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MECHANISM OF OXIDATION OF α,β-UNSATURATED THIONES BY SINGLET OXYGEN

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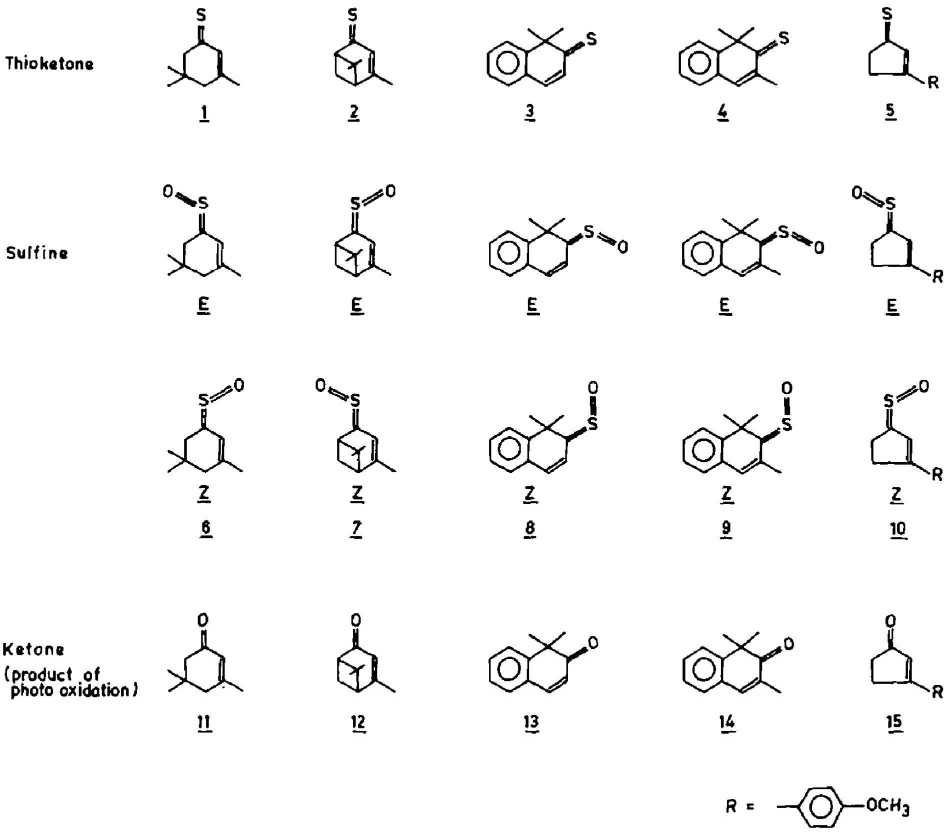
Abstract—Photo-oxidation of α,β-unsaturated thiones yields the corresponding ketones as the only product. Studies carried out on three systems, namely thioketones, α,β-unsaturated thiones and thioketenes, have revealed that there exists a similarity in their mechanism of oxidation. It has been suggested that the thiocarbonyl chromophore is the site of attack by singlet oxygen in α,β-unsaturated thiones and that the adjacent C—C double bond is inert under these conditions. Absence of sulphine during the oxidation of α,β-unsaturated thiones is attributed to the electronic factors operating on the zwitterionic/diradical intermediate. While α,β-unsaturated ketones are poorly reactive, α,β-unsaturated thiones are highly reactive toward singlet oxygen.

One of the earliest photoreactions of thiones to be recognized was the reaction of excited thione with oxygen. Following Gattermann and Schulze's[1] report of the light catalysed oxidation of thiones, Schonberg and Mustafa[2] found that thiobenzophenone reacts with oxygen even in the dark to give benzophenone which is also the product of the light catalysed reaction. In sunlight a trisulphide is also formed. Oster *et al.*[3] conducted the reaction with visible light and found quantitative conversion to benzophenone. A direct reaction between $n\pi^*$ thione and triplet oxygen was speculated. The quantum yield of oxidation, which is dependent on oxygen concentration, was estimated to be *ca* 0.05. Light catalysed oxidation to give the corresponding ketones as the sole products for a number of thiones has been reported by several groups of workers.[4] Kinetic studies obviated earlier speculations that the reaction proceeds via $n\pi^*$ thione and triplet oxygen and suggested that the excited thione photosensitizes the formation of singlet oxygen. Singlet oxygen, thus formed, reacts with thione to form thiadioxetane as an intermediate. Analogous to the reactions of singlet oxygen with olefins, the rupture of the C—S bond of thiadioxetane may be expected to be accompanied by chemiluminescence. Indeed, such a phenomenon has been reported during the oxidation of several diaryl thiones.[5] Photo-oxidation of several diaryl thiones in the solid state also yields the corresponding ketones. However, an impressive difference in the oxidizability of several diaryl thiones is observed during their photolysis in the solid state.[6]

A deviation from the generally observed quantitative conversion to ketone was reported during the photo-oxidation of di-t-butylthione.[7] The major product was the corresponding sulphine. The light induced formation of sulphines, which hitherto had been observed only during the dark reaction of thiobenzophenone,[8] added a new dimension to the photo-oxidation of thione and triggered a systematic mechanistic investigation.[9] Aerated solutions of diaryl, dialkyl and aryl alkyl thiones undergo ready oxidation to the corresponding sulphine and/or ketone upon $n\pi^*$ excitation. Electron withdrawing substituents in diaryl and aryl alkyl thiones favour sulphine formation. In [2.2.1] bicyclic thiones, the presence of Me groups at the C-7 position promotes sulphine formation. A striking difference in the yield of sulphine is noticed between di-t-butylthione and 2,2,4,4-tetramethylcyclobutanethione.[10] A proposed general mechanism involves the attack of singlet oxygen on the 'n' lobe of the thiocarbonyl chromophore.[11] A zwitterionic/diradical intermediate is regarded to be the precursor for thiadioxetane and sulphine. A steric factor has been invoked to rationalize the product distribution in dialkylthiones. The variation in the product distribution in the diaryl and aryl alkyl series effected by substituents is rationalized in terms of electronic factors operating on the zwitterionic/diradical intermediate. Rates of quenching of singlet oxygen by thiones have been estimated to be in the range of *ca* $10^5\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$.[12]

Photo-oxidation of a new class of heterocumulenes, namely thioketenes, has also been reported.[13] Oxidation of thioketenes by singlet oxygen, unlike ketenes[14] and ketenimines,[15] yields several products. Two thioketenes, namely di-t-butylthioketene and 2,2,6,6 - tetramethylcyclohexylidenemethanethio - ketone, have been studied in detail. Except for the formation of 2,2,6,6-tetramethylcyclohexanone, all the other products of oxidation of the above two thioketenes are unexpected based on the established behaviour of ketenes and ketenimines. It is believed that the initial attack of singlet oxygen, similar to thioketenes, occurs on the sulphur of the thioketene chromophore. However, during the oxidation of ketenes and ketenimines it has been suggested that the singlet oxygen attacks the central carbon to generate the zