(5), 107 (59), 106 (6), 93 (3), 80 (10), 79 (100), 52 (8). The product from **1a** in P-1 was a mixture of **4a** and **5a**, and the solution was heated at 80 °C to yield the solution of pure **5a**. The product from **1b** was usually a mixture of cis (meso) and trans-(±) (*dl*) isomers of 2,11-dimethyl-6,7,12a,12b-tetrahydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazine (**4b** and **5b**, respectively) in both procedures of P-1 and P-2. The pure **4b** was obtained by irradiating the solution of the mixture with a 500-W Hg lamp equipped with a UV-29 glass filter for 20 min. MS for **4b**: *m/z* 214 (M^+, 100), 213 (57), 120 (22), 93 (22), 91 (25). Pure **5b** was obtained by heating the solution of **4b** in a sealed tube at 80 °C for 4 h. MS for **5b**: *m/z* 214 (M^+, 40), 121 (28), 120 (11), 119 (14), 108 (11), 105 (3), 94 (13), 93 (100), 66 (13). The product from **1c** was also a mixture of cis and trans-(±) isomers of 2,11-di-*tert*-butyl-6,7,12a,12b-tetrahydrodipyrido[1,2-*a*:2′1′-*c*]pyrazine (**4c** and **5c**, respectively). The pure forms were yielded in a similar manner as above. MS for **4c**: *m/z* 298 (M^+, 9), 163 (100), 135 (68), 120 (51). MS for **5c**: *m/z* 298 (M^+, 11), 163 (100), 135 (64), 120 (46).

The concentration of each solution of cyclomers was determined in acetonitrile by following spectroscopically the slow formation of methylviologen cation radical (ϵ = 13000 at 605 nm)[11] from methylviologen dichloride.

Instrumentation. UV-vis spectra were measured on a Cary Model 14 spectrophotometer, ESR spectra were recorded on a Varian Model E-109E EPR spectrometer, and NMR spectra were recorded on a JEOL 90Q NMR spectrometer. The ^1H off-resonance decoupling and INEPT techniques were used to analyze ^{13}C NMR spectra. Irradiation was carried out with a Ushio 500-W Hg lamp and Toshiba filters. Mass spectra were obtained by using a JEOL Model LMS-DX300 mass spectrometer.

Kinetic Treatment of Thermal Conversion. Thermal conversions of **4** into **5** were kinetically treated by measuring the change of a ^1H NMR spectrum with time at various temperatures. Change of the integrated signal intensities of H-12a,12b protons of **4** and **5** were analyzed as the first-order reaction. The sample was dissolved in CD_3CN, degassed, and then sealed in a tube.

Acknowledgment. We are grateful to Associate Professor Shozo Tero-Kubota and Dr. Kimio Akiyama for their helpful discussions. The present work was partially supported by Grants-in-Aid for Scientific Research Nos. 60430001 and 63540324 from the Ministry of Education, Science and Culture.

Reactions of an Allylic Sulfide, Sulfoxide, and Sulfone with Singlet Oxygen. The Observation of a Remarkable Diastereoselective Oxidation

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Contribution from the Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071. *Received December 5, 1988*

Abstract: The reactions of singlet oxygen with 1-[(4-methylphenyl)sulfinyl]-2,3-dimethyl-2-butene (**6**), 1-[(4-methylphenyl)sulfonyl]-2,3-dimethyl-2-butene (**7**), and 2,3-dimethyl-2-butenyl *p*-methylphenyl sulfide (**8**) have been examined. The formation of transient intermediates and products in the reaction of **8** have been followed as a function of extent of reaction and a remarkable diastereoselective reaction has been uncovered. The implications of this discovery for the mechanism of sulfide oxidation is discussed.

The photooxidation of sulfides (eq 1), first reported by Schenck[1] more than 25 years ago, remains an active area of investigation.

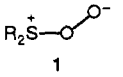
$$2R_2S + {}^1O_2 \rightarrow 2R_2SO \qquad (1)$$

The unraveling of the mechanistic complexities of this deceptively simple reaction has provided an intriguing challenge for the physical organic chemist.[2] In addition, the possibility that singlet oxygen is involved in the posttranslational modification of methionine to the sulfoxide and ultimately responsible for the loss of activity in several enzymes has attracted the interest of biochemists.[3]

Foote's group[4] in particular has extensively contributed to an understanding of dialkyl sulfide photooxidation. In aprotic solvents such as benzene or acetonitrile this reaction produces several interesting experimental observations which include the following: (1) For every mole of oxygen consumed, 2 mol of sulfoxide are produced. (2) Greater than 95% of all interactions of diethyl sulfide with singlet oxygen at room temperature are unproductive and lead to physical quenching and only 5% produce an oxidized product. (3) At lower temperatures (−78 °C) physical quenching is suppressed and product formation is accelerated. (4) The extent of physical quenching is independent of sulfide concentration. (5) Addition of diphenyl sulfoxide inhibits physical quenching. (6) The total rate of singlet-oxygen removal by the sulfide substrate is sensitive to steric bulk around the sulfur. (7) Decreasing concentrations of sulfide favors sulfone formation. (8) Increasing concentrations of sulfide favors sulfoxide formation. (9) Sulfides and sulfoxides do not compete for the same intermediate.

To explain these experimental observations, the mechanism invoking two intermediates, A and B, in Figure 1 was proposed. This mechanism satisfies the requirements that sulfide substrate and diphenyl sulfoxide do not compete for the same intermediate (experimental observation 9) and that physical quenching (k_q) is independent of sulfide concentration (experimental observation 4) but dependent on the concentration of added diphenyl sulfoxide (experimental observation 5).

No direct structural information is available on intermediates A or B. Diaryl sulfides, however, function as nucleophilic trapping agents[5] and diaryl sulfoxides as electrophilic trapping agents,[6] suggesting that A is best described as a persulfoxide **1** and B as



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2

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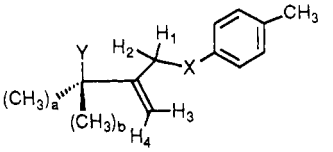
0002-7863/89/1511-5787$01.50/0

Table I. Proton NMR Data for **9**[a]



9

	(H_1, H_2)[b]	(H_3, H_4)	$(CH_3)_a$	$(CH_3)_b$	$ArCH_3$	Ar	OH/OOH
9a	3.58 (14)	5.38 (1.7)	1.23	1.46	2.43	7.44 (8)	10.9
	3.77 (14)	5.49				7.67 (8)	
9a′	3.58 (13)	4.80 (0.7)	1.33	1.35	2.4	7.4 (9)	4.1
	3.91 (13)	5.21				7.7 (9)	
9b	4.04	5.39	1.29	1.29	2.46	7.48 (9)	10.29
		5.45				7.85 (9)	
9b′	4.10	5.10	1.28	1.28	2.45	7.45 (9)	*c*
		5.36				7.82 (9)	
9c	3.77	5.17	1.39	1.39	2.30	7.1 (8)	10.25
		5.20				7.3 (8)	
9c′	3.74	5.07	1.38	1.38	2.30	7.1 (8)	3.8
		5.20				7.3 (8)	

[a] In acetone-d_6 referenced to internal TMS. [b] Chemical shift in ppm followed by coupling constants in parentheses in hertz. [c] Not observed.

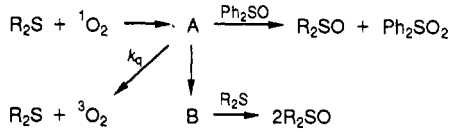
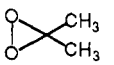


Figure 1. Foote mechanism for sulfide photooxidation.

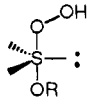
a thiadioxirane **2**. A recent theoretical study[7] of the additions of singlet oxygen to H_2S and Me_2S, however, was unable to locate a minimum on the potential energy surface corresponding to the thiadioxirane. This is a surprising outcome in view of the fact that dioxirane **3**[8] and dimethyldioxirane **4**[9] are well-characterized species.

3



4

The photooxidations of sulfides in methanol are very different reactions than those observed in aprotic solvents. Physical quenching does not compete with chemical reaction even at room temperature, and as a result, the formation of oxidized products are more efficient in methanol than in benzene. In addition, in protic solvents it is unnecessary to invoke a second intermediate to describe the kinetic behavior of sulfoxide-trapping experiments.[10] The absence of a detectable second intermediate has been attributed to either stabilization of the persulfoxide by hydrogen bonding or rapid conversion to a sulfurane **5**.[11] No direct experimental evidence for either intermediate was presented.



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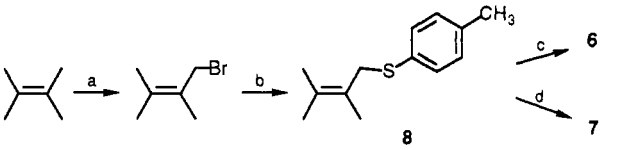
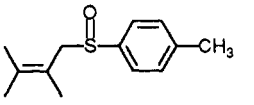


(a) $(PhCO_2)_2$, *N*-bromosuccimide, CCl_4, (b) Sodium *p*-methylthiophenoxide, EtOH, (c) 1 equiv of MCPBA, (d) 2 equiv of MCPBA.

Figure 2. Substrate synthesis.

In this paper we report a study of the photooxidations of the allylic sulfoxide **6**, sulfone **7**, and sulfide **8**[12] which implicates the sulfurane as an authentic intermediate.



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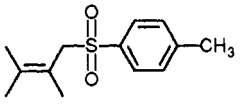

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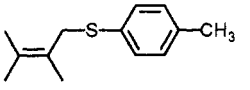

8

Results and Discussion

Substrates **6–8** were synthesized in the straightforward manner outlined in Figure 2. The oxidation reactions were maximized for sulfoxide formation by using slightly less than 1 equiv of *m*-chloroperbenzoic acid (MCPBA) and for sulfone formation by using greater than 1 equiv of MCPBA. Under these conditions, underoxidation or overoxidation was never completely eliminated but chromatographic separations readily produced pure samples of **6** and **7**. Epoxide formation was not detected in reactions maximized for sulfoxide or sulfone production.

Photooxidations were conducted by irradiation of 5×10^{-2} M oxygen-saturated acetone-d_6 solutions of **6–8** containing 2×10^{-5} M Rose Bengal at −78 °C. A 1-cm 0.5% potassium dichromate filter solution was placed between a 750-W projection lamp and the sample to insure that light was absorbed by the sensitizer but not the substrates or products. The reaction mixtures were presaturated with oxygen to maximize dye interaction with oxygen and to minimize dye–substrate interactions. Singlet oxygen is the oxidative intermediate in these reactions as verified by the ob-

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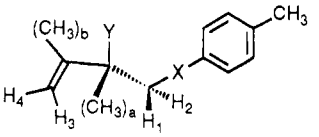
Table II. Proton NMR Data for **10**[a]



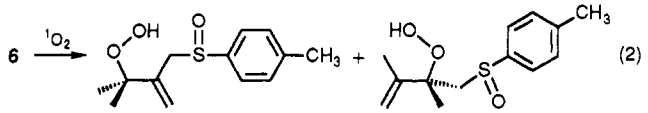
10

	(H_1, H_2)[b]	(H_3, H_4)	$(CH_3)_a$	$(CH_3)_b$	$ArCH_3$	Ar	OH/OOH
10a	3.3–3.4	4.85	1.54	1.84	2.41	7.4 (8)	10.6
		4.91				7.6 (8)	
10a′	2.95 (13.7)	4.88	1.57	1.81	2.40	7.4 (8)	4.7
	3.14 (13.7)	5.20				7.6 (8)	
10b	3.3–3.4	5.03	1.48	1.86	2.40	7.4 (8)	10.8
		5.08				7.6 (8)	
10b′	2.91 (13)	4.99	1.38	1.88	2.40	7.4 (8)	4.8
	3.18 (13)	5.28				7.6 (8)	
10c	3.74	4.90	1.58	1.76	2.45	7.45 (9)	10.2
		4.93				7.85 (9)	
10c′	3.48 (13.9)	4.78	1.44	1.65	2.44	7.45 (9)	*c*
	3.65 (13.9)	5.13				7.82 (9)	
10d	3.29	4.96	1.43	1.75	2.30	7.1 (8)	10.28
		5.02				7.3 (8)	
10d′	3.15 (13)	4.84	1.39	1.77	2.28	7.11 (8)	3.81
	3.26 (13)	5.11				7.29 (8)	

[a] In acetone-d_6 referenced to internal TMS. [b] Chemical shift in ppm followed by coupling constants in parentheses in hertz. [c] Not observed.

servation of identical product ratios (vide infra) in reactions using Rose Bengal and tetraphenylporphyrin as sensitizers.

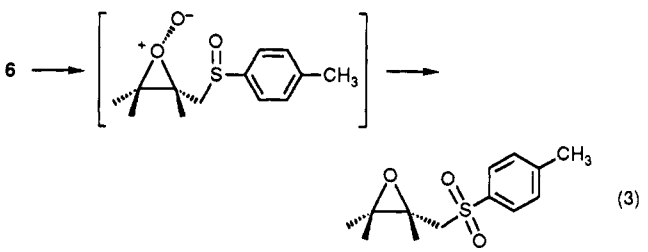
Under these carefully controlled conditions photooxidation of **6** resulted in the formation of hydroperoxide **9a** and the two diastereomeric hydroperoxides **10a** and **10b** (eq 2). Examination



(2)

9a 75% **10a/10b** 11%/14%

of this reaction mixture at various times by proton NMR reveals that the ratios **9a**/**10** and **10a**/**10b** are invariant as a function of extent of reaction. No additional peaks were observed at any point during the reaction which could be attributed to the sulfones formed by oxidation at sulfur or by trapping of a perepoxide[13] (eq 3). The hydroperoxide products were not isolated but were

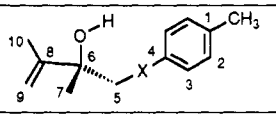


(3)

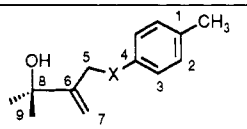
quantitatively reduced with triphenylphosphine to form a mixture of alcohols (**9a′**, **10a′**, and **10b′**) in the same ratio as the hydroperoxide precursors. The alcohols were separated by thin-layer chromatography and were identified by standard spectroscopic means. The proton NMR data for the hydroperoxides and the alcohols in Tables I and II and the ^{13}C NMR data for the alcohols in Table III provide convincing evidence for the structures of these adducts.

The diastereomeric alcohols **10** are members of a synthetically useful class of compounds, the β-hydroxy sulfoxides.[14] Solladie[15]

Table III. ^{13}C NMR Data for Allylic Alcohols[a]



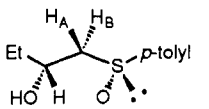
	10a′	**10b′**	**10d′**
C_1	140.7	140.6	132.9
C_2	130.1 (162)	130.1 (160)	129.7 (159)[b]
C_3	124.1 (162)	123.9 (164)	130.7 (162)[b]
C_4	141.9	142.0	136.6
C_5	66.3 (145)	64.6 (144)	47.2 (140)
C_6	74.8	75.7	74.6
C_7	26.7	28.6 (128)	26.8 (127)
C_8	148.9	147.2	148.9
C_9	111.1 (161)	113.1 (160)	111.1 (156)
C_{10}	18.8 (125)	19.7 (127)	19.3 (125)
$ArCH_3$	21.4 (127)	21.4 (127)	21.0 (123)



	9a′	**9c′**
C_1	139.6	132.3
C_2	129.8 (161)	130.8 (160)[b]
C_3	124.5 (164)	129.7 (160)[b]
C_4	141.8	136.8
C_5	59.5 (144)	37.2 (141)
C_6	146.8	150.3
C_7	116.5 (160)	112.3 (158)
C_8	71.0	73.2
C_9	29.9 (122), 30.3 (123)	30.1 (123)
$ArCH_3$	21.4 (127)	21.1 (125)

[a] In CD_3Cl versus TMS; coupling constants are in parentheses in hertz. [b] Assignments may be switched.

and co-workers during a study of the reduction of β-oxo sulfoxides[16] chemically correlated β-hydroxy sulfoxide **11** with the



11

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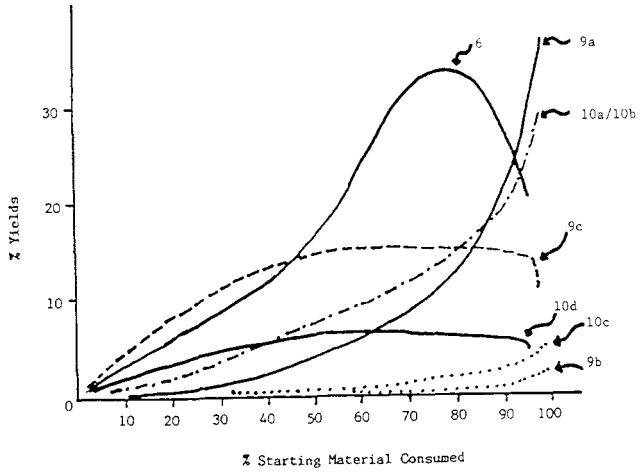
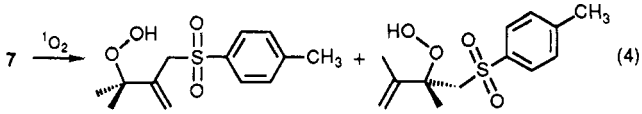


Figure 3. Reaction-mixture composition in the photooxidation of **8** as a function of unreacted **8** at −78 °C.

benzoate ester of (+)-(*S*)-2-butanol. They demonstrated that the chemical shift difference in $CDCl_3$ between the diastereotopic protons α to sulfur, $\Delta\delta$(AB), in the AB region of the ABX spectrum was greater for the *SR* than the *RR* diastereomer. On the basis of this observation, we tentatively assign the minor diastereomer **10a** the *RS*/*SR* configuration and the major diastereomer **10b** the *RR*/*SS* configuration.[17]

Sulfone **7** was photooxidized under the same conditions utilized for sulfide **6**. The hydroperoxides **9b** and **10c** were formed in a 83/17 ratio (eq 4). The hydroperoxide structures were deduced

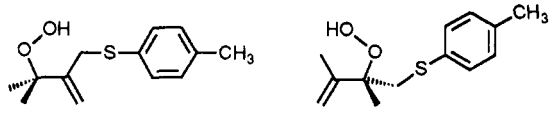

(4)

9b **10c**

by examination of their proton NMR (Tables I and II) and by their reductions to the corresponding alcohols (**9b**′ and **10c**′) with PPh_3. The ratio **9b**/**10c** was invariant as a function of extent of reaction. The formation of **9b** as the major product in this reaction was previously attributed to a conformational effect in **7** which places the carbon–hydrogen bond on the methyl group geminal to the substituent nearest to the preferred perpendicular arrangement relative to the olefinic plane.[18]

The exhaustive photooxidation of sulfide **8** under our standard conditions produced a complex mixture of **9a,b** and **10a–c**. Despite the complexity of the proton NMR spectrum of the reaction mixture, all peaks could be unambiguously assigned by reference to the previous work conducted with sulfoxide **6** and sulfone **7**.

Examination of the photooxidation of **8** by proton NMR as a function of time revealed formation of three transient intermediates, sulfoxide **6** and sulfides **9c** and **10d**. The time evolution



9c **10d**

of these transient intermediates and the final products are shown diagrammatically in Figure 3. Sulfoxide **6** was easily identified by comparison to an authentic sample. The structures of sulfides **9c** and **10d** became apparent when their proton NMR were

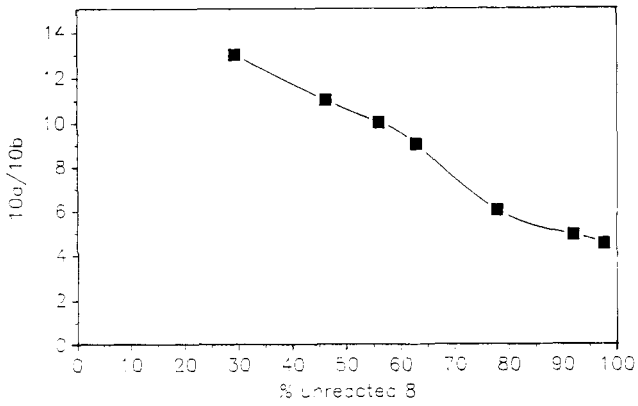
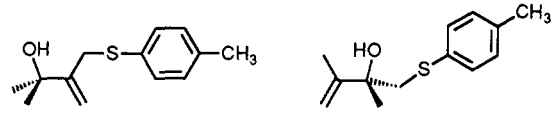


Figure 4. Diastereoselectivity in the reaction of sulfide **8** as a function of unreacted **8** at −78 °C.

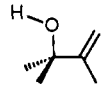
compared to those of the analogous compounds observed in the reactions of **6** and **7** (see Tables I and II). As a further check on the identity of these hydroperoxy sulfides, an incompletely oxidized reaction mixture was reduced with PPh_3 and the alcohols **9c**′ and **10d**′ were isolated and purified. Both the proton and



9c′ **10d**′

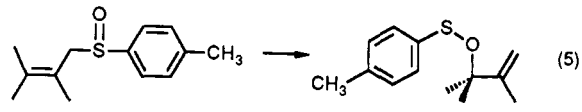
carbon NMR of these alcohols confirm the structural assignments (Tables I–III).

The partially oxidized reactions mixtures were warmed to room temperature and analyzed immediately by proton NMR. The rapid analysis was necessitated by a thermal reaction which occurred within a few hours to give alcohol **12**. This alcohol was



12

identical with an authentic sample produced by reduction of the hydroperoxide formed in the singlet oxidation of 2,3-dimethyl-2-butene.[19] Alcohol **12** is also produced after several hours when a mixture of **6** and **8** are allowed to sit in acetone-d_6 at room temperature. A 2,3-sigmatropic shift[20] in **6** (eq 5) followed by


(5)

6

8 acting as a thiophilic reducing agent would provide a rational explanation for the formation of **12**. Isolation of the sulfur-containing products or further investigation of this reaction was not pursued.

In contrast to the behavior observed in the reaction of sulfoxide **6**, the ratio of the diastereomeric hydroperoxides **10a** and **10b** formed in the singlet oxidation of **8** was greater than 13/1 and decreased as the reaction proceeded (Figure 4). These results rules out the possibility that allylic sulfoxide **6**, which must produce a diastereomeric ratio of 1/1.3, is the immediate precursor to **10a** and **10b**.

These results can be explained if hydroperoxy sulfide **10d** rather than sulfoxide **6** is the immediate precursor producing **10a** and **10b**. This suggestion is supported by an examination of the initial product composition as a function of temperature (Table IV), which demonstrates that ene reactions to produce **9c** and **10d** are the predominate processes at all temperatures. This is especially

(17) The positions of the AB doublets in the two diastereomers reverse in $CDCl_3$ in comparison to acetone-d_6 (Table I). **10a**: ^{1}H NMR ($CDCl_3$) δ 1.71 (s, 3 H), 1.77 (s, 3 H), 2.42 (s, 3 H) 2.84 (d, J = 14 Hz, 1 H), 3.03 (d, J = 14 Hz, 1 H), 4.3 (s, 1 H), 4.89 (s, 1 H), 5.14 (s, 1 H), 7.34 (d, J = 8 Hz, 2 H), 7.55 (d, J = 8 Hz, 2 H). **10b**: ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 3 H), 1.92 (s, 3 H), 2.42 (s, 3 H), 2.91 (d, J = 13 Hz, 1 H), 3.02 (d, J = 13 Hz, 1 H), 4.7 (s, 1 H), 5.14 (s, 1 H), 5.41 (s, 1 H), 7.34 (d, J = 8 Hz, 2 H), 7.53 (d, J = 8 Hz, 2 H).

