 4749.

(27) Buchanan, J. G.; Sable, H. Z. In *Selective Organic Transformations*; Thyagarajan, B. S., Ed.; Wiley-Interscience: New York, 1972; Vol. 2, p 1. Stirling, C. J. M. *Chem. Rev.* **1978**, *78*, 517. Rao, A. S.; Paknikar, S. K.; Kirtane, J. G. *Tetrahedron* **1983**, *39*, 2323. Gorzynski, Smith, J. *Synthesis* **1984**, 629.

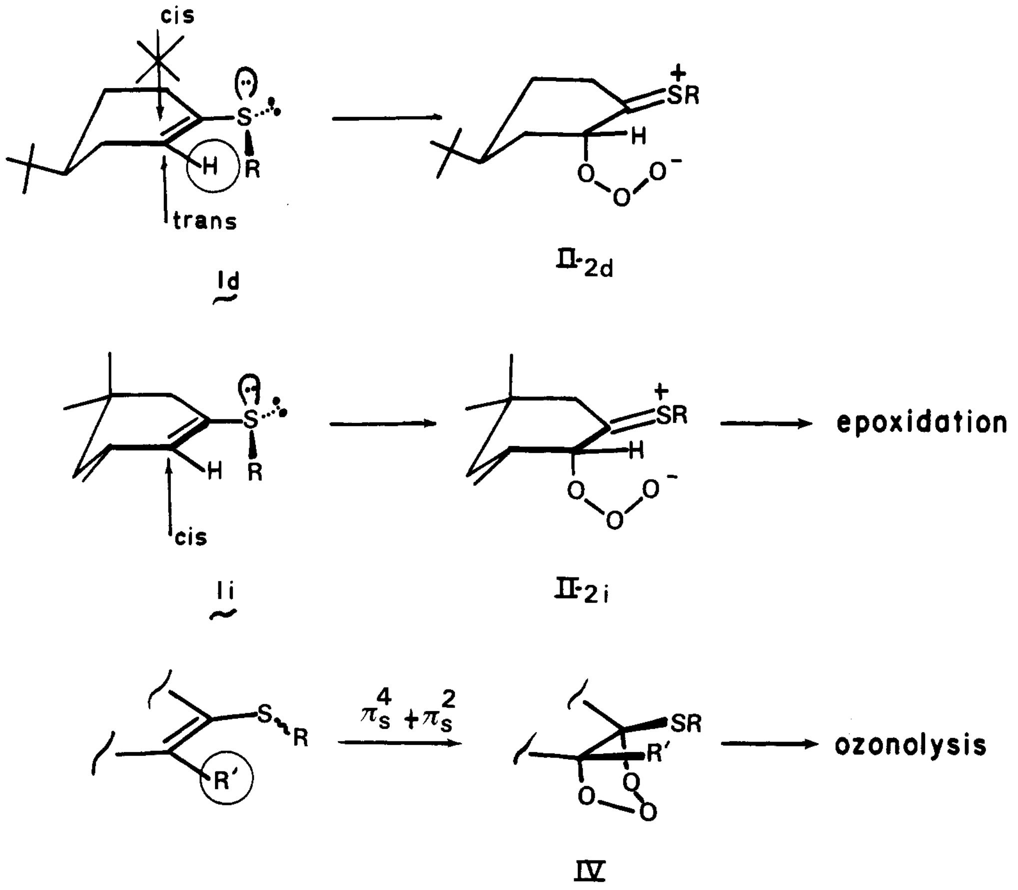
(28) Electron-releasing groups are known to facilitate bond breaking between oxygen and carbon to which they are bound, see: Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737 and also Capon, B.; McManus, S. P. *Neighbouring Group Participation*; Plenum: New York, 1976; Vol. I, p 195.

(29) The probably preferred conformation is V_A with the electronegative substituent in the axial configuration. See: Lessart, J.; Minh Tau, P. V.; Martino, R.; Saunders, H. K. *Can. J. Chem.* **1977**, *55*, 1015.

(30) Direct rearrangement of epoxides **2** into β-keto sulfides **4** via abstraction of the equatorial proton in V_A has not been observed.

(31) Bailey, P. S.; Lane, A. G. *J. Am. Chem. Soc.* **1967**, *89*, 4473. See also: Bailey, P. S.; Hwang, H. H.; Chiang, C. Y. *J. Org. Chem.* **1985**, *50*, 231.

Scheme III. Conformational Changes during the First Stage of the Reaction



by loss of molecular oxygen to give epoxide III. Its production has most often been reported to be sterically controlled. The second mechanistic pathway[32] involves a primary ozonide IV which subsequently results in normal ozonolysis products, via Criegee intermediates. Refinements of this general scheme have been complemented by further theoretical conclusions.[32c] To understand the dichotomy of routes, it is particularly attractive, at first, to consider the dienophilic reactivity of vinyl sulfides toward ozone as being chiefly substrate dependent (Scheme III).

The initial reactive conformations of unsaturated thioethers **1d** and **1i** are reasonably depicted as in Scheme III by taking into account the fact that the more populated conformer exists in a planar S-cis conformation[33a] with the maximum number of equatorial substituents.[33b] Therefore, the vinyl sulfide, with the S in a conformation such that its nonbonding electrons overlap those of the π bond, may constitute a 4π electron system[34] (an allyl anion analogue) as does ozone itself. By orbital symmetry-type arguments,[35] there will be a barrier to the concerted formation of a five-membered 1,2,3-trioxolane. The alternative formation of the dipolar ion II-2, particularly where there is a positive charge stabilizing electron donor, becomes the low-energy, preferred path. The epoxide results when the dipolar ion is formed. The epoxide formation inhibiting effect of the cis-β-R′ substituent is accounted for by a conformational change in the vinyl sulfide that forces the nonbonding electrons on the sulfur out of conjugation with the π electrons of the double bond.[36] The alkene, in this case, is just a simple 2π electron system, and the reaction proceeds as a normal [4 + 2] concerted addition[37] to yield the 1,2,3-trioxolane IV, which leads to ozonolysis products. As vinyl sulfides **1d** and **1i** are transformed almost completely to epoxides without solvent polarity effects, do zwitterion intermediates deal effectively with the results? The inference is that [2 + 1] cycloaddition of ozone delivering II-1 as well as formation of II-2 should be more solvent dependent than substrate dependent.

Fortunately, the above conclusions suggest an alternative reaction pathway involving a polarized cyclic intermediate like IV$_A$ of low-ionic character. The structural arrangement within IV$_A$ is seen to be properly predisposed for conversion to both epoxides and ozonolysis products. Moreover, as an early transition state would resemble a two-plane orientation of the reactants (eq 1, Scheme IV); this mechanism also appears to require the electrophilic ozone species to approach in a plane perpendicular to the C=C bond.

---

(32) For a discussion of 1,3-dipolar cycloaddition: (a) Wei, Y. K.; Cvetanovic, R. J. *Can. J. Chem.* **1963**, *41*, 913. Huisgen, R. *J. Org. Chem.* **1976**, *41*, 403. (b) Firestone, R. A. *Tetrahedron* **1977**, *33*, 3009. Lluch, J. M.; Bertrân, J. *Tetrahedron* **1982**, *38*, 1847. Haque, M. S. *J. Chem. Ed.* **1984**, *61*, 490. (c) Harding, L. B.; Goddart, W. A. III., *J. Am. Chem. Soc.* **1978**, *100*, 7180. Cremet, D. J. *Chem. Phys.* **1979**, *70*, 1898.

(33) (a) Koole, N. J.; DeBie, M. J. A.; Hansen, P. E. *Org. Magn. Reson.* **1984**, *22*, 146. For comparison with the enol ethers, see: Taskinen, E.; Mukkala, V. M. *Tetrahedron* **1982**, *38*, 613. Dodziuk, H.; Von Voithenberg, H.; Allinger, N. L. *Tetrahedron* **1982**, *38*, 2811. (b) Barton, D. H. R. *J. Chem. Soc.* **1953**, 1027.

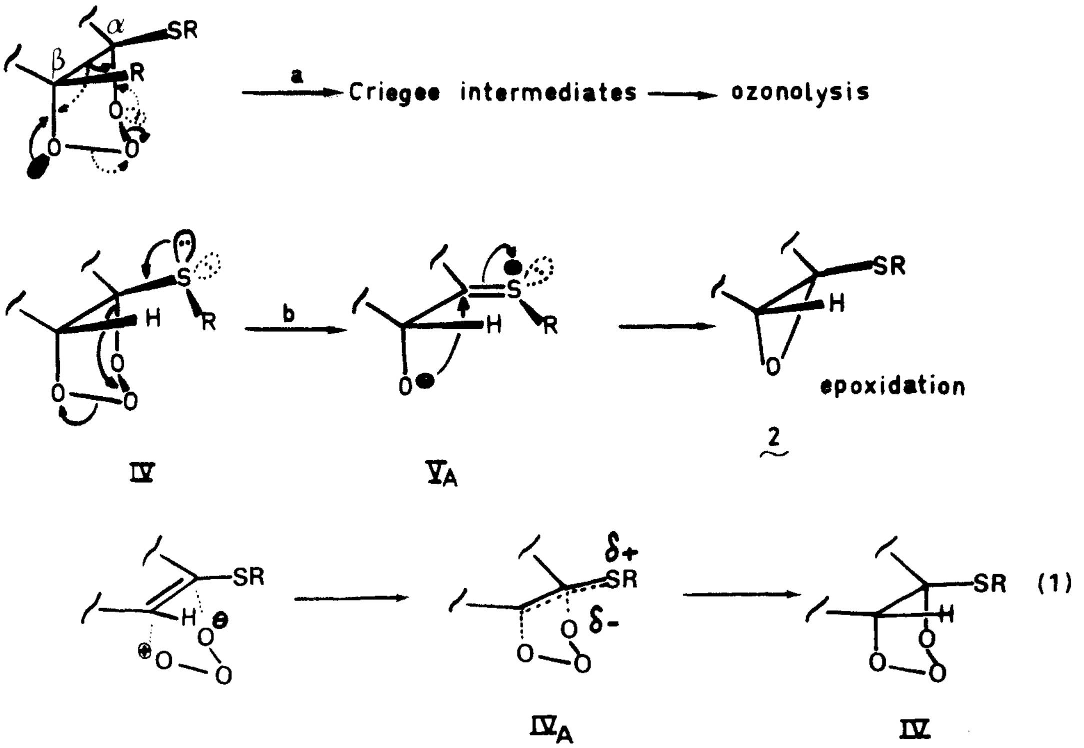
(34) With regard to five-membered-ring formation, the lone pair of electrons on the sulfur can simply function as a perturbation. But, in this case, the conjugative effects with the double bond may also be viewed in favor of a two-step mechanism leading to the 1,2,3-trioxolane IV.

(35) Woodward, R. B.; Hoffman, R. *The Conservation of Orbital Symmetry*; Academic: New York, 1970.

(36) This observation was suggested by a reviewer, whom we thank for his comments.

(37) An alternative scenario for cycloaddition may be envisioned. For example, an initial electrophilic attack of ozone on sulfur would produce a doubly charged intermediate which, by a [3.3] sigmatropic rearrangement followed by intramolecular quenching, may lead to IV. For several reasons (A strain, stereoselectivity, etc...), this process is not readily reconciled with our results.

Scheme IV. Schematic of Competitive Mechanisms[44] for Vinyl Sulfides with Ozone



Decomposition of the 1,2,3-Trioxolane IV. To our knowledge there is no direct evidence in olefin chemistry that initial ozonides IV are intermediates in the formation of epoxides. The expected high reactivity of sulfur-substituted 1,2,3-trioxolane IV has prevented any characterization by physical methods under our working conditions. Such a reactivity derives presumably from the interaction between sulfur atom and neighboring O–O bond. The nature of this interaction is outlined in Scheme IV.

One of the striking observations here is that oxidative cleavage (pathway a) occurs exclusively when a β-alkyl substituent, cis to the SR group, is present. The original Criegee proposal[38] probably holds in this situation, but a successful mechanism for ozonolysis would require more data before a final conclusion on the preferentially produced carbonyl oxide[39] can be made.

