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Oxidations of Thioketones by Singlet and Triplet Oxygen

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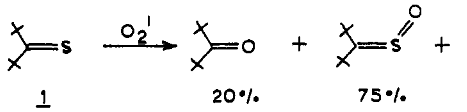
Oxidation of di-*tert*-butyl thioketone (1) and 2,2,4,4-tetramethylcyclobutyl thioketone (2) by singlet oxygen yields the corresponding sulfine and ketone; in the case of 1 the sulfine is the major product, whereas in 2 it is the ketone. 1,2,3-Dioxathietane has been suggested as the precursor for the ketones, and the zwitterionic/diradical peroxide is believed to be a common primary intermediate for both sulfine and ketone. Steric influence is felt both during primary interaction between singlet oxygen and thioketone and during the partitioning of the peroxide intermediate. Steric interaction is suggested as the reason for variations in the product distribution between 1 and 2. Singlet oxygen is also generated through energy transfer from the triplet state of thioketones. These excited states also directly react with oxygen to yield ketone.

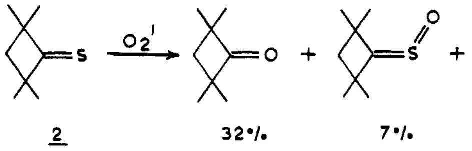
Oxidation of organic chromophores by singlet oxygen has sustained the interest of chemists for over a decade.[1] Photooxidation of the thiocarbonyl chromophore is no exception. In the course of time several reports have appeared on the photooxidation of thiocarbonyl compounds. These reported the formation of ketone as the sole product.[2] Singlet oxygen, generated by self-sensitization, has been speculated as the active species. Recently, we noted that di-*tert*-butyl thioketone is an exception to this general behavior and yields the corresponding sulfine as the major product.[3] Believing that bulky *tert*-butyl groups play a significant role in this anomalous behavior, we have studied in detail the photooxidation and oxidation by singlet oxygen of the highly hindered di-*tert*-butyl thioketone (1) and the similar but less hindered 2,2,4,4-tetramethylcyclobutyl thioketone (2). Surprisingly, these two thioketones showed marked differences in their behavior toward singlet and triplet oxygen as described below.

Results

Singlet oxygen, generated by dye sensitization or by thermal decomposition of triphenyl phosphite ozonide reacted with 1 and 2 to give the corresponding sulfine and ketone as identified by their spectral data (eq 1 and 2).



$SO\ (2SO \longrightarrow S + SO_2)$ (1)



$SO\ (2SO \longrightarrow S + SO_2)$ (2)

The product distribution in the case of 1 was found to be independent of the solvent, the thioketone concentration, and the source of singlet oxygen (Tables I and II). The rates of singlet oxygen quenching as measured by the inhibition of the self-sensitized rubrene photooxidation method[4] was estimated to be 1×10^4 and 3.1×10^5 (±10%) $M^{-1}s^{-1}$ for 1 and 2, respectively. In addition to ketone and sulfine, sulfur and sulfur dioxide were identified among the reaction products. Sulfur dioxide evolved during the oxidation was estimated gravimetrically,[5] and on the basis of this, the expected yield of the ketone was estimated and is shown in Table I. Efforts to characterize the reactive intermediates during the oxidation by using alcoholic solvents (methanol and ethanol), tetracyanoethylene, and other thioketones were singularly unsuccessful.

Direct excitation (500-W tungsten lamp) of 1 and 2 in aerated solvents gave the corresponding sulfine and ketone. However, the photooxidation of 2 was complicated by side reactions (reduction, α cleavage, and polymerization), and this discouraged detailed investigation. The product distribution during direct excitation of 1 was slightly solvent dependent (Table III). The photooxidation of 1 was quenched by singlet oxygen quenchers such as Dabco, 1,3-diphenylisobenzofuran, dimethyl sulfide, dihydropyran, cyclohexadiene, and tetramethylethylene (Table IV). Surprisingly, although the formation of sulfine was completely quenched, the formation of ketone persisted, albeit at a much lower rate. Excitation of 1 in the presence of chemical quenchers of singlet oxygen led to the oxidation of the quenchers, suggesting the generation of singlet oxygen. The efficiency of singlet oxygen generation was estimated by following 1,3-diphenylisobenzofuran method[6] and was found to be 0.85 at infinite dilution of 1.[7] Sensitization and quenching studies were conducted to identify the reactive state of 1 involved during the photooxidation. The formation of ketone and sulfine was sensitized by triplet sensitizers (4,4′-dibromobiphenyl and 1,4-dibromonaphthalene) and quenched by the triplet quencher alloocimine (Table IV). As controls it was noted that sulfines of 1 and 2 were stable toward singlet oxygen.