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Table IV. Photooxidation of Sulfide **8** as a Function of Temperature

temp, °C	products, %[a]			
	10d	**9c**	**6**	**8**[b]
14	3.87 (48.9)	4.04 (51.1)	0	92.1
−6	8.6 (45.0)	10.6 (55.0)	0	80.8
−29	6.3 (42.0)	8.7 (58.0)	0	85.0
−55	4.8 (35.0)	7.9 (57.5)	1.0 (7.3)	86.3
−78	2.2 (24.4)	3.9 (44.0)	2.8 (31.6)	91.1

[a] Values in parentheses are the percentages of the total oxidized material. [b] Percentage of starting material left.

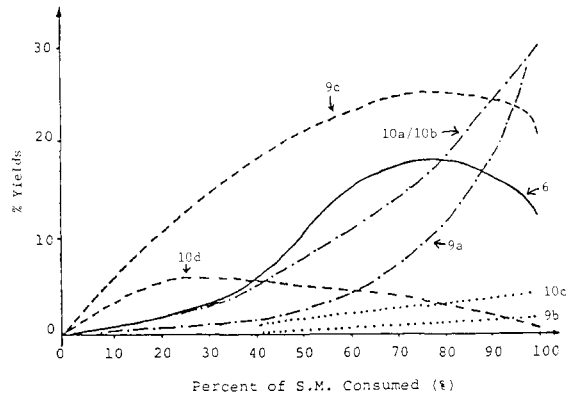


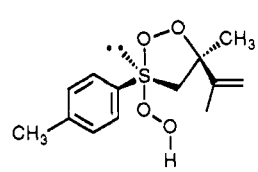
Figure 5. Reaction-mixture composition in the photooxidation of 2,3-dimethyl-2-butenylphenyl sulfide at −78 °C. The number scheme refers to compounds analogous to those formed in the reaction of **8** but without the 4-methyl group.

apparent in the reaction of singlet oxygen with the parent para-H compound[21] (Figure 5) in which the diastereomer ratio is greater than 20/1. Sulfur oxidation to produce **6**, however, does increase with decreasing temperature. This is consistent with previous reports[22] that in aprotic solvents physical quenching of singlet oxygen by sulfides becomes less important and chemical reaction becomes more important with decreasing temperature.

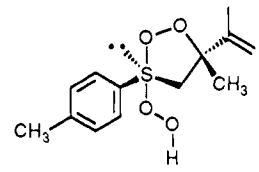
The remarkably high[23] diastereoselectivity in the reaction of the acyclic sulfide **8** can potentially occur at several locations on the Foote reaction surface (Figure 1). The diastereoselection could reflect the energy differences between diastereomeric persulfoxides A and thiadioxiranes B or in the transition states for sulfide trapping of the thiadioxirane. Photooxidation of sulfide **10d′**, however, produces **10a′** and **10b′** in a ratio of 1/2. This much-reduced diastereoselectivity and the reversal of diastereoselection in the singlet oxidation of **10d′** in comparison to **8** suggest that there is something unique about hydroperoxy sulfide **10d**.

We suggest that the large preference for diastereomer **10a** in the photooxidation of **8** reflects the energy difference in the two sulfuranes **13a** and **13b**. The ability to stabilize a hypervalent species by the five membered ring effect[24] is not available during the singlet oxidation of **10d′**.

Martin and co-workers[25] have extensively examined the formation, structure, and properties of sulfuranes. It appears that both electronic effects and ligand structure play an important role



13a



13b

in stabilizing sulfuranes. The most stable conformations of **13a** and **13b** are those depicted above in which the most electronegative oxygen ligands occupy the apical positions. This is a consequence of the electron-rich nature of the four electron three centered hypervalent apical–apical bond which is stabilized when electron-withdrawing groups occupy the apical positions and σ-donor groups occupy the equatorial positions of the trigonal-bipyramidal structure.[26]

It is the reduction of sulfurane **13a** with the two largest groups, the isopropenyl and the *p*-tolyl, cis to one another on the five-membered ring which leads to the predominate diastereomer **10a**. Thermochemical data[27] on the five-membered rings *cis*- and *trans*-1,3-dimethylcyclopentane also indicate that the cis isomer [ΔH_f(l or c) = −40.66 kcal/mol] is slightly more stable than its trans isomer [ΔH_f(l or c) = −40.17 kcal/mol).