In contrast, the second mechanism (pathway b) can be viewed as the result of mutual influences of competing heteroatoms at the α-position in the absence of any steric effect. The structure of IV appears to be a compromise between the minimization of steric interactions and the lone pair–lone pair repulsions. Such a situation leads to a near-planar arrangement of the H–C_β–C_α–S–R fragment and confers an orbital properly oriented on the sulfur atom for controlling the course of ozonide rearrangement.[40] Deslonchamps and Lehn[41] have provided a theory and extensive work on the selective cleavage of tetrahedral intermediates in ester and amide hydrolysis. In that theory, the specific decomposition of such intermediates is controlled by trans antiperiplanar lone pairs. The same type of reasoning here may explain the epoxide formation. Then, in spite of the instability of primary ozonide IV due to its proclivity to generate Criegee intermediates, stereoelectronic cleavage of the C_α–O bond would occur because of the antiperiplanar oriented orbital on sulfur to the departing oxygen molecule. The resulting thionium ion V_A (thiocarbocation) may be intramolecularly captured by the reactive nucleophilic oxygen to give sulfur-substituted epoxide 2. Similar behavior associated with methylene sulfonium ion toward nucleophilic attack is well-illustrated in the Pummerer reaction.[42]

Simple rationalization of the stereochemical requirement for epoxidation may be seen originally in terms of eclipsing effects: while A strain developed in the corresponding transition state of the orbital, assisted mechanism b places no new steric congestion on the system, the strain already present in the starting primary ozonide that bears a β-alkyl substituent cis to the SR group would introduce a strong bias for the ozonolysis mechanism a. The nature of the group attached to the sulfur atom has been noted also to influence the fate of the initial ozonide IV. The ability of (phenylthio)alkenes (**1f** for example) to enter into this scheme can be explained by postulating that the phenyl sulfide bond "ties up" the nonbonding electrons of the sulfur so that they cannot interact effectively with the 1,2,3-trioxolane system. From all these conclusions, we are led to believe that the initial adduct formed by addition of ozone to vinyl sulfides might be a primary ozonide IV;[43]

---

[38] Criegee, R.; Wenner, G. *Justus Liebigs Ann. Chem.* **1949**, *9*, 564.

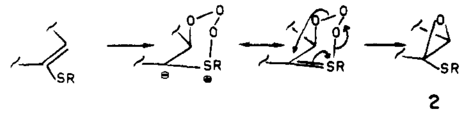
[39] For a nearly exclusive breakdown of the initial ozonide obtained from ozonolysis of methyl vinyl ether into $H_2\ ^{+}COO^{-}$ see: Keul, H.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1984**, *106*, 5370. From ozonolysis of monochlorinated olefins: Meister, M.; Zwick, G.; Griesbaun, K. *Can. J. Chem.* **1983**, *61*, 2385.

[40] In view of stereoelectronic control over the decomposition of the primary ozonide IV_A, the nature of the group attached to sulfur atom may play a role. In this regard, the alkyl substituent proved to be superior to the phenyl one (cf. **1d** to **1f**, Table I).

[41] Lehn, J. M.; Wipff, G. *J. Am. Chem. Soc.* **1974**, *96*, 4048. Deslongchamps, P. *Tetrahedron* **1975**, *31*, 2463. Deslongchamps, P.; Taillefer, R. J. *Can. J. Chem.* **1975**, *53*, 3029.

[42] Tillet, J. G. *Chem. Rev.* **1976**, *76*, 747. For recent and particular examples of intramolecular trapping see also: Ueda, N.; Shimizu, H.; Kataoka, T.; Hori, M. *Tetrahedron Lett.* **1984**, *25*, 757 and Byers, J. H.; Spencer, T. A. *Tetrahedron Lett.* **1985**, *26*, 713.

[43] This reasonable assumption accounts, apparently, for ozonolysis as well as ozonation. A pathway in which suitable vinyl sulfides might react in a [3 + 3] fashion as represented below is not completely ruled out for epoxidation.



the reaction course then followed being highly dependent on substituents at the β- and β'-sites.[44]

Conclusion

The ozone-mediated epoxidation of cycloalkenyl sulfides has been demonstrated to proceed readily and regioselectively to give transposed allylic alcohols in reasonable to high yield. Several experiments have indicated the intermediacy of alkylthio carbenium ions which are known to constitute an important class of intermediates in organic reactions. Moreover, the investigation of the five-membered-ring (alkylthio)-1,2,3-trioxolane IV reactivity as a function of steric, electronic, and conformational factors has enabled us to devise general schemes for explaining most of the observations concerning ozone–vinyl sulfide reactions, including ozonation and ozonolysis. On the other hand, the above results suggest that the vinyl sulfide is more promising than other electron-rich alkenes for the overall success of ozone-mediated epoxidation. Of particular interest is the sulfur-substituted epoxide isomerization into an axial allylic alcohol since this new method of introducing a hydroxyl group might find various applications in synthesis. We are currently studying the scope of this reaction and its synthetic utility.

Experimental Section

Melting points were determined on a Reichert microscope and are uncorrected. Infrared spectra were run on a Perkin Elmer 221 or 225 spectrophotometer in CCl_4 solution, unless otherwise stated. ^1H NMR spectra were recorded with Varian A 60 D or EM 360 instrument in $CDCl_3$ relative to Me_4Si as internal standard. For each signal, chemical shifts (ppm), multiplicity, intensity, and coupling constant (Hz) are reported in that order by using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; and $W_{1/2}$, width of peak at half height. ^{13}C NMR spectra were taken on a Bruker spectrospin WP 60 apparatus operating at 15.08 MHz and measured in $CDCl_3$ solution relative to Me_4Si (δ 0.00). Mass spectra were recorded on a Varian CH 5 spectrometer at an ionizing voltage of 70 eV. Microanalysis were performed by the center of analyses of the C.N.R.S., 69390 Vernaison. Preparative separations were performed by column chromatography packed with either 0.063–0.200 mm mesh Merck silica gel or Woelm neutral alumina adsorbant. VPC analyses were carried out on a 3 m × $^3/_8$ in. SEDC 550 5% on Chromosorb GAW 60/80 column in a Girdel series 3000 chromatograph. The ozone source was a laboratory Trailigaz-Welsbach T 23 type ozone generator using pure dry oxygen as the feed gas.

Materials. Dichloromethane was distilled from phosphorus pentoxide prior to use. Pyridine was distilled from calcium hydride and stored over KOH pellets. The cycloalkenyl sulfides **1d,e,f,h** were synthesized by conversion of the commercial ketones to thioalkyl or thiophenyl ketals followed by thermal cracking distillation[15] at atmospheric pressure and were previously described, except **1h**. Reductive thioalkylation under Birch conditions[45] of thioisophorone afforded the expected regio-defined vinyl sulfide **1i**.

3,3,5,5-Tetramethyl-1-(phenylthio)cyclohexene (1h): 80% yield by column chromatography on silica gel, mp 57 °C: ^1H NMR δ 0.93 (s, 6 H), 1.07 (s, 6 H), 1.32 (s, 2 H), 1.83 (d, 2 H, J = 2 Hz), 5.84 (t, 1 H, J = 2 Hz), 7.0–7.7 (m, 5 H).