Discussion

Oxidation of Thioketones by Singlet Oxygen. Interesting aspects of our results on the oxidation of 1 and

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[1] Wasserman, H. H., Murray, R. W., Eds. "Singlet Oxygen"; Academic Press: New York, 1979.

[2] Schonberg, A.; Schulz, O.; Nickel, S. *Ber.* **1928**, *61*, 2195. Schonberg, A.; Mostafa, A. *J. Chem. Soc.* **1943**, 275. Ishibe, M.; Odani, M.; Sunami, M. *J. Chem. Soc. B.* **1971**, 1837. Worman, J. J.; Shen, M.; Nichols, P. C. *Can. J. Chem.* **1972**, *50*, 3923. Rajee, R.; Ramamurthy, V. *Tetrahedron Lett.* **1978**, 143.

[3] Tamagaki, S.; Akatsuka, R.; Nakamura, M.; Kozuka, S. *Tetrahedron Lett.* **1979**, 3665. Jayathirtha Rao, V.; Ramamurthy, V. *Indian J. Chem., Sect. B* **1980**, *19B*, 143. Ramnath, N.; Ramesh, V.; Ramamurthy, V. *J. Chem. Soc., Chem. Commun.* **1981**, 112.

[4] Monroe, B. *J. Phys. Chem.* **1977**, *81*, 1861.

[5] Vogel, A. I. "A Textbook of Quantitative Analysis"; ELBS and Longman Group Ltd.: London, 1970; pp 370, 462.

[6] Gorman, A. A.; Gould, I. R.; Hamblett, I. *Tetrahedron Lett.* **1980**, 1087. Wu, K. C.; Trozzolo, A. R. *J. Phys. Chem.* **1979**, *83*, 2823.

[7] The efficiency of singlet oxygen generation has been extrapolated to zero concentration of thioketone since self-quenching of thioketone competes with the above process. The details of the procedure are discussed in the following paper: Ramesh, V.; Ramnath, N.; Ramamurthy, V. *J. Photochem.*, in press.

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Scheme I. General Mechanism for the Oxidation of Thioketones by Singlet Oxygen

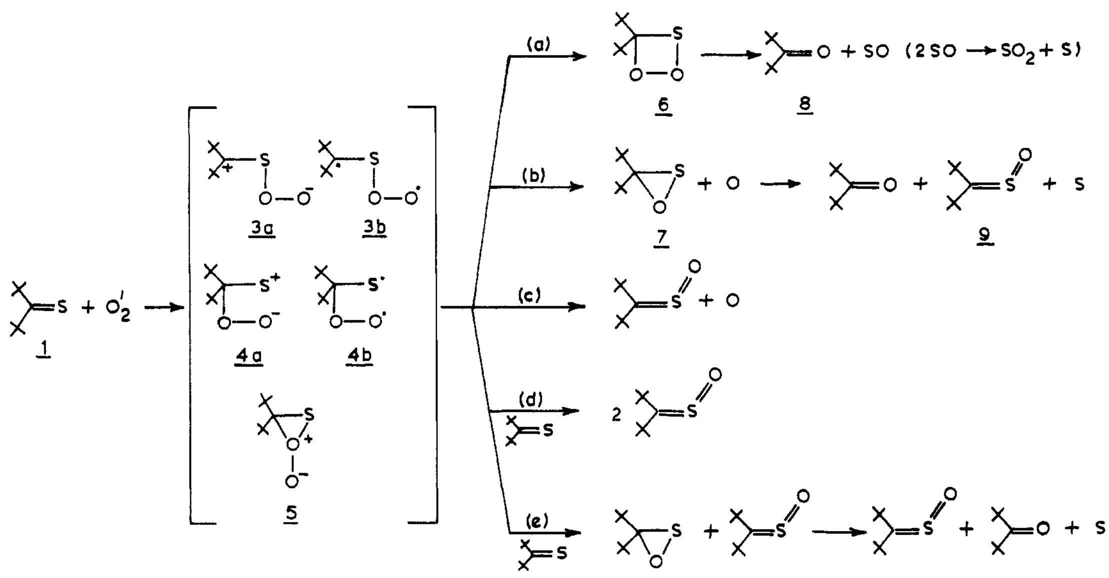

Table I. Product Distribution upon Singlet Oxygen Oxidation of 1 and 2[a]