At the time of maximum diastereoselectivity (Figure 4) the predominate reducing agent in solution is sulfide **8** rather than hydroperoxy sulfide **10d**. The reduction of **13a** with **8** would produce increasing amounts of sulfoxide **6** as the reaction proceeds. Ultimately it is the formation of this sulfoxide which leads to the sharp decline in the diastereoselectivity as a function of extent of reaction.

Conclusion

The examinations of the simple ene reactions of singlet oxygen with an allylic sulfoxide and sulfone have made possible a detailed study of the complex photooxidation of an allylic sulfide. A time-evolution study of intermediates and products in the photooxidation of **8** has uncovered a remarkably high diastereoselective reaction. It has been established that the hydroperoxy sulfide **10d** reacts with singlet oxygen at −78 °C to produce a hydroperoxy sulfoxide with greater than 13/1 diastereoselectivity. In contrast, the singlet oxidation of the homologous alcohol **10d′** shows only a small diastereoselection for the other diastereomer. To rationalize this behavior, the formation of a transient sulfurane in the reaction of the hydroperoxy sulfide has been proposed.

Additional work to further clarify the mechanistic details of the singlet oxidations of **8** and other sulfides containing potential participating groups is in progress and will be reported in the near future.

Experimental Section

Preparative gas-chromatographic separations were carried out on a GOW-MAC Series 550 thermal conductivity detector gas chromatograph utilizing a 0.25 in by 10 ft column packed with 20% Carbowax 20M on NAW Chromosorb W 80/100. Chromatographic separations were carried out on a Harrison Research Model 7624T Chromatotron using plates coated with EM Science 7749 silica gel 60PF_{254}.

Proton and carbon NMR spectra were obtained on a JEOL FX270 at 270 and 67.83 MHz, respectively, and the chemical shifts were referenced to Me_4Si.

Rose Bengal, tetraphenylporphyrin, *N*-bromosuccinimide, triphenylphosphine, *p*-methylthiophenol, and tetramethylethylene were all obtained from Aldrich and used without further purification. Reagent-grade benzoyl peroxide was obtained from Fisher Scientific and used as received. Sodium 4-methylthiophenoxide was prepared according to a literature procedure.[28] $CDCl_3$ (99.8 atom % D) and acetone-d_6 were obtained from Aldrich Chemical Co. and were dried over 4A molecular sieves before use. CCl_4 was purrified by distillation from P_2O_5, and hexane and ethyl acetate were purified by simple distillation.

1-Bromo-2,3-dimethyl-2-butene. To a solution of 3.4 g (40.5 mmol) of 2,3-dimethyl-2-butene in 25 mL of carbon tetrachloride was added 7.1

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g (40.5 mmol) of *N*-bromosuccinimide and 0.03 g of dibenzoyl peroxide. This solution was stirred and refluxed under a nitrogen atmosphere for 3 h. The solution was then cooled to room temperature and the succinimide was removed by suction filtration. The succinimide was washed with two 5-mL portions of CCl_4, and the filtrates were combined. The CCl_4 was removed under reduced pressure to give 4.2 g (64% yield) after distillation: bp 65 °C (24 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.71 (s, 3 H), 1.77 (s, 6 H), 4.08 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.2 (q, J = 127 Hz), 20.2 (q, J = 127 Hz), 21.3 (q, J = 125 Hz), 37.0 (t, J = 162 Hz), 124.8 (s), 133.1 (s).

2,3-Dimethyl-2-butenyl *p*-Methylphenyl Sulfide (8). A solution of 0.55 g (4.2 mmol) of sodium 4-methylthiophenoxide and 0.68 g (4.2 mmol) of 1-bromo-2,3-dimethyl-2-butene in 10 mL of absolute ethanol was stirred for 30 min. The well-mixed solution was then poured into 20 mL of saturated NaCl and extracted with several portions of petroleum ether. The organic layer was dried with $MgSO_4$ and removed under reduced pressure to give 0.62 g (80% yield) of **8**. The sulfide product was purified by preparative gas chromatography (retention time 18 min) and by distillation: bp 82 °C (0.03 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.52 (s, 3 H), 1.64 (s, 3 H), 1.77 (s, 3 H), 2.31 (s, 3 H), 3.53 (s, 2 H), 7.07 (d, J = 8 Hz, 2 H), 7.26 (d, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.1 (q, J = 125 Hz), 20.2 (q, J = 125 Hz), 20.8 (q, J = 125 Hz), 21.0 (q, J = 125 Hz), 39.9 (t, J = 140 Hz), 123.0 (s), 129.4 (d, J = 162 Hz), 129.5 (s), 131.2 (d, J = 160 Hz), 133.5 (s), 136.3 (s).

1-[(4-Methylphenyl)sulfinyl]-2,3-dimethyl-2-butene (6). A 5-mL CH_2Cl_2 solution of 254 mg of MCPBA (85%) was added to 10 mL of methylene chloride containing 260 mg of **8** at 0 °C. This mixture was warmed to room temperature and stirred for 1 h. It was then poured into 10 mL of 10% aqueous $NaHCO_3$. The organic layer was separated, washed with saturated NaCl, and dried with $MgSO_4$. The solvent was removed under reduced pressure and the sulfoxide was purified by passing it down a 20-cm long, 3-cm diameter flash column containing 8 g of silica gel (60-200 mesh) column with hexane/ethyl acetate (9/1) elution: 83% yield; ^{1}H NMR ($CDCl_3$) δ 1.46 (s, 3 H), 1.64 (s, 3 H), 1.67 (s, 3 H), 2.42 (s, 3 H), 3.43 (d, J = 12 Hz, 1 H), 3.77 (d, J = 12 Hz, 1 H), 7.29 (d, J = 8 Hz, 2 H), 7.49 (d, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.7 (q, J = 126 Hz), 20.7 (q, J = 126 Hz), 21.0 (q, J = 126 Hz), 21.4 (q, J = 125 Hz), 64.5 (t, J = 140 Hz), 117.4 (s), 124.3 (d, J = 163 Hz), 129.6 (d, J = 165 Hz), 134.2 (s), 140.9 (s), 141.4 (s).

1-[(4-Methylphenyl)sulfonyl]-2,3-dimethyl-2-butene (7). Two equivalents of MCPBA was added to a 10 mL CH_2Cl_2 solution of 85 mg of **8** at 0 °C. This solution was stirred for 1 h, warmed to room temperature, and washed with saturated aqueous $NaHCO_3$ and water. The organic layer was separated and dried over $MgSO_4$, the solvent was removed at low pressure, and the sulfone was purified by chromatography: 67% yield; ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 3 H), 1.62 (s, 3 H), 1.77 (s, 3 H), 2.46 (s, 3 H), 3.92 (s, 2 H), 7.44 (d, J = 8.2 Hz, 2 H), 7.74 (d, J = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.45 (q, J = 125 Hz), 20.6 (q, J = 125 Hz), 21.0 (q, J = 125 Hz), 21.6 (q, J = 125 Hz), 61.8 (t, J = 140 Hz), 116.0 (s), 128.4 (d, J = 160 Hz), 129.5 (d, J = 160 Hz), 135.8 (s), 136.3 (s), 144.4 (s).

General Photolysis Conditions. The singlet-oxygen reactions were performed in 5-mm NMR tubes containing 0.5 mL of acetone-d_6. The temperature was maintained by submersion in a methanol bath held at -78 °C by the use of a refrigerator probe (FTS Systems Inc. Flexicool). Prior to photolysis, the samples were saturated with oxygen for 20 min. The concentrations of the starting materials and dye were approximately 5×10^{-2} M and 2×10^{-5} M, respectively. The irradiation was conducted under continuous oxygen bubbling by using a 750-W, 120-V tungsten halogen lamp and by filtering out the high-energy light with a 1-cm 0.5% $K_2Cr_2O_7$ filter solution. The samples were deoxygenated prior to monitoring by NMR by bubbling argon through the NMR tube for 15 min. Removal of the oxygen results in an improved NMR spectrum.

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Stereochemical Course of Diels-Alder Cycloadditions to Hydroxymethyl-Substituted Plane-Nonsymmetric Cyclopentadienes[1]

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Abstract: Steric, electronic, and potential hydrogen-bonding factors governing π-facial stereoselectivity in hydroxymethyl-substituted cyclopentadienes **4** and **6** have been investigated. The stereochemical response of **4** is no different than that of hydrocarbon **5**. In both examples, only below-plane dienophilic capture operates. The predominance of *anti*-7-hydroxymethyl isomers in these cycloadditions involving **6** has been ascribed predominantly to differential steric factors. Kinetically preferred endo stereoalignment in all of the adducts derived from **6** signals additionally that hydrogen bonding has no evident kinetic consequence. Accordingly, a properly positioned CH_2OH substituent does not find it possible to contravene approach to **4** and **6** from their less sterically hindered surfaces.

In the 50 years that have elapsed since its discovery,[4] the Diels-Alder reaction has been heavily exploited to take advantage of its superb regio- and stereochemistry.[5] The end result often involves the elaboration of as many as four contiguous stereogenic centers in a single laboratory step. However, [4 + 2] cycloadditions have the latent capacity for still greater stereochemical latitude in those situations where plane-nonsymmetric 1,3-dienes are involved. Because the reactive faces of such 4π reagents are

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(1) Part 41 in the series dealing with isodicyclopentadienes and related molecules. (a) For part 40, see: Paquette, L. A.; Moriarty, K. J.; Meunier, P.; Gautheron, B.; Crocq, V. *Organometallics* **1988**, *7*, 1873. (b) For part 39, consult: Paquette, L. A.; Gugelchuk, M. *J. Org. Chem.* **1988**, *53*, 1835.

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