The remaining samples were irradiated at 366 nm for a period of 1 h at various temperatures. The product mixtures were analyzed by capillary GC, and the results are given in Table V.

Thermolysis of 11. Degassed, sealed NMR samples of DBH and **11** in toluene-d_8 were thermolyzed simultaneously at 161.6 °C. The disappearance of azoalkane bridgehead hydrogen(s) was followed by NMR with the solvent aromatic protons as a standard. Plots of ln of the corrected peak area versus time were linear with slopes of -1.59×10^{-4} s^{-1} ($r = -0.9982$) for DBH and -4.72×10^{-4} s^{-1} ($r = -0.9988$) for **11**.

A degassed, sealed NMR sample of **11** was thermolyzed in a 1/1 mixture of toluene-d_8 and benzene-d_6 at 143 °C. Product analyses under the standard conditions showed 98% **45** and 0.06% **46**.

Biradical Trapping with CHD. Six solutions of 0.0542 M azoalkane **11**, 0.0392 M decane, 4.57×10^{-3} M Michler's ketone, and 1,4-cyclohexadiene in C_6H_5F were prepared. The concentrations of CHD were 0.2082, 0.4116, 0.6140, 0.8048, 1.604, and 2.806 M. The solutions were irradiated at 366 nm and 24.7 °C for 1 h. The products were analyzed by capillary GC, giving the results in Table IV.

Acknowledgment. We thank the National Science Foundation and the Robert A. Welch Foundation for support of this research. Helpful comments frrom Professor Martin Newcomb (Texas A & M University) and Dr. Charles E. Doubleday (Columbia University) are much appreciated.

Supplementary Material Available: Synthesis and spectral properties of authentic hydrocarbons **30a-33a** and **30b-33b** (5 pages). Ordering information is given on any current masthead page.

Cooxidation Reaction in the Singlet Oxygenation of Cyclic and Benzylic Sulfides: *S*-Hydroperoxysulfonium Ylide Intermediate As a New Epoxidizing Species

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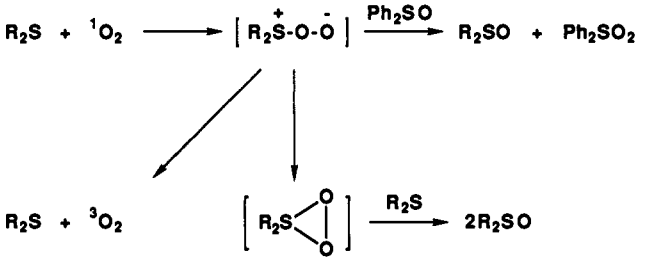
Contribution from the Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan. *Received September 7, 1990*

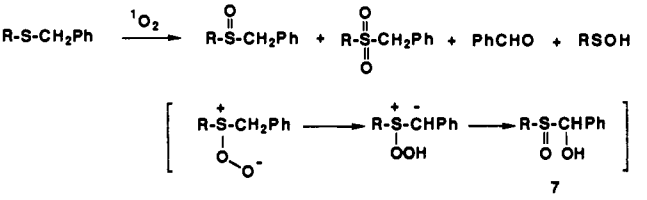
Abstract: The reaction of singlet oxygen with a series of 3-benzoyl-4-(methoxycarbonyl)thiazolidine derivatives and alkyl benzyl sulfides in methylene chloride in the presence of olefins has been investigated. The reaction of singlet oxygen with the sulfides caused cooxidation of olefins to the corresponding epoxides in substantial yields. The epoxidation of olefins by the active oxidizing species generated in photosensitized oxygenation of the sulfides is provided, suggesting that the new epoxidizing species is probably the *S*-hydroperoxysulfonium ylide intermediate derived from a persulfoxide intermediate by intramolecular α-proton abstraction.

The photooxidation of sulfides continues to yield fascinating results. In the past more than two decades, the reactions of singlet oxygen ($^1O_2$) with a wide variety of sulfur-containing compounds including sulfides[1-9] and disulfides[10] have been reported. Since some of the naturally occurring sulfur compounds isolated so far have sulfur-oxygen bonds, these S-oxidation products can play important roles in biochemical reactions.[11] For instance, me-

Scheme I



Scheme II



(1) For reviews, see: Ando, W.; Takata, T. In *Singlet O_2*; Frimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. 3, Chapter 1, p 1 and references cited therein.

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(5) (a) Skold, C. N.; Schlessinger, R. H. *Tetrahedron Lett.* **1970**, 791. (b) Wasserman, H. H.; Strehlow, W. *Ibid.* **1970**, 795. (c) Murray, R. W.; Jindal, S. L. *Photochem. Photobiol.* **1972**, *16*, 147. (d) Casagrande, M.; Gennari, G.; Cauzzo, G. *Gazz. Chim. Ital.* **1974**, *104*, 1251. (e) Stary, F. E.; Jindal, S. L.; Murray, R. W. *J. Org. Chem.* **1975**, *40*, 58. (f) Cauzzo, G.; Gennari, G.; Da Re, F.; Curci, R. *Gazz. Chim. Ital.* **1979**, *109*, 541. (g) Monroe, B. M. *Photochem. Photobiol.* **1979**, *29*, 761.