General Procedures for Ozonation. Ozone concentration was calculated by bubbling the gas stream through a 10% aqueous solution of KI for a measured period of time and by titrating the liberated iodine with a 0.1 N sodium thiosulfate solution. Under standard working conditions (P_{O_2}, 1.5 bar; flow rate, 50 L/h; power, 50 W) the flow rate of ozone was approximately 1 mmol/min. The ozonations were performed in an oven-dried Pyrex vessel equipped with a gas inlet tube and connected to a bubbler containing a KI solution. In all cases, the progress of the reaction was followed by TLC or ^1H NMR. In a typical experiment, a solution of thioenol ether **1** (20 mmol) in 50 mL of dry CH_2Cl_2 and 0.5 mL (5 mmol) of pyridine was ozonized at the temperature of a solid CO_2–acetone cooling bath. When a stoichiometric amount (method A) or 2 molar equiv of ozone (method B) were consumed, the crude solution was allowed to warm up to room temperature, and then, after removal of the solvent, the residual mixture was purified by chromatography.

Method A. In most cases, the initial allylic alcohol **3** isomerized during workup. Nevertheless, attempts to purify **3** have been made upon neutral alumina (unless otherwise stated) by eluting the column initially with petroleum ether and then with minor amounts of ethyl acetate. Fractions containing by order of elution, if present, ketones **4**, ozonolysis product **5**, and allylic alcohol **3** were freed from solvent in vacuo.

(a) Ozonation of 4-*tert*-butyl-1-(methylthio)cyclohexene (**1d**): 3.7 g (20 mmol) of **1d** gave 0.6 g (15%) of ketones **4d** (E/Z:4/1), 0.18 g (5%) of ozonolysis product **5d**, and 2.20 g (55%) of allylic alcohol **3d**.

(*Z*)-5-*tert*-Butyl-2-(methylthio)cyclohexanone (4d): IR 1695 cm^{-1} ($\nu_{C=O}$); ^1H NMR δ 0.88 (s, 9 H), 1.5–3.0 (m, 7 H), 2.03 (s, 3 H), 3.17 (br t, 1 H_{eq}, $W_{1/2}$ = 7 Hz); ^{13}C NMR δ 15.1, 21.7, 27.2, 31.1, 32.8, 37.9, 49.4, 52.5, 209.2; **(E)-4d:** IR 1710 cm^{-1} ($\nu_{C=O}$); ^1H NMR δ 0.90(s, 9 h), 1.15–3.0 (m, 7 H), 2.10 (s, 3 H), 3.38 (dd, 1 H_{ax}, J = 6 and 12 Hz); ^{13}C NMR δ 14.0, 27.0, 27.2, 32.8, 43.5, 49.3, 52.4, 207.6. Anal. Calcd for $C_{11}H_{20}OS$ (E/Z mixture): C, 65.94; H, 10.06; O, 7.98. Found: C, 66.23; H, 10.06; O, 8.33.

***S*-Methyl 4-*tert*-butyl-6-oxohexanethioate (5d)** (as a clear oil): IR 1685 and 1720 cm^{-1} ($\nu_{C=O}$); ^1H NMR δ 0.72 (s, 9 H), 1.6–3.0 (m, 7 H), 2.30 (s, 3 H), 9.85 (t, 1 H, J = 1 Hz); ^{13}C NMR δ 11.5, 27.1, 27.4, 30.8, 41.8, 43.0, 45.8, 199.6, 207.0; MS, m/e (rel intensity) 216 (5), 169 (25), 123 (20), 57 (95), 41 (100).

(*E*)-5-*tert*-Butyl-2-(methylthio)cyclohex-2-en-1-ol (3d) as a colorless oil or a semisolid near 0 °C: IR 1625 cm^{-1} ($\nu_{C=C}$); ^1H NMR δ 0.90 (s, 9 H), 1.0–2.4 (m, 5 H), 2.00 (masked, OH), 2.23 (s, 3 H), 4.17 (br t, 1 H, $W_{1/2}$ = 7 Hz), 5.67 (dd, 1 H, J = 2 and 5 Hz), ^{13}C NMR δ 14.6, 27.3, 28.3, 31.6, 32.4, 37.3, 64.2, 125.1, 135.6.

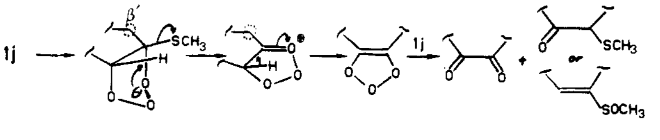
(b) Ozonation of **1e** (4.0 g, 20 mmol) afforded by silica gel chromatography 2.10 g (45%) of ketones **4e** (E/Z:9/1), 0.45 g (10%) of ozonolysis product **5e**, and 1.35 g (25%) of allylic alcohol **3e**.

(*Z*)-5-*tert*-Butyl-2-(ethylthio)cyclohexanone (4e) as a clear oil: IR 1710 cm^{-1} ($\nu_{C=O}$): ^1H NMR δ 0.90 (s, 9 H), 1.22 (t, 3 H, J = 7.5 Hz), 2.43 (q, 2 H, J = 7.5 Hz), 1.2–3.1 (m, 7 H), 3.18 (br t, 1 H eq, $W_{1/2}$ = 8 Hz); ^{13}C NMR δ 14.4, 21.8, 26.0, 27.2, 31.4, 32.8, 38.0, 49.5, 50.2, 209.7; MS, m/e (rel intensity) 214 (50), 154 (100). **(*E*)-4e:** IR 1715 cm^{-1} ($\nu_{C=O}$); ^1H NMR δ 0.90 (s, 9 H), 1.23 (t, 3 H, J = 7.5 Hz), 1.5–3.0 (m, 9 H), 3.50 (dd, 1 H_{ax}, J = 6 and 13 Hz); ^{13}C NMR δ 14.4, 24.3, 26.4, 27.6, 30.7, 33.2, 43.2, 49.7, 53.6, 207.7. Anal. Calcd for $C_{12}H_{22}OS$ (E/Z mixture): C, 67.23; H, 10.35; O, 7.46. Found: C, 66.75; H, 10.34; O, 8.16.