	chloroform		acetonitrile		methanol	
source of singlet oxygen	% ketone	% sulfine	% ketone	% sulfine	% ketone	% sulfine
	(1) Di-*tert*-butyl Thioketone[b]					
methylene blue	25 (28)[c]	75	16 (20)[c]	84	18	82
rhodamin-B			18	82	12	88
crystal violet			27	73	20	80
eosin	26	74			12	88
triphenyl phosphite ozonide[d]	28	72			22	78
	(2) 2,2,4,4-Tetramethylcyclobutyl Thioketone[b]					
methylene blue	32 (35)[c]	7				
triphenyl phosphite ozonide[d]	35	10				

[a] Product distribution calculated by NMR integration (average of three independent runs); error limits are ±10%. In the case of 1 only sulfine and ketone were obtained whereas 2 yielded additional unidentified products. [b] $[\text{Thioketone}]_0$ = 0.1 M. [c] Expected yield of ketone based on sulfur dioxide estimation; error limit is ±5%; average of three estimations. [d] Dichloromethane as solvent.

Table II. Dye-Sensitized Irradiation of Di-*tert*-butyl Thioketone:[a] Concentration-Independent Product Distribution[b]

	chloroform		acetonitrile	
[thioketone], M	% ketone	% sulfine	% ketone	% sulfine
0.25	28	72	17	83
0.20	29	71	14	86
0.15	30	70	18	82
0.10	30	70	15	85
0.05	28	72	16	84
0.01	27	73	17	83

[a] Methylene blue used as the sensitizer; irradiation ($\lambda >$ 600 nm) was conducted by using a 500-W tungsten lamp and filter combinations. [b] Percentages by NMR integration and GC analysis; average of three independent runs; error limit is ±10%. Product distribution was measured at the end of ~30% conversion.

Table III. Product Yields in Various Solvents upon Direct Excitation (>450 nm) of 1 (0.1 M)[a]

	% yield		rel rate of thioketone disappearance[b]
solvent	sulfine	ketone	
cyclohexane	47	52	1.00
carbon tetrachloride	39	61	
diglyme	36	64	0.93
benzene	54	46 (50)[d]	
dioxane	42	58	1.27
chloroform	55	45 (40)[d]	1.87
acetonitrile	67	33	3.40
methanol[c]	63		2.31

[a] Product yields were estimated by NMR integration, average of at least four independent runs; error limit is ±10%. [b] Relative rate followed by monitoring the disappearance of 1 at λ_{max} = 540 nm. [c] Oxidation was accompaniedby polymerization. [d] Expected yield of ketone based on SO_2 estimation; error limit is ±5%.

2 by singlet oxygen are that the product distribution in these two cases are different; in the former, sulfine is the major product whereas in the latter it is the ketone, and the reactivity of 1 and 2 toward singlet oxygen differs by an order of magnitude. These results may be rationalized in terms of the general mechanism outlined in Scheme I. One of the products of oxidation is sulfur dioxide, and this can arise only if path a is involved. Although ketone formation can occur through paths b and e, sulfur dioxide evolution would not be observed. More importantly, the amount of sulfur dioxide evolved, estimated gravimetrically, corresponds to the amount of ketone formed, suggesting that all the ketone arises through path a. Sulfine can be formed through paths b–e. If sulfine is formed through paths d and e, the ratio of sulfine to ketone would depend upon the concentration of 1, but the observed results are to the contrary (Table II). Therefore, we suggest that both ketone and sulfine are formed through

Scheme II. Steric Effect on the Partitioning of Zwitterionic/Diradical Intermediate to Sulfine and Ketone

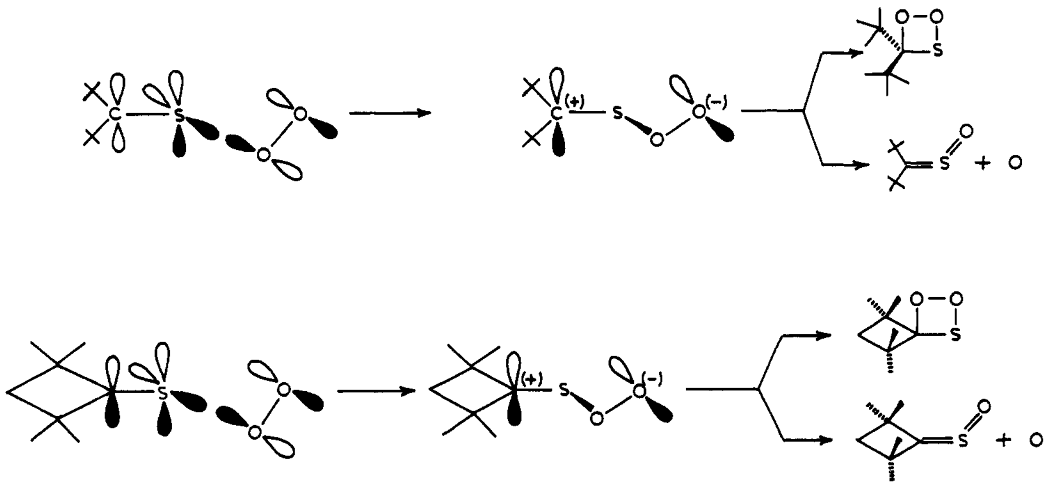

Table IV. Quenching and Sensitization Studies on the Photooxidation of 1[a]

solvent	quencher/sensitizer (concn, M)	% yield sulfine	% yield ketone
acetonitrile	Dabco (0.1)[b]	29	71
	dimethyl sulfide (0.1)[b]	12	88
	1,3-diphenylisobenzofuran (0.05)[b]	21	79
	alloocimine (0.1)[c]	70	30
	4,4'-dibromobiphenyl[d]	68	32
	1,4-dibromonaphthalene[d]	67	33
chloroform	Dabco (0.1)	42	58
	dimethyl sulfide (0.1)	14	86
	1,3-diphenylisobenzofuran (0.05)	20	80
	alloocimine (0.1)	61	39
	4,4'-dibromobiphenyl	57	43
	1,4-dibromonaphthalene	59	41

[a] [Thioketone] = 0.1 M; product distribution by NMR integration; average of three independent runs; error limit is ±10%. [b] Singlet oxygen quenchers. The oxidation was slowed down. The yield represents the products with respect to thioketone reacted. [c] Excited triplet quenchers ($E_T \simeq 47$ kcal/mol). The oxidation was slowed down. [d] Triplet sensitizers. Selective excitation of the sensitizer was achieved by using Corning glass filter CS-3.70.

unimolecular pathways a–c. Consistent with our conclusion are the results of oxygen consumption experiments. In the cases of 1 and 2, 1 mol of oxygen is required to oxidize 1 mol of thioketone; if paths d and e are involved, less than 1 mol of oxygen would be sufficient. Attempts to provide further support for this conclusion through competitive experiments using other thioketones were mitigated by the fact that all the thioketones thus far investigated quenched singlet oxygen more readily than 1.[8] If sulfine formation occurs through path b, then oxathiirane 7 would be expected to decompose exclusively to sulfine as ketone formation seems to be accompanied by sulfur dioxide evolution as noted earlier. At this stage, we have no direct evidence for the involvement of 1,2,3-dioxathietane 6, but the evolution of an equivalent amount of sulfur dioxide indirectly favors the above intermediate. Furthermore, the fate of an oxygen atom is unknown.

Possible intermediates resulting from the interaction of singlet oxygen with thioketone are listed in Scheme I. Singlet oxygen, an electrophile, with its empty π^* orbital is expected to interact with the filled n or π orbitals of the thiocarbonyl chromophore. The dominant interaction between these orbitals will be determined by the energy difference between the orbitals and the steric factors. We suggest that in the cases of 1 and 2, where the energy difference between n and π orbitals is large (>50 kcal/mol based on $n\pi^*$ and $\pi\pi^*$ absorptions) and where n electrons have lower ionization potentials than π electrons,[9] the singlet oxygen interacts preferentially with the n orbital. This is supported by our recent measurements of rates of singlet oxygen quenching by a number of dialkyl thioketones.[8] A plot of rate constants vs. ionization potentials for a limited number of dialkyl thioketones showed a linear correlation with n-electron but not with π-electron ionization potentials.[8] The lower rate of singlet oxygen quenching by 1 compared to that by 2 can be understood in terms of steric hindrance for the singlet oxygen approach by *tert*-butyl groups of 1. In the case of 2, where the methyl groups are held back by the cyclobutane ring, thus reducing the hindrance for n-orbital approach, the rate is expected to be higher and is indeed so. According to this model the formation of intermediate 3 would be favored; formation of 4–6 would not be consistent since these require the singlet oxygen to approach along the π orbital of the thiocarbonyl chromophore.[10]

The zwitterionic/diradical intermediate 3 can either close to dioxathietane 6 or eliminate oxygen as shown in Scheme II. The ease of closure of 3, however, will depend upon the substituents on the thiocarbonyl carbon. The bulky *tert*-butyl groups may sufficiently hinder the closure of 3 and thus lower the rate of path a compared to that for c. If this is the case, sulfine would be expected as the major product for 1, and this is indeed found to be true. The percentage of sulfine drops appreciably in 2 where one can visualize the *tert*-butyl group being drawn back to form a cyclobutane ring, thereby releasing the steric crowding and easing the closure of 3. A drop in the percentage of sulfine is therefore expected as is observed. Attempts to

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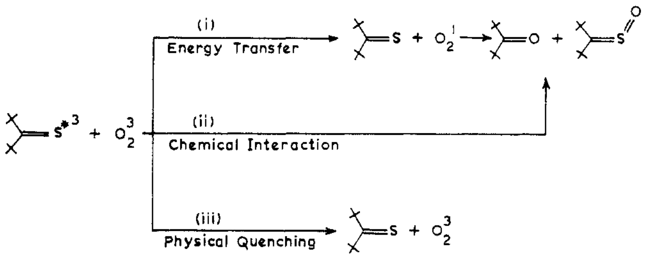
[8] Ramesh, V.; Ramnath, N.; Jayathirtha Rao, V.; Ramamurthy, V. *J. Photochem.*, in press.

[9] Ionization potentials for n and π electrons of 1 are measured to be 7.8 and 9.8 eV by UV PES. Similar measurements have not been carried out for 2. However, for closely similar compounds, tetramethylcyclobutane-1,3-dithione (n, 8.32 and 8.74 eV; π, 10.2 eV) and tetramethyl-3-thio-1,3-cyclobutanedione (n, 8.48 eV; 10.5 eV) have been reported. Tantry, K. N.; Basu, P. K.; Ramamurthy, V.; Rao, C. N. R.; Seddon, E. A.; Green, J. C. *Tetrahedron Lett.* **1979**, 4787.

[10] Recently, according to CNDO/B calculation, primary formation of oxathiirane *O*-oxide (5) has been favored as an intermediate during singlet oxygen addition to thioformaldehyde. Carlsen, L. *J. Chem. Soc., Perkin Trans. 2* **1980**, 188.

Scheme III. Interaction between Excited Thioketone and Triplet Oxygen



trap the suggested intermediate **3** through alcoholic solvents, tetracyanoethylene and xanthione were unsuccessful.[11]

Oxidation of Thioketones by Triplet Oxygen. Direct excitation of **1** and **2** in aerated solvents yields the corresponding sulfine and ketone. Since the photooxidation of **2** is complicated by side reactions, the photooxidation of **1** alone will form the content of the following discussion. Involvement of the triplet state of **1** in the above oxidation is evident from sensitization and quenching studies. The interaction of the triplet state of **1** with ground-state oxygen can result in three pathways as described in Scheme III. Accordingly, formation of sulfine and ketone can arise through two pathways: one wherein singlet oxygen, generated by energy transfer, oxidizes the ground-state thioketone and the other wherein ground-state oxygen oxidizes the excited triplet thioketone. This approach is consistent with the mechanism proposed by Tamagaki and coworkers.[3] Sufficient evidence exists for the involvement of path i: the rate of oxidation is slowed by the singlet oxygen quenchers, sulfine formation is quenched, and chemical quenchers of singlet oxygen are oxidized during the direct excitation of **1**. In fact, the efficiency of singlet oxygen generation is fairly high (0.85).[7] That the efficiency is less than unity indicates the interaction of triplet thione with ground-state oxygen also leads to paths ii and/or iii. We believe that the ketone, whose formation cannot be completely quenched by singlet oxygen quenchers, arises through path ii in addition to path i which is consistent with the above measured efficiency.

The mechanism of oxidation of excited triplet thioketone **1** by ground-state triplet can be speculated on in terms of Scheme I. Absence of the involvement of a second molecule of **1** in the above process is suggested by the nonvariation in the ketone–sulfine ratio with thioketone concentration (0.01–0.25 M). Correlation of the amount of sulfur dioxide evolved with the amount of ketone formed indicates that dioxathietane **6** might be the sole precursor of the ketone (Table III). The triplet excited state of **1** has partially filled n and π orbitals susceptible for attack by ground-state oxygen. It is known that $n\pi^*$ triplet carbonyls are attacked along either the n or π face by olefins.[12] Similarly, attack by oxygen along the n face would result in singlet diradical **3b** and along the π face would yield the diradical **4b**. During the direct excitation of **1**, the formation of sulfine can be completely quenched by singlet oxygen quenchers, suggesting that oxidation by triplet oxygen yields only the ketone. Since **3b** would be expected to yield both sulfine and ketone as observed during singlet oxygen oxidation, we speculate that triplet oxygen attacks the thiocarbonyl chromophore along the π face to yield **4b**. This probably prefers ring closure to yield **6**.

Perusal of Table III reveals that polar solvents slightly favor the formation of sulfine at the expense of ketone. We suggest that the energy transfer step (path i) yielding singlet oxygen (to give sulfine and ketone) is favored over direct chemical interaction (to yield ketone) by polar solvents. This is consistent with the literature reports[13] that activation of oxygen by aromatics and carbonyl triplets (through energy transfer) involves a certain amount of charge-transfer character. The relative rate of thioketone oxidation is slightly higher in polar solvents (Table III) as would be expected on the basis of the above rationale. In conclusion, the current work further substantiates the observations of Tamagaki and co-workers on the oxidation of **1**.

Thus we have shown that ground and excited states of thioketones can be oxidized by excited- and ground-state oxygen, respectively. The products of oxidation, sulfine and ketone, probably arise from the same primary intermediate, zwitterionic/diradical peroxide **3**, during oxidation by singlet oxygen. Involvement of 1,2,3-dioxathietane is suggested by our observations, but firm evidence has not been demonstrated yet. Singlet oxygen is generated during direct excitation of thioketones. This fact combined with the thioketones' absorption in the visible region and their solubility in nonpolar solvents, indicate that thioketones may be good singlet oxygen sensitizers. Much more experimental work is needed to clearly define the various aspects of the complicated photooxidation mechanism.

Experimental Section

Synthesis of 1 and 2. Di-*tert*-butyl thioketone (**1**) was prepared by following the published procedure.[14] 2,2,4,4-Tetramethylcyclobutyl thioketone (**2**) was prepared in 60% yield by bubbling HCl and H_2S gases through the methanolic solution of the corresponding ketone[15] for 15 h. Thioketones obtained were purified by column chromatography (silica gel, hexane). Di-*tert*-butyl thioketone: IR 1115 cm^{-1} (C═S); UV (cyclohexane) 540 nm (ϵ 7), 240 (7900); ^{1}H NMR (CCl_4) 1.42 (s); ^{13}C NMR ($CDCl_3$) 277.18 (s), 53.46 (s), 32.924 (q). 2,2,4,4-Tetramethylcyclobutyl thioketone: IR 1140 cm^{-1} (C═S); UV (cyclohexane) 510 nm (ϵ 9.2), 240 (8100); ^{1}H NMR (CCl_4), 1.33 (s), 2.33 (s); ^{13}C NMR ($CDCl_3$) 289 (s), 56.8 (s), 47.0 (t), 27.95 (q).