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(8) Correa, P. E.; Riley, D. P. *J. Org. Chem.* **1985**, *50*, 1787.

(9) (a) Clennan, E. L.; Chen, X. *J. Am. Chem. Soc.* **1989**, *111*, 5787. (b) Clennan, E. L.; Chen, X. *Ibid.* **1989**, *111*, 8212. (c) Clennan, E. L.; Yang, K. *Ibid.* **1990**, *112*, 4043.

(10) (a) Murray, R. W.; Jindal, S. L. *J. Org. Chem.* **1972**, *37*, 3516. (b) Stary, F. E.; Jindal, S. L.; Murray, R. W. *Ibid.* **1975**, *40*, 58.

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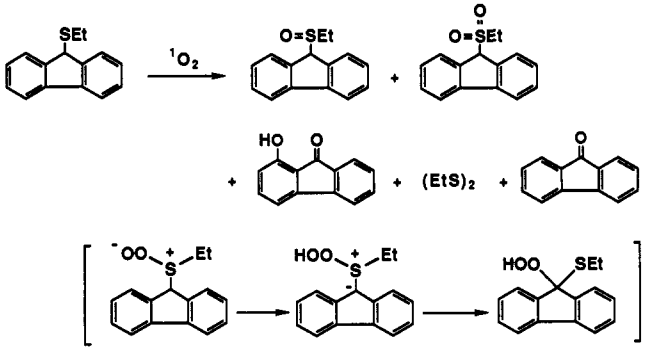
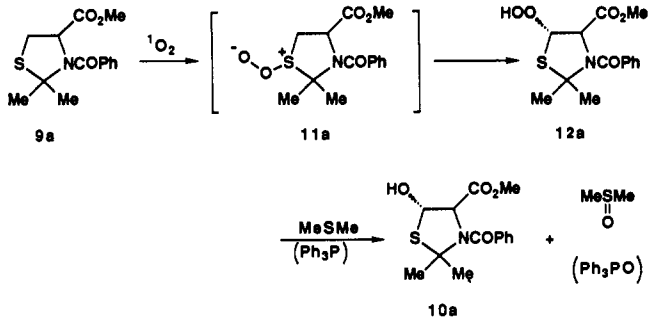
Scheme III

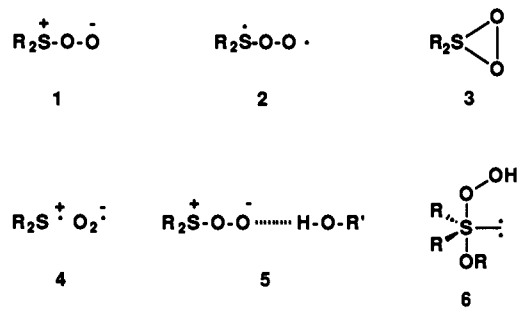


Scheme IV

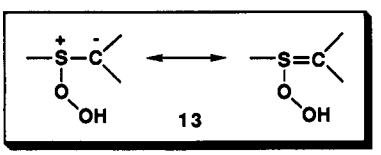


thionine undergoes photooxygenation to give the sulfoxide.[12] The degradation of methionine is responsible for the loss of activity of several important enzymes that are damaged in photodynamic action.[13]

The photooxidation of sulfide was first described by Schenck et al.[2] They reported that dialkyl sulfides undergo photooxidation to give 2 mol of sulfoxide per mol of absorbed oxygen. Much attention has been devoted to their structures and the reactivities of initially formed reactive intermediates,[1-9] for which persulfoxide **1**, diradical **2**, thiadioxirane **3**, or tight ion pair **4**[14] structures have been suggested. Foote et al.[3g] elegantly proposed that there are



two intermediates in the $^1O_2$ reaction of sulfide in aprotic solvents in which an initial nucleophilic persulfoxide intermediate **1** reacts with an electrophile such as diphenyl sulfoxide, loses triplet oxygen, or collapses to an electrophilic thiadioxirane intermediate **2** that reacts with a nucleophile such as sulfide (Scheme I). Meanwhile, in protic solvents the persulfoxide intermediate is stabilized by hydrogen bonding as **5**.[3c,6] The function of the alcohol was interpreted as decreasing the negative charge density on the persulfoxide, thus promoting nucleophilic attack by a second sulfide. Clennan et al.[9] reported the experimental evidence for the formation of a sulfurane intermediate **6**. Since no direct trapping of the intermediates formed in $^1O_2$ reaction of sulfides has been achieved, however, the structures of the intermediates are still controversial.[1] Recently, we have provided the first observation of the matrix-isolated sulfide–oxygen adducts by FT-IR spectroscopy.[4h] The IR spectra suggest that the adduct is best formulated as a persulfoxide. We also reported the experimental evidence for the trapping of a persulfoxide intermediate derived from $^1O_2$ reaction of a thiirane by methanol to afford the peroxysulfenic acid intermediate that oxidizes olefins to epoxides and sulfides to sulfoxides.[4i] Meanwhile, Corey[15] and Ando[16] reported that singlet oxygenation of sulfides bearing active α-C–H bonds, such as benzyl sulfide and 9-fluorenyl ethyl sulfide, affords fragmentation products by C–S bond cleavage along with the usual S-oxidized products, sulfoxides, and sulfones (Scheme II and III). The primary intermediate in both reactions is thought to be a persulfoxide followed by intramolecular α-hydrogen abstraction to give the secondary intermediate. Corey et al. proposed an α-hydroxy sulfoxide **7** as a key intermediate derived from the persulfoxide by rearrangement.[15] Ando et al., however, pointed out the reasonable intermediacy of α-hydroperoxy sulfide **8** on the basis of detailed product analysis.[16] Recently, we have found that singlet oxygenation of thiazolidine derivatives **9a** and subsequent reduction selectively affords the corresponding α-hydroxy sulfide **10a** in high yields.[17] Abstraction of an α-proton in the persulfoxide intermediate **11a** leading to α-hydroperoxythiazolidine **12a** via Pummerer-type rearrangement competes with S-oxidation (Scheme IV).[17a] This hydroperoxide **12a** is stable at 0 °C and is capable of oxidizing sulfide and phosphine to give the corresponding sulfoxide and phosphine oxide.[4c] In relation to photodynamic action, however, oxidation of olefin is of more interest and importance, since an unsaturated bond is contained in many biologically important compounds such as lipids. We report here cooxidation of olefin to epoxide in singlet oxygenation of thiazolidine derivatives **9** and alkyl benzyl sulfides in the presence of olefin. Hydroperoxide **12a** has no ability to epoxidize olefin to epoxide. In both cases, *S*-hydroperoxysulfonium ylide intermediates **13** are proposed as a new active oxidizing species that oxidizes olefins to epoxides.



Results and Discussion

Singlet Oxygenation of Thiazolidine 9a in the Presence of Olefins. Oxygen was bubbled through a benzene solution of thiazolidine **9a** (0.25 M) that was photoirradiated at 0 °C in the presence of excess norbornene with tetraphenylporphine as a sensitizer. After disappearance of the starting material, excess dimethyl sulfide was added. The resulting mixture was subjected to analytical GLC and ^1H NMR. Norbornene oxide was apparently produced in 16% yield together with a quantitative amount of alcohol **10a**[17a] and dimethyl sulfoxide (DMSO) in 49% yield. If the oxygenation is carried out in the absence of a sensitizer or light, no reaction occurs. The oxygenation was inhibited by addition of 1,4-diazabicyclo[2.2.2]octane (DABCO), a known singlet oxygen quencher.[18] These control experiments make it probable that $^1O_2$ is the primary oxygenating species. The reaction conditions are not optimized. Very similar results were obtained with cyclohexene. Photoepoxidation of olefins did not take place

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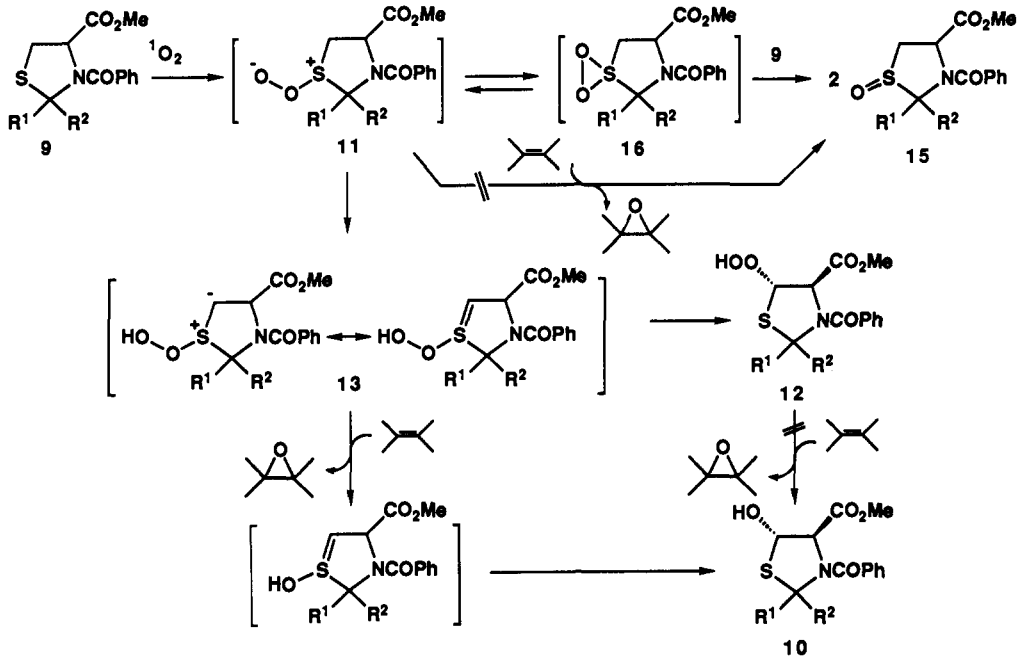
Scheme V