***S*-Ethyl 4-*tert*-butyl-6-oxohexanethioate (5e)** as a semisolid: IR 1690 and 1730 cm^{-1} ($\nu_{C=O}$); ^1H NMR δ 0.90 (s, 9 H), 1.23 (t,

---

[44] From consideration of the specificity of mechanisms in Scheme IV, it was anticipated that substitution at β'-carbon would strongly affect the partial cleavage mode. To test briefly this hypothesis, we did ozonation of 1-(methylthio)-3,3,5,5-tetramethylcyclopentene (**1j**) and isolated besides α-methylthio ketone or the vinyl sulfoxide, depending on conditions used, the corresponding 1,2-diketone. This result is not unprecedented.[46] Since a complete description of this new mechanism deserves a study of its own, it is interesting to note that the postulated trioxolene intermediary[47] VII has been often used as a probe of diketone synthesis and is a known potent oxenoid agent.[48]



[45] Metzner, P.; Vialle, J. *Bull. Soc. Chim. Fr.* **1972**, 3138; **1973**, 1703.

[46] Chaussin, R.; Leriverend, P.; Paquer, D. *J. Chem. Soc., Chem. Commun.* **1978**, 1032.

[47] Miller, D. J.; Nemo, T. E.; Hull, L. A. *J. Org. Chem.* **1975**, *40*, 2675. Jackson, S.; Hull, L. A. *J. Org. Chem.* **1976**, *41*, 3340.

[48] Keay, R. E.; Hamilton, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 6578.

3 H, J = 7.5 Hz), 2.82 (q, 2 H, J = 7.5 Hz), 1.5–3.0 (m, 7 H), 9.78 (t, 1 H, J = 1 Hz); ^{13}C NMR δ 14.7, 23.2, 27.4, 31.3, 33.5, 41.6, 43.1, 45.7, 199.0, 202.2.

(*E*)-5-*tert*-Butyl-2-(ethylthio)cyclohex-2-en-1-ol (3e) as a clear oil: IR 1630 cm^{-1} ($\nu_{C=C}$); ^{1}H NMR δ 0.90 (s, 9 H), 1.26 (t, 3 H, J = 7.5 Hz), 1.40–2.70 (m, 5 H), 2.59 (q, 2 H, J = 7.5 Hz), 4.14 (br t, 1 H, $W_{1/2}$ = 7 Hz), 5.80–6.05 (m, 1 H).

(c) Ozonation of **1f** (4.9 g, 20 mmol) led to 2.5 g (45%) of ozonolysis product **5f** and among undefined oils, 0.5 g (10%) of ketones **4f** (*E*/*Z*:5/1).

***S*-Phenyl 4-*tert*-butyl-6-oxohexanethioate (5f)** as a pale yellow oil: IR 1695 and 1720 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR δ 0.75 (s, 9 H), 1.20–2.90 (m, 7 H), 7.34 (s, 5 H), 9.76 (t, 1 H, J = 1 Hz).

5-*tert*-Butyl-2-(phenylthio)cyclohexanone (4f) (*E*/*Z* mixture) as a yellow oil: IR 1700 and 1710 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR δ 0.87 (*E*) and 0.90 (*Z*) (2 s, 9 H), 1.2–2.9 (m, 7 H); 3.73 (*E*) and 3.85–4.20 (*Z*) (m, $W_{1/2}$ = 7 Hz and m, respectively, 1 H), 6.9–7.6 (m, 5 H).

(d) Ozonation of **1h** (4.9 g, 20 mmol) led to ozonolysis product **5h** (2–3%), 1.1 g (20%) of ketone **4h**, and 3.10 g (60%) of alcohol **3h**. In this case, **3h** isomerized to **4h** during workup.

4,4,6,6-Tetramethyl-2-(phenylthio)cyclohexanone (4h) as yellow oil: IR 1710 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR δ 0.98 (s, 3 H), 1.10 (s, 3 H), 1.15 (s, 3 H), 1.24 (s, 3 H), 1.60 (s, 2 H), ABX system: δ_A 1.70, δ_B 1.91 (AB part, dq, 2 H, J_{AB} = 10 Hz), δ_X 4.36 (X part, dd, 1 H, J_{AX} = 12 Hz, J_{BX} = 6 Hz), 7.15–7.85 (m, 5 H); ^{13}C NMR δ 27.7, 27.9, 28.1, 31.6, 32.9, 45.2, 46.7, 51.6, 53.3, 127.1, 129.0, 131.7, 133.0, 211.6. Anal. Calcd for $C_{16}H_{22}OS$: C, 73.23; H, 8.45. Found: C, 72.76; H, 8.60.

***S*-Phenyl 3,3,5,5-tetramethyl-6-oxohexanethioate (5h)** as a colorless oil: IR 1710 and 1730 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR δ 1.02 (s, 6 H), 1.07 (s, 6 H), 1.72 (s, 2 H), 2.50 (s, 2 H), 7.35 (br s, 5 H), 9.43 (s, 1 H); ^{13}C NMR δ 197.6, 206.2, (C=O); MS, *m/e* (rel intensity) 278 (3), 250 (5), 218 (85), 169 (85), 109 (100).

4,4,6,6-Tetramethyl-2-(phenylthio)cyclohex-2-en-1-ol (3h) as a clear oil: IR 1570 cm^{-1} ($\nu_{C=C}$); ^{1}H NMR δ 0.93 (s, 6 H), 1.05 (s, 3 H), 1.10 (s, 3 H), 1.45 (d, 2 H, J = 14 Hz), 1.90–2.05 (br s, 1 H), 3.44 (s, 1 H), 5.80 (s, 1 H), 7.0–7.5 (m, 5 H); ^{13}C NMR δ 25.1, 29.3, 30.5, 33.9, 34.4, 35.6, 45.0, 74.1, 124.8, 127.6, 130.6, 134.8, 141.3, 144.3.

(e) Ozonation of **1i** (3.7 g, 20 mmol) led to 3.4 g (85%) of allylic alcohol **3i** from silica gel chromatography. Minor products were not isolated. Further purification was accomplished by preparative VPC (10% SE-30, 180 °C).

4,4,6-Trimethyl-2-(methylthio)cyclohex-2-en-1-ol (3i) as a colorless liquid: IR 1625 cm^{-1} ($\nu_{C=C}$); ^{1}H NMR δ 0.97 (s, 3 H), 1.00 (s, 3 H), 1.03 (d, 3 H, J = 7 Hz), 1.20–1.95 (m, 3 H), 2.20 (s, 3 H), 2.34 (br s, OH), 3.78 (d, 1 H, J = 3.4 Hz), 5.23 (s, 1 H); ^{13}C NMR δ 14.6, 17.4, 27.8, 31.2, 31.6, 34.7, 38.8, 69.8, 133.5, 134.6. Anal. Calcd for $C_{10}H_{18}OS$: C, 64.46; H, 9.74. Found: C, 64.30; H, 9.95.

Method B. The treatment of thioenol ethers **1** (20 mmol) with 2 molar equiv of ozone provided diastereomeric epoxy sulfoxides **6** and **7** (ratio 1:1) as major products and small amounts of ozonolysis products **5**. No attempts have been made to isolate minor products arising from oxidation on sulfur. The purification step over silica gel (petroleum ether/ethylacetate:70/30:v/v as eluent) was generally followed by recrystallization of **6** and **7** in petroleum ether (twice) or pentane. See Table II for structural data R/S.

(a) Ozonation of **1d** (3.7 g, 20 mmol) gave 0.8 g (20%) of ozonolysis product **5d** and 2.15 g (50%) of epimeric epoxy sulfoxides **6d** and **7d**.

4-*tert*-Butyl-1,2-epoxycyclohexyl methyl sulfoxide (6d) (*S*$_S$,*S*,*S*) as colorless crystals: mp 72 °C; IR 1063 and 1078 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 9 H), 1.0–2.40 (m, 6 H), 2.50 (s, 3 H), 2.66 and 2.78 (dd, 1 H, J = 13 and 6 Hz), 3.64 (br s, 1 H, $W_{1/2}$ = 5 Hz); (C_6D_6) δ 0.63 (s, 9 H), 0.9–1.95 (m, 6 H), 2.09 (s, 3 H), 2.62 and 2.84 (dd, 1 H, J = 13 and 6 Hz), 3.25 (br s, 1 H, $W_{1/2}$ = 5 Hz); ^{13}C NMR δ 17.7, 22.9, 26.5, 27.1, 31.8, 33.3, 39.6, 62.0, 70.5. Anal. Calcd for $C_{11}H_{20}O_2S$: C, 61.07; H, 9.32; O, 14.79. Found: C, 61.35; H, 9.53; O, 15.11.

7d (*R*$_S$,*S*,*S*) as colorless crystals: mp 76 °C; IR 1069 and 1080 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR ($CDCl_3$) δ 0.83 (s, 9 H), 1.10–2.35 (m, 7 H), 2.50 (s, 3 H), 3.73 (br s, 1 H, $W_{1/2}$ = 5 Hz); (C_6D_6) δ 0.63 (s, 9 H), 0.90–1.90 (m, 7 H), 2.03 (s, 3 H), 3.62 (br s, 1 H, $W_{1/2}$ = 5 Hz); ^{13}C NMR δ 22.9, 24.2, 26.2, 27.2, 31.0, 32.5, 39.7, 57.6, 72.4. Anal. Calcd for $C_{11}H_{20}O_2S$: C, 61.07; H, 9.32; O, 14.79. Found: C, 61.15; H, 9.60; O, 14.86.

(b) Ozonation of **1e** (4.0 g, 20 mmol) gave 0.46 g (10%) of the ozonolysis product **5e** and 2.7 g (60%) of epoxy sulfoxides **6e** and **7e**.

4-*tert*-Butyl-1,2-epoxycyclohexyl ethyl sulfoxide (6e) (*S*$_S$,*S*,*S*) as colorless crystals: mp 60 °C; IR 1062 and 1074 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR δ ($CDCl_3$) 0.83 (s, 9 H), 1.32 (t, 3 H, J = 7 Hz), 1.2–2.6 (m, 7 H), 2.73 (q, 2 H, J = 7 Hz), 3.60 (br t, 1 H, $W_{1/2}$ = 5 Hz); (C_6D_6) δ 0.63 (s, 9 H), 1.05 (t, 3 H, J = 7 Hz), 0.8–2.2 (m, 6 H), 2.42 (q, 2 H, J = 7 Hz), 2.72 (dd, 1 H, J = 13 and 6 Hz), 3.26 (br s, 1 H, $W_{1/2}$ = 5 Hz); ^{13}C NMR δ 7.2, 18.9, 23.3, 26.6, 27.2, 31.9, 39.9, 41.6, 61.1, 70.4. Anal. Calcd for $C_{12}H_{22}O_2S$: C, 62.56; H, 9.63; O, 13.89. Found: C, 62.66; H, 9.70; O, 13.93.

7e (*R*$_S$,*S*,*S*) as colorless prisms: mp 85 °C; IR 1069 and 1080 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR ($CDCl_3$) δ 0.83 (s, 9 H), 1.37 (t, 3 H, J = 7 Hz), 1.30–2.60 (m, 7 H), 2.72 (q, 2 H, J = 7 Hz), 3.66 (br t, 1 H, $W_{1/2}$ = 5 Hz); (C_6D_6) δ 0.63 (s, 9 H) 1.10 (t, 3 H, J = 7 Hz), 1.2–2.80 (m, 9 H), 3.62 (br t , 1 H, J = 5 Hz); ^{13}C NMR δ 7.4, 22.9, 24.5, 26.1, 27.2, 31.9, 39.6, 40.8, 56.7, 71.8. Anal. Calcd for $C_{12}H_{22}O_2S$: C, 62.56; H, 9.63; O, 13.89. Found: C, 62.59; H, 9.51; O, 13.67.

(c) Ozonation of **1g** has been previously described.[5] Only for comparison with the above results ^{1}H NMR spectra in $CDCl_3$ and C_6H_6 of diastereomeric epoxy sulfoxides **6g** and **7g** are reported.

1,2-Epoxy-3,3,5,5-tetramethylcyclohexyl methyl sulfoxide (6g) (*S*$_S$,*S*,*S*): ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 6 H), 1.07 (s, 3 H), 1.18 (s, 3 H + 2 H masked), 1.58 and 2.32 (ABq, 2 H, J = 15 Hz, signal at 2.32 shows a long range coupling J = 1 Hz), 2.52 (s, 3 H), 3.22 (br s, 1 H); (C_6H_6) δ 0.75 (s, 3 H), 0.81, 0.85 and 0.89 (3 s, 9 H + 2 H masked), 1.27 and 2.29 (ABq, 2 H, J = 15 Hz, long range coupling, J = 1 Hz, for H at 2.29), 2.03 (s, 3 H), 2.93 (br s, 1 H).

7g (*R*$_S$,*S*,*S*): ^{1}H NMR ($CDCl_3$) δ 0.95 (s, 3 H), 1.00 (s, 3 H), 1.10 and 1.17 (2 s, 6 H + 2 H masked), 1.58 (s, 2 H), 2.52 (s, 3 H), 3.37 (s, 1 H); (C_6H_6) δ 0.69 (s, 6 H), 0.80 and 0.95 (2 s, 6 H + 2 H masked), 1.17 (s, 2 H), 2.06 (s, 3 H), 3.41 (s, 1 H).

(d) Ozonation of **1h** (4.9 g, 20 mmol) gave 0.25 g (5%) of ozonolysis product **5h** and 4.15 g (75%) of two epoxy sulfoxides **6h** and **7h**.

1,2-Epoxy-3,3,5,5-tetramethylcyclohexyl phenyl sulfoxide (6h) (*R*$_S$,*S*,*S*) as colorless prisms: mp 118 °C; IR (KBr) 1050 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR ($CDCl_3$) δ 0.79 (s, 6 H) 1.05 and 1.15 (two s, 6 H, + 2 H masked), 1.03 and 1.95 (ABq, 2 H, J = 15 Hz), 3.44 (s, 1 H), 7.35–7.90 (m, 5 H); (C_6D_6) δ 0.57 (s, 3 H), 0.84 and 0.87 (two s, 6 H + 2 H masked), 0.94 (s, 3 H), 0.97 and 2.18 (ABq, 2 H, J_{AB} = 15 Hz, long-range coupling J = 2 Hz for H at 2.18), 3.23 (s, 1 H), 7.0–7.35 (m, 3 H), 7.70–8.10 (m, 2 H); ^{13}C NMR δ 27.2, 28.5, 29.3, 29.7, 30.8, 31.7, 32.1, 46.4, 65.6, 74.8, 125.0, 128.8, 131.2, 140.2. Anal. Calcd for $C_{16}H_{22}O_2S$: C, 69.02; H, 7.97; O, 11.52. Found: C, 69.43; H, 8.03; O, 11.16.

7h (*S*$_S$,*S*,*S*) as colorless needles: mp 98 °C; IR (KBr) 1045 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR ($CDCl_3$) δ 0.75 (s, 3 H), 0.81 (s, 3 H), 1.07 (s, 3 H), 1.11 (s, 3 H), 1.23 and 1.73 (ABq, 2 H, J = 15 Hz + 2 H masked), 3.39 (s, 1 H), 7.4–7.85 (m, 5 H); (C_6D_6) δ 0.45 (s, 3 H), 0.58 (s, 3 H), 0.77 (s, 3 H), 0.95 (s, 3 H), 0.80 (masked) and 1.17 (ABq, 2 H, J = 11 Hz), 1.27 and 1.75 (ABq, 2 H, J = 15 Hz, long-range coupling for H at 1.75, J = 2 Hz), 3.32 (s, 1 H), 7.0–7.35 (m, 3 H), 7.50–7.70 (m, 2 H); ^{13}C NMR δ 27.4, 28.8, 29.3, 30.1, 30.7, 32.1, 35.4, 46.6, 62.6, 76.4, 125.9, 129.2, 131.9, 140.1; MS, *m/e* (rel intensity) 278 (1), 262 (2), 247 (2), 153 (50), 69 (100). Anal. Calcd for $C_{16}H_{22}O_2S$: C, 69.02; H, 7.97; O, 11.52. Found: C, 69.17; H, 7.98; O, 11.58.

(e) Ozonation of **1i** (3.5 g, 20 mmol) yielded ca. 3.30 g (80%) of epimeric epoxy sulfoxides **6i** and **7i**.

1,2-Epoxy-3,5,5-trimethylcyclohexyl methyl sulfoxide (6i) (*S*$_S$,*S*,*S*) as a semisolid near room temperature; IR ($CDCl_3$) 1050 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR ($CDCl_3$) δ 0.96 (d, 3 H, J = 6 Hz), 0.97 (s, 3 H, plus 2 H masked), 1.12 (s, 3 H), 1.52 and 2.28 (ABq, 2 H, J = 15 Hz, long-range coupling, J = 2 Hz for H at 2.28), 1.70–2.40 (m, 1 H), 2.46 (s, 3 H), 3.43 (d, 1 H, J = 2 Hz); (C_6D_6) δ 0.75 (s, 3 H), 0.78 (s, 3 H), 0.87 (d, 3 H + 2 H masked), 1.22 and 2.20 (ABq, 2 H, J = 15 Hz), 1.50–2.10 (m, 1 H), 3.04 (d, 1 H, J = 2 Hz); ^{13}C NMR δ 17.8, 25.8, 26.9, 29.3, 30.2, 31.2, 33.3, 39.9, 63.7, 71.2. Anal. Calcd for $C_{10}H_{18}O_2S$: C, 59.36; H, 8.97; O, 15.82; Found: C, 58.85; H, 8.86; O, 16.00.

J. Org. Chem. **1986**, *51*, 2285–2289

7i (***R***$_S$**,*S*,*S***) as a colorless oil: IR ($CDCl_3$) 1058 cm^{-1} ($\nu_{S=O}$); ^1H NMR ($CDCl_3$) δ 0.94 (s, 3 H), 0.95 (s, 3 H), 1.10 (d, 3 H, J = 6 Hz), 1.10–1.35 (masked m, 2 H), 1.53 (s, 2 H), 1.85–2.40 (m; 1 H), 2.51 (s, 3 H), 3.57 (d, 1 H, J = 2 Hz); (C_6D_6) δ 0.62 (s, 3 H), 0.69 (s, 3 H), 0.75–1.0 (masked m, 2 H), 1.22 (s, 2 H), 2.10 (s, 3 H), 3.47 (d, 1 H, J = 2 Hz); ^{13}C NMR δ 17.9, 25.9, 26.4, 29.7, 31.1, 32.4, 36.4, 39.8, 59.3, 73.0. Anal. Calcd for $C_{10}H_{18}O_2S$: C, 59.36; H, 8.97; O, 15.82. Found: C, 59.36; H, 9.12; O, 15.62.

Characterization of the Intermediate α-(Methylthio) Epoxide 2i. The reaction of 3,5,5-Trimethyl-1-(methylthio)cyclohexene (**1i**) with 1 molar equiv of ozone in chloroform, according to the above general procedure (method A), was monitored by ^1H NMR as follows: at the end of the reaction, a crude sample was transferred from reaction vessel into the NMR tube. Its spectrum was immediately recorded at −80 °C. Then, from −80 °C to room temperature, NMR spectra were taken regularly. The characteristic signal for the epoxidic proton of **2i** (doublet at 3.2 ppm) disappeared near 0 °C, giving way to new signals of the corresponding allylic alcohol **3i**.

1,2-Epoxy-3,5,5-trimethylcyclohexyl methyl sulfide (2i): ^1H NMR ($CDCl_3$, −78 → 0 °C) δ 0.85–1.2 (m, 14 H), 1.85 (s, 2 H), 2.15 (s, 3 H), 3.24 (d, 1 H, J = 2 Hz).

Solvent and Temperature Effects. When the reactions of **1g** and **1i** with ozone (method A) were conducted in pentane or anhydrous ether with or without pyridine, at −78 °C, there were no significative differences between the ^1H NMR spectra of the crude concentrated mixtures. In these runs, allylic alcohols **3g** and **3i** were obtained as major products (∼85% yields). Nevertheless, pyridine was still effective as a reducing agent since ozonide formation could occur to some extent.

Temperature effects were found to be more pronounced. When **1d** (1.2 g, 6 mmol) was allowed to react with 1 equiv of ozone in CH_2Cl_2 above 0 °C, the expected allylic alcohol **3d** was formed in 60% yield together with epoxy sulfoxides **6d** and **7d** (10–15%) and the ozonolysis compound **5d** (15% in isolated yield). Under the same conditions, with more hindered vinyl sulfides **1g** and **1i**, 25% of the corresponding vinyl sulfoxides were produced along with the allylic alcohols (about 50%). In the former case, besides some unreacted vinyl sulfide **1g**, also isolated was 2,3-epoxy-4,4,6,6-tetramethyl-2-(methylsulfinyl)cyclohexanol[5] (10%).

Pyrolysis and Photolysis of 6,7-Diazatricyclo[3.2.2.1^{2,4}]dec-6-ene

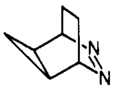
Tyze-Kuan Yin and Weston Thatcher Borden*

Department of Chemistry, University of Washington, Seattle, Washington 98195

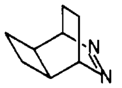
Received March 6, 1986

Pyrolysis at 200 °C and direct and sensitized photolysis of the title compound (**3a**) produced only *cis*-1,3-divinylcyclobutane (**6a**) and tricyclo[4.1.1.0^{2,5}]octane (**7a**). The latter hydrocarbon was prepared by an independent synthesis, which involved photochemical ring closure of bicyclo[4.1.1]octa-2,4-diene (**8**) to tricyclo[4.1.1.0^{2,5}]oct-3-ene (**9**), followed by hydrogenation of **9**. The ratio of **6a** to **7a** was 2.4:1 in the pyrolysis reaction, 3.3:1 in the direct photolysis, and >50:1 when the photolysis of **3a** was photosensitized. The kinetics of nitrogen loss from **3a** were measured at three different temperatures to yield $\log k$ (s^{-1}) = 15.0 ± 1.0 − (38 300 ± 2200)/2.3RT, with R in cal/mol·K. The stereochemistry of product formation was determined by preparation of the deuterium labeled azo compound **3b**. The **6** that resulted from pyrolysis and direct and sensitized photolysis of **3b** contained a 1:1 mixture of vinyl groups with E and Z stereochemistry. The ratio of **7b** to **7c** was 1.2:1 in the pyrolysis reaction and 1:2.4 in the direct photolysis, indicating 10% excess double retention of configuration in the former reaction and 40% excess double inversion in the latter. These results are discussed, and it is concluded that the high-lying filled orbitals of the 1,3-bridged cyclobutane ring of **3** have no apparent effect on its deazetation.

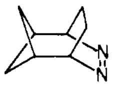
The bent bonds of suitably oriented cyclopropane rings have been shown to participate in concerted, $_\sigma2_s + {}_\sigma2_s + {}_\sigma2_s$ extrusion of nitrogen from azo compounds.[1] For example, the cyclopropane ring in **1** accelerates the rate of nitrogen loss from **1** dramatically compared to that from 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO).[2,3] The activation enthalpy of 21.5 kcal/mol for **1**[4] is less than half that of 43.5–45.0 kcal/mol for DBO.[5] Moreover, the only organic product formed in the thermally induced loss of nitrogen from **1** is 1,4-cycloheptadiene,[2,3] which is the product expected from cleavage of the participating cyclopropane ring bond.



1



2



3

Edge participation by cyclobutane in nitrogen extrusion reactions is less well established. For example, although the enthalpy of activation of 38.5 kcal/mol for nitrogen loss from **2**[3] is lower than that for DBO, the energy lowering may simply reflect greater strain relief in the transition state for deazetation of **2**.[6] Evidence against edge participation by cyclobutane in the transition state for nitrogen loss from **2** comes from the observation that, in addition to 1,5-cyclooctadiene, small amounts of *anti*-tricyclo[4.2.0.0^{2,5}]octane are formed.[6] Of course, the two products could be generated by separate pathways, the major involving edge participation by cyclobutane and the minor one diradical formation; and it has been argued that cyclobutane edge participation is a borderline situation.[7,8]

Azo compounds like **3**, containing a 1,3-bridged cyclobutane ring, have not been studied. Although edge participation of the cyclobutane ring in the transition state for deazetation of such an azo compound is impossible, the high-lying filled orbitals of the four-membered ring[9] can interact strongly with the orbitals that comprise the bonds between the bridgehead carbons and the departing nitrogen molecule. Interactions between the orbitals of cyclobutane and unsaturated 1,3-bridging groups have been

---

[1] For an excellent review of azo chemistry, see: Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

[2] Martin, M.; Roth, W. *Chem. Ber.* **1969**, *102*, 811.

[3] Allred, E. L.; Hinshaw, J. C. *J. Chem. Soc., Chem. Commun.* **1969**, 1021.

[4] Snyder, J. P.; Harpp, D. N. *J. Am. Chem. Soc.* **1976**, *98*, 7821.

[5] (a) Cohen, S. G.; Zand, R. *J. Am. Chem. Soc.* **1962**, *84*, 586. (b) Engel, P. S.; Hayes, R. A.; Kiefer, L.; Szilagyi, S.; Timberlake, J. W. *Ibid.* **1978**, *100*, 1876.

[6] Allred, E. A.; Hinshaw, J. C. *Tetrahedron Lett.* **1972**, 387.

[7] Berson, J. A.; Olin, S. S.; Petrillo, E. W.; Bickart, P. *Tetrahedron*, **1974**, *30*, 1639.

[8] Martin, H.-D.; Heiser, B.; Kunze, M. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 696.

[9] Hoffman, R.; Davidson, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 5699.

0022-3263/86/1951-2285$01.50/0 © 1986 American Chemical Society