Dye-Sensitized Oxidation of 1 and 2. Dye-sensitized irradiations were conducted by irradiating aerated solutions of **1** and **2** (0.1 M) in the presence of appropriate dyes (10^{-4} M; methylene blue, crystal violet, eosin, and rhodamin B). Selective excitation of the dye was achieved by using Corning glass filter CS-2.58. The reaction was followed by TLC, after complete consumption of thioketone, the solvent was evaporated, and the products were isolated by column chromatography (silica gel, hexane/benzene). The products obtained were the corresponding ketone and sulfine as identified by their spectral data and by comparison with authentic samples[16] (Table I). Di-*tert*-butyl sulfine: IR 1180, 1080 cm^{-1} (characteristic of sulfine); ^{1}H NMR (CCl_4) 1.536 (s), 1.369 (s); ^{13}C NMR ($CDCl_3$) 216.49 (s), 43.52 (s), 40.42 (s), 30.69 (q), 29.54 (q); mass spectrum, m/e 174 (M$^+$). Anal. Calcd for $C_9H_{18}OS$: C, 62.04; H, 10.41. Found: C, 61.06; H, 10.50. 2,2,4,4-Tetra-

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[11] Trapping of zwitterionic intermediates during singlet oxygen addition to olefins and ketones has been achieved by using alcoholic solvents. Jefford, C. W.; Rimbault, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 295. Turro, N. J.; Ito, Y.; Chow, M. F.; Adam, W.; Rodriguez, O.; Yany, F. *Ibid.* **1977**, *99*, 5836.

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[13] Gizeman, O. L. J. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1143. Gizeman, O. L. J.; Kaufaman, F. *Ibid.* **1973**, *69*, 721. Garner, A.; Wilkinson, F. *Ibid.* **1976**, *72*, 1010. Garner, A.; Wilkinson, F. *Chem. Phys. Lett.* **1977**, *45*, 432.

[14] Ohno, A.; Nakamura, K.; Nakazima, Y.; Oka, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2403.

[15] Wedekind, E.; Weisswange, W. *Ber.* **1906**, *39*, 1631. Herzog, H. L.; Buchman, E. R. *J. Org. Chem.* **1951**, *16*, 99. Hartzler, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 4527.

[16] Authentic samples of sulfines were prepared by *m*-chloroperbenzoic acid oxidation of the corresponding thioketones. Ketones were prepared by the reported procedures.[15]

methylcyclobutyl sulfine: IR 1060 cm^{-1} (characteristic of sulfine); ^{1}H NMR (CCl_4) 1.4 (s), 1.567 (s), 1.83 (s).

Dye sensitization of 1 was also conducted by varying the concentration of thioketone (0.01–0.25 M), and the ratio of sulfine to ketone was determined by ^{1}H NMR integration and by gas chromatographic analysis (10 ft × $^1/_8$ in., 10% Carbowax 20M on 80–100-mesh Chromosorb W) within 30% conversion (Table II).

Oxidation of 1 and 2 by Singlet Oxygen Generated by the Decomposition of Triphenyl Phosphite Ozonide. Triphenyl phosphite ozonide was prepared at −78 °C in dichloromethane/methanol by following the reported procedure.[17] The above solution was warmed to −10 °C at which time oxygen evolution was visible, and at this stage thioketone 1 and 2 was added. When the reaction mixture was kept at room temperature for about 1 h, the thioketone color disappeared, and products were isolated by column chromatography (Table I).

Estimation of Sulfur Dioxide Evolved. A chloroform solution (200 mL) of the thioketone (500 mg) and methylene blue (10 mg) was placed in a Pyrex immersion well consisting of a gas inlet and an outlet. The outlet was connected to a trap containing aqueous sodium hydroxide (0.3 M) solution. The immersion well was irradiated (500-W tungsten lamp) while oxygen was continuously bubbled through the inlet. The sulfur dioxide evolved ($2SO \rightarrow SO_2 + S$) was collected as sodium sulfite in the trap and was oxidized to the sulfate by the addition of bromine. The sulfate was gravimetrically estimated by following the reported procedure.[5]

Oxidation of 1 upon Direct Excitation. Aerated solutions of 1 (0.01–0.25 M) in various solvents were irradiated with 500-W tungsten lamp. Irradiation was followed by NMR, and the product ratio was determined by NMR integration. After complete conversion, products were isolated by column chromatography and identified as the corresponding sulfine and ketone. Sulfur dioxide evolved during direct excitation was determined by the above procedure.

Relative rates of oxidation of 1 in various solvents were determined by irradiating (450-W medium-pressure mercury lamp, Corning glass filter CS-3.68) 3-mL aerated solutions of 1 (0.1 M) in various solvents in a merry-go-round style. After about 5 h of irradiation the amount of thioketone oxidized was estimated by measuring the optical density of 1 at 540 nm. With the rate in cyclohexane taken as 1.00, the relative rates are shown in Table III.

Quenching and Sensitization Studies. Aerated solutions of 1 (0.1 M) in chloroform/acetonitrile were irradiated in the presence of singlet oxygen quenchers (0.05–0.1 M). The quenchers used were Dabco, 1,3-diphenylisobenzofuran, dimethyl sulfide, 2,3-dimethylbut-2-ene, dihydropyran, and cyclohexadiene. In the presence of quenchers the oxidation was very slow. Products were isolated by column chromatography after complete decolorization of the thioketone solution. In addition to di-*tert*-butyl sulfine and di-*tert*-butyl ketone, oxidation products of quenchers were isolated and identified by comparison with authentic samples.[18] 1,3-Diphenylisobenzofuran yielded *o*-dibenzoylbenzene, dimethyl sulfide gave dimethyl sulfoxide, 2,3-dimethylbut-2-ene gave 2,3-dimethyl-3-(hydroperoxy)but-1-ene, and cyclohexadiene yielded the cyclohexadiene endoperoxide.

Triplet-sensitized irradiation was conducted in chloroform/acetonitrile by using 4,4′-dibromobiphenyl ($E_T \simeq 62$ kcal/mol) and 1,4-dibromonaphthalene ($E_T \simeq 59$ kcal/mol) as triplet sensitizers. A 10-mL solution of thioketone 1 (0.1 M) with 0.005 M sensitizer was irradiated (450-W medium-pressure mercury lamp, Corning glass filter CS-7.60) until decolorization. Product yields were determined by ^{1}H NMR integration (Table IV). Since the thioketone concentration is much higher than the dissolved oxygen concentration, we assume that energy transfer occurs preferentially to the thioketone.

The triplet quenching study was conducted by using alloocimene as the triplet quencher ($E_T \simeq 47$ kcal/mol) in acetonitrile and chloroform. Five samples of 3-mL solutions of 0.1 M 1 and varying concentrations of the quencher (0, 0.1, 0.15, 0.2, and 0.25 M) were irradiated for 5 h in a merry-go-round style with a 450-W medium-pressure mercury lamp and Corning glass filter CS-3.68. The amount of thione reacted was estimated by electronic absorption spectrometry. A linear Stern–Volmer plot was obtained, and at 0.25 M alloocimene the oxidation was 90% quenched.

Determination of Rate Constants for Singlet Oxygen Quenching by 1 and 2 and Efficiency of Singlet Oxygen Generation. The rate of singlet oxygen quenching by 1 and 2 was measured by the inhibition of self-sensitized rubrene photooxidation method developed by Monroe.[4] The efficiency of singlet oxygen generation was measured by the method of sensitized oxidation of 1,3-diphenylisobenzofuran.[6]

Control Experiments. Thioketones 1 and 2 are stable indefinitely in the dark in aerated media both as a pure liquid and in organic solvents. Sulfines of 1 and 2 are also stable in aerated media both in the absence and presence of visible light. Sulfines of 1 and 2 resisted oxidation by singlet oxygen (dye sensitization). Direct excitation of 1 in a nitrogen atmosphere in organic solvents did not bring about any change (>10 days). Similar irradiation of 2 resulted in disulfide and sulfur incorporation (<2 days).

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Registry No. 1, 54396-69-9; 2, 64273-93-4; di-*tert*-butyl sulfine, 56956-25-3; 2,2,4,4-tetramethylcyclobutyl sulfine, 79735-00-5.

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(18) Authentic samples of oxidation products of quenchers, for comparison, were prepared by dye-sensitized oxidation of the quenchers.