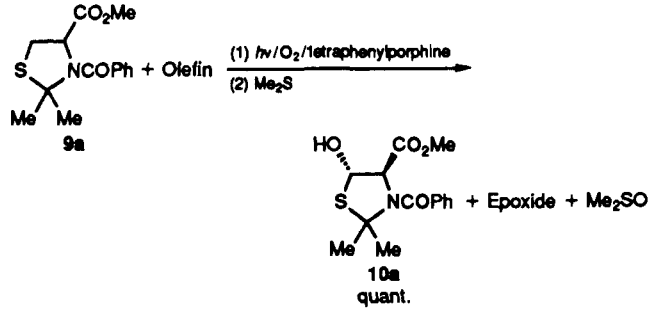


at all in the absence of **9a**.[4i] An oxenoid mechanism, which could resemble that in biological epoxidations,[19] is suggested for the epoxidation reaction. Addition of a radical trap (triphenylmethane) in concentrations up to 5×10^{-2} M did not have any influence on epoxidation; norbornene oxide: 16% in the absence and 14% in the presence of a trap at 0 °C. Similarly, cyclohexene was converted into the corresponding epoxide in 9% yield at 0 °C in a benzene solution of **9a** (Table I).

To clarify whether or not hydroperoxide **12a** has an ability to epoxidize olefin to epoxide, the following experiments have been done. Thiazolidine **9a** in benzene (2.5×10^{-1} M) was photooxygenated at 0 °C. After disappearance of **9a** and formation of hydroperoxide **12a** were monitored by ^{1}H NMR,[17a] excess olefin such as norbornene or cyclohexene was added and then the resulting mixture was left to stand for 1.5 h at 0 °C. Dimethyl sulfide was also added to reduce the remaining **12a**. The solvent was removed under reduced pressure, and the residue was subjected to analytical GLC and ^{1}H NMR. α-Hydroxythiazolidine **10a** was obtained quantitatively along with dimethyl sulfoxide (DMSO), but no epoxide was detected. This apparently suggests that hydroperoxide **12a** has no ability to oxidize olefin to epoxide. These results indicate that an intermediate in the reaction of thiazolidine with $^1O_2$ is actually responsible for this epoxidation. Since less nucleophilic olefins such as stilbene and styrene were not oxidized, the active intermediate in this epoxidation reaction seems to have an electrophilic nature. Possible reactions leading to the observed products are shown in Scheme V.

The mechanism of the photooxidation of thiazolidine **9a** may be explained by assuming the Pummerer-type rearrangement of the persulfoxide (**11a**) via abstraction of an α-proton affording α-hydroperoxythiazolidine **12a**. As mentioned previously, however, hydroperoxide **12a** has no ability to oxidize olefin. It has been known that photooxygenation of diethyl sulfide in the presence of norbornene gave the sulfoxide quantitatively while no epoxidation took place.[4i] The primary intermediate **11** is also not likely to react with olefin to afford the sulfoxide and epoxide. The fact that the sulfoxide was not obtained at all in the singlet oxygenation of **9a** makes it possible to rule out the epoxidation by **11a**. On the basis of these observations, electrophilic *S*-

Table I. Singlet Oxygenation of **9a** in the Presence of Olefin



reaction condns (solvent/T(°C)/ time(h)/(equiv))	olefin, amt (equiv)	products and yields (%)	
		epoxide	Me_2SO
C_6H_6/0/1.5	norbornene, 30	14	80
C_4H_8O/0/9	norbornene, 30	16	49
C_4H_8O/−78/8	norbornene, 30	14	58
C_6H_6/0/1.5/ Ph_3CH, 0.2	norbornene, 30	14	43
C_6H_6/0/1.5	cyclohexene, 30[a]	9	76
C_6H_6/0/1.5	*trans*-stilbene, 30	0	
C_6H_6/0/1.5	styrene, 30	0	66

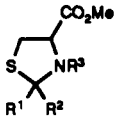
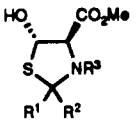
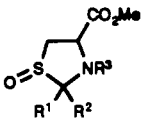
[a] Yields determined as 2-methoxycyclohexanol after acid-catalyzed methanolysis.

hydroperoxysulfonium ylide **13** derived from persulfoxide **11** by abstraction of an intramolecular α-proton seems to be a key epoxidizing species.

Substituent Effect in Singlet Oxygenation of Thiazolidines. To elucidate the previous reaction mechanism, a series of thiazolidines **9** was also submitted to reaction with $^1O_2$ in the presence of norbornene (Table II). The electronic and/or steric effects may be important in accounting for the differences in epoxidizing ability. A higher extent of methyl substitution at the 2-position in **14** suppressed the sulfoxide formation and raised the yield of the abstraction product.[17b] When dimethyl or monomethyl derivatives (**9a** or **9b**) were photooxygenated in the presence of norbornene, the epoxidation reaction took place. In the reaction of unsubstituted thiazolidine **9c** in which abstraction of α-proton might be suppressed, however, only a trace of epoxide was obtained. These results might support that an intermediate generated by abstraction of the α-proton in persulfoxide **11** is responsible for the epoxidation reaction. The acidity of the α-proton in

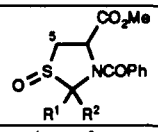
(19) Hamilton, G. A. In *Molecular Mechanisms of Oxygen Activation*; Hayaishi, O., Ed.; Academic Press: New York, 1985; p 405. For recent articles, see: (a) Heimbrook, D. C.; Mulholland, R. L., Jr.; Hecht, S. M. *J. Am. Chem. Soc.* **1986**, *108*, 7839. (b) Nam, W.; Valentine, J. S. *Ibid.* **1990**, *112*, 4977. (c) Collman, J. P.; Zhang, X.; Hembre, R. T.; Brauman, J. I. *Ibid.* **1990**, *112*, 5356.

Table II. Singlet Oxygenation of Thiazolidines **9** and **14**

	reactn condns	products and yields (%) 		norbornene oxide	Me_2SO
14a, $R^1 = R^2 = Me$; $R^3 = COMe$	(1) $^1O_2$, (2) Me_2S	100[a]	0[a]		
9a, $R^1 = R^2 = Me$; $R^3 = COPh$	(1) $^1O_2$/norbornene, (2) Me_2S	100	0	14	80
14b, $R^1 = Me$; $R^2 = H$; $R^3 = COMe$	(1) $^1O_2$, (2) Me_2S	40[a]	60[a]		
9b, $R^1 = Me$; $R^2 = H$; $R^3 = COPh$	(1) $^1O_2$/norbornene, (2) Me_2S			14	32
14c, $R^1 = R^2 = H$; $R^3 = COMe$	(1) $^1O_2$, (2) Me_2S	5[a]	95[a]		
9c, $R^1 = R^2 = H$; $R^3 = COPh$	(1) $^1O_2$/norbornene, (2) Me_2S			trace	34

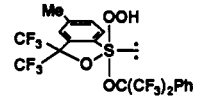
[a] Reference 17b.

Table III. $J_{^{13}C-H}$ Values and s Character of Thiazolidine *S*-oxides **15a–c**

	$J_{^{13}C-H}$ (Hz) at 5-position	s character (%)[a]
15a, $R^1 = R^2 = Me$	146.4	29.3
15b, $R^1 = Me$; $R^2 = H$	142.6	28.5
15c, $R^1 = R^2 = H$	143.9	28.8

[a] s character = $1/(1 + \lambda^2)$; $J_{^{13}C-H} = 500/(1 + \lambda^2)$.

persulfoxide **11** may be one of the important factors responsible for this substituent effect. It is known that the higher the acidity of α-proton is, the larger the C–H coupling constant measured by ^{13}C NMR becomes.[20] Since the sulfoxides could have the structures most similar to those of the persulfoxide intermediates (Table III), the C–H coupling constants at the C-5 position of each sulfoxide **15a–c** were determined by ^{13}C NMR measurement. On the basis of the C–H coupling constants, there is hardly any difference in s characters calculated from the following equation; $J_{^{13}C-H} = 500/(1 + \lambda^2)$, s character $= 1/(1 + \lambda^2)$.[20a] Thus, it seems that there is not enough difference in the acidity of α-protons so as to give such a substituent effect to the reaction. The observed substituent effect may, therefore, depend upon the bulkiness of the C-2 substituent on persulfoxide **11**. Persulfoxide **11** cyclizes to thiadioxirane **16**, which reacts with another **9** to afford 2 mol of sulfoxide **15** (Scheme V).[3g] However, in the case of **9a**, steric hindrance around the sulfur atom prevents this bimolecular reaction. The ring opening of **16** may take place to reform **11**. Judging from the results on the substituent effect, the cooxidation of olefin to epoxide might be caused by *S*-hydroperoxysulfonium ylide intermediate **13**, which would be a first trivalent sulfur compound substituted with a hydroperoxy group. Sulfurane intermediates **17**[21] and **18**[9a,b] can be classified as a tetravalent type of compound having a hydroperoxy group on the sulfur atom, while peroxysulfenic acid intermediate **19**[4i] is an example of a divalent type.



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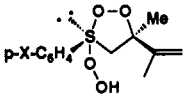
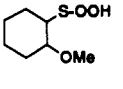


18



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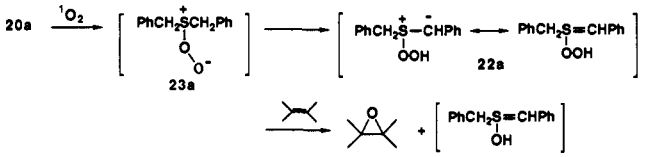
Singlet Oxygenation of Benzyl Sulfide in the Presence of Norbornene. To delineate the limitation and scope of the cooxidation of olefins to the corresponding epoxides by the active oxidizing species generated in singlet oxygenation of sulfides, a series of alkyl benzyl sulfides was also submitted to reaction with $^1O_2$ in the presence of norbornene. Benzyl sulfide (**20a**, 0.25 M) in deuteriated chloroform was photooxygenated at 0 °C in the presence of excess norbornene with methylene blue as a sensitizer under bubbling oxygen. After disappearance of the starting materials, excess dimethyl sulfide was added. Norbornene oxide and benzaldehyde as a fragmentation product by oxidative C–S bond cleavage[15] were obtained together with the corresponding sulfoxide (**21a**) and sulfone (Table IV). The formation of *S*-benzyl phenylmethanethiosulfinate[22] was confirmed by means of ^1H NMR. The photooxygenation in the absence of a sensitizer does not give any product. Moreover, the oxidation is inhibited by addition of DABCO.[18] These results clearly demonstrate that singlet oxygen is the active oxygen species responsible for this oxidation. This epoxidation reaction seems to proceed via the intermediate **22a** generated by the abstraction of α-proton on the persulfoxide intermediate (**23a**) (Scheme VI), similar to the case of thiazolidine **9** (Scheme V). In order to trap persulfoxide **23a**, the reaction in the presence of both methyl phenyl sulfoxide as an electrophilic oxygen acceptor[23] and norbornene was carried out (Table IV). Interestingly, methyl phenyl sulfone was obtained in 17% yield together with the S-oxidation product such as benzyl sulfoxide and sulfone in 92% and 7% yields, respectively. However, neither norbornene oxide nor benzaldehyde was observed. These results support that persulfoxide **23a** is surely involved in the early stage of this epoxidation reaction.

Scheme VI



Substituent Effect in Singlet Oxygenation of Alkyl Benzyl Sulfides. In order to clarify the cooxidation of olefin in singlet oxygenation of benzyl sulfides, photooxygenation of alkyl benzyl sulfides **20b–e** in the presence of norbornene was carried out. A deuteriated chloroform solution of the sulfide with methylene blue as a sensitizer was photoirradiated until the sulfide was consumed by means of GLC. The reaction mixture was analyzed by ^1H NMR. In each case, benzaldehyde was obtained as the C–S bond cleavage product together with the corresponding sulfoxide and sulfone (Table V). The formation of the corresponding *S*-alkyl alkanethiosulfinate[10a] was confirmed by means of ^1H NMR. When the sulfide was substituted with a bulky alkyl group, the yield of benzaldehyde increased. In the presence of excess norbornene, sulfides **20b–e** were also photooxygenated under the same reaction conditions, and the reaction mixture was analyzed by GLC and ^1H NMR. In each case, the corresponding sulfoxide and sulfone, benzaldehyde, and norbornene oxide were obtained as shown in Table V. In the case of sulfides **20c–e** with small substituents, S-oxidation becomes the main path and a small amount of benzaldehyde was obtained. However, in the case of sulfide **20b** having a sterically more hindered substituent, ab-

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Table IV. Singlet Oxygenation of **20a** in the Presence of Norbornene

reaction condns (sensitizer/solvent/T(°C))	additives, amt (equiv)	products and yields (%) $(PhCH_2)_2SO$ (**21a**)	$(PhCH_2)_2SO_2$	PhCHO	norbornene oxide
MB[a]/$CDCl_3$/0	norbornene, 30	48	20	25	17 (68[b])
MB[a]/$CDCl_3$/0	norbornene, 3	66	13	19	trace
MB[a]/CH_2Cl_2/0	norbornene, 30	92	7	0	0
	PhS(O)Me, 20				$PhSO_2Me$, 17

[a] MB is methylene blue. [b] Based on the yield of benzaldehyde produced.

Table V. Singlet Oxygenation of **20b–e** in the Presence of Norbornene

$PhCH_2SR$	condns time (min)	condns norbornene (equiv)	products and yields (%) $PhCH_2S(O)R$ (**21**)	$PhCH_2S(O_2)R$	PhCHO	norbornene oxide
20b; R = *t*-Bu	120		42	6	37	
		30	36	5	46	22 (47)[a]
20c; R = *i*-Pr	60		66	9	19	
		30	60	15	16	11 (64)[a]
20d; R = Et	60		66	7	13	
		30	71	9	14	7 (53)[a]
20e; R = Me	60		61	6	7	
		30	76	11	6	5 (78)[a]

[a] The yields in the parentheses are based on the amount of benzaldehyde produced.

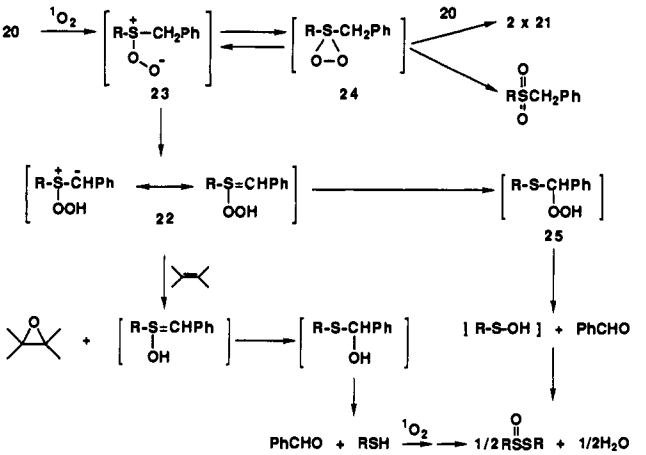
Table VI. $J_{^{13}C-H}$ Values and s Character of Alkyl Benzyl Sulfoxides **21b–e**

$PhCH_2S(O)R$	$J_{^{13}C-H}$, (Hz)	s character (%)[a]
21b; R = *t*-Bu	138.85	27.78
21c; R = *i*-Pr	139.05	27.82
21d; R = Et	139.25	27.85
21e; R = Me	139.35	27.87

[a] s character = $1/(1 + \lambda^2)$; $J_{^{13}C-H} = 500/(1 + \lambda^2)$.

straction of α-proton in the persulfoxide intermediate predominantly takes place and S-oxidation is suppressed. Meanwhile, the yields of the epoxide are higher for the sulfides substituted with a more bulky group, similar to those of benzaldehyde. There seems to be no substituent effect on the yields of epoxide on the basis of those of benzaldehyde produced. The alkyl substituents on the sulfur atom affect not the oxidizing ability of the active intermediate but the proportion of S-oxidation path to α-proton abstraction path. Since the acidity of α-proton may be one of the important factors responsible for this substituent effect, the C–H coupling constants at α-position of the benzyl group of sulfoxides **21b–e** were determined by ^{13}C NMR as in the case of thiazolidines.[20] The C–H coupling constants obtained and the corresponding s characters calculated from them[20a] are listed in Table VI. There is no significant difference in s characters. Thus, it seems that there is not enough difference in the acidity of α-protons to give such a substituent effect as described previously. If α-proton abstraction in the persulfoxide intermediate occurs on the alkyl group, the resulting product will be acetaldehyde from the ethyl group and formaldehyde from the methyl group.[15] Benzyl disulfide and the corresponding thiolsulfinate should also be produced from the benzyl group. The fact that none of these were produced in the reaction reveals that the hydrogen abstraction occurrs on the benzyl group. On the basis of these observations, the epoxidation mechanism might be described as shown in Scheme VII. Benzylic sulfide reacts with $^1O_2$ to give persulfoxide **23** as an initial intermediate followed by cyclization to thiadioxirane **24** as a secondary one, which reacts with another sulfide to afford 2 mol of sulfoxide or intramolecularly rearranges to a sulfone.[3g] When the alkyl group on the sulfide is bulky, the bimolecular reaction will be sterically inhibited. Thus, the ring opening of **24** leads back to the persulfoxide **23**, which then abstracts the α-proton to give *S*-hydroperoxysulfonium ylide **22**. Then, **22** proceeds to give α-hydroperoxide **25** via Pummerer-type rearrangement. Judging from the results that no remarkable difference is observed in the acidity of α-protons in the sulfoxides, the bulkiness of the substituent may accelerate the returning from **24** to **23** rather than the formation of **22** from **23**. There may

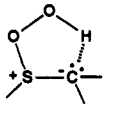
Scheme VII



be three possible intermediates, **22**, **24**, and **25**, as active oxidizing species for epoxidation of olefins. As the yield of the epoxide is in proportion to the yield of benzaldehyde, epoxidation by thiadioxirane **24** could be ruled out. α-Hydroperoxide **25**, an acyclic analogue of **12**, might have no ability to oxidize olefin, similar to the case of thiazolidines. Therefore, *S*-hydroperoxysulfonium ylide **22** rather than **25** is more likely to be an active oxidizing species in this cooxidation reaction of olefin to epoxide.

Conclusion

Singlet oxygenation of sulfides bearing active α-C–H bonds such as thiazolidine derivatives and benzylic sulfides caused cooxidation of olefin to epoxide. Intramolecular α-proton abstraction in the initially formed persulfoxide intermediate gives a *S*-hydroperoxysulfonium ylide intermediate that is capable of epoxidizing olefin and in itself inert toward singlet oxygen. There is one possibility that can account for the epoxidizing ability of the *S*-hydroperoxysulfonium ylide intermediate. An intramolecular hydrogen bonding may stabilize the intermediate **26** and would activate the electrophilic oxygen, so that it could react with olefin, similar to the case of peracid **27**. Thus, in singlet oxygenation of sulfides, an active oxidizing species much stronger



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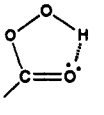

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than singlet oxygen itself and a primary intermediate such as persulfoxide **1** and thiadioxirane **3** can be formed as a secondary intermediate.

Experimental Section

IR spectra were recorded with a Hitachi 260-50 spectrometer, ^{1}H NMR spectra with a JEOL PMX 60SI spectrometer and a Bruker AM-500 spectrometer, and ^{13}C NMR spectra with a Bruker AM-500 spectrometer. Deuteriated chloroform was used as the solvent. Chemical shift values are reported (δ) relative to internal tetramethylsilane standard. Mass spectral data were obtained on a Hitachi RMU-6MG mass spectrometer. GLC analysis was done on a Hitachi 263-70 gas chromatograph equipped with a fid detector.

Reagent-grade solvents were used for the experiments in benzene, tetrahydrofuran, and methylene chloride. Benzene was distilled in the presence of lithium aluminum hydride before use. Tetrahydrofuran was distilled twice in the presence of lithium aluminum hydride before use. Methylene chloride was washed with water, dried over calcium chloride, and then distilled in the presence of calcium hydride. Tetraphenylporphine (Strem Chemicals), methylene blue (Kanto Chemical), and deuteriated chloroform for spectroscopy (Merck) were used as received. Norbornene (Tokyo Kasei) was used as received and its epoxide was prepared according to the literature method.[24] Thiazolidines **9a**[17a] and **9b**,**c**[25] were prepared from L-cysteine methyl ester according to the literature method. Their *S*-oxides were synthesized by oxidation with 3-chloroperoxybenzoic acid.[25] Benzyl methyl sulfide (Tokyo Kasei) was used as received. Benzyl ethyl, isopropyl, and *tert*-butyl sulfides were prepared by the reported method.[26] Their sulfoxides were prepared by oxidation of the corresponding sulfides with 3-chloroperoxybenzoic acid.[27] Their sulfone derivatives benzyl methyl,[28] benzyl ethyl,[29] benzyl isopropyl,[29] and benzyl *tert*-butyl[27] sulfone were synthesized by the literature method.

The light source was two 500-W tungsten–halogen lamps. Irradiations were carried out in a Pyrex tube on an ice–water bath while oxygen was passed through.

Reaction of Hydroperoxide 12a with Olefins. A 2.5 M benzene solution of thiazolidine **9a** containing tetraphenylporphine as a sensitizer was photooxygenated at 0 °C. After disappearance of **9a** and formation of **12a** were monitored by ^{1}H NMR,[17a] either norbornene or cyclohexene (75 M) was added and the resulting mixture was left to stand for 1.5 h at 0 °C in dark. Dimethyl sulfide (25 M) was then added, and the mixture was left at room temperature in the dark for overnight. Only the corresponding α-hydroxythiazolidine **10a** was obtained quantitatively along with DMSO by means of NMR and GLC analysis, and none of the corresponding epoxide was obtained at all.

Photooxygenation of Thiazolidine in the Presence of Olefins. A 0.25 M solution of thiazolidine **9a** containing tetraphenylporphine as a sensitizer was photooxygenated in the presence of norbornene until the starting material was consumed. After photolysis, dimethyl sulfide (2.5 M) was added to the reaction mixture at room temperature to decompose any of the peroxidic products formed. The mixture was left to stand for overnight in dark. The solvent was removed under reduced pressure, and the residue was subjected to ^{1}H NMR and analytical GLC (4 mm × 2 m glass column packed with 2% Silicon OV-1 on Uniport HP). The formation of *exo*-norbornene oxide was analyzed by GLC. DMSO and **10a** were identified by means of ^{1}H NMR. When the reaction mixture was separated by column chromatography with benzene and ethyl acetate as eluent, **10a** was isolated in 84% yield. The results obtained are summarized in Table I. Similarly, in the presence of cyclohexene, the corresponding epoxide was identified by means of GLC analysis. The yield was determined as 2-methoxycyclohexanol[30] after acid-catalyzed methanolysis of the reaction mixture. In the presence of stilbene or styrene, none of the corresponding epoxide was detected by GLC analysis. Photooxygenation of thiazolidines **9b** and **9c** in the presence of norbornene was also carried out under the same reaction conditions.

Photooxygenation of Benzyl Sulfide in the Presence of Norbornene. A chloroform solution of benzyl sulfide (**20a**, 0.25 M), norbornene (7.5 M), and methylene blue as sensitizer was photooxygenated. After complete consumption of the sulfide, the yields of the corresponding sulfoxide and sulfone were determined by means of ^{1}H NMR. The formation of the epoxide and benzaldehyde was analyzed by GLC. Similarly, in the presence of methyl phenyl sulfoxide (5 M) under the same reaction conditions, none of the epoxide and benzaldehyde was obtained. The yield of methyl phenyl sulfone was determined by GLC analysis (4 mm × 2 m glass column packed with 5% PEG-20MP on Uniport HP). The results obtained are shown in Table IV.

Photooxygenation of Alkyl Benzyl Sulfides. General Procedure. A 0.5 M deuteriated chloroform solution of the sulfide containing methylene blue as sensitizer was photooxygenated in a 5-mm NMR tube. After complete consumption of the sulfide, the products were analyzed by means of ^{1}H NMR. The results obtained are summarized in Table V.

Photooxygenation of Alkyl Benzyl Sulfides in the Presence of Norbornene. A methylene chloride solution of the sulfide (0.25 M), norbornene, and methylene blue as sensitizer was photooxygenated. The yields of the epoxide and benzaldehyde were determined by GLC analysis. The solvent was then removed under pressure, and the residue was subjected to ^{1}H NMR to analyze the formation of the corresponding sulfoxide and sulfone. The results obtained are summarized in Table V. In the absence of a sensitizer under the same reaction condition, it was observed by GLC and ^{1}H NMR that no reaction took place. Similarly, addition of DABCO (0.08 M), a singlet oxygen quencher,[18] completely inhibited this oxidation.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 64607003) from the Ministry of Education, Science, and Culture of Japan.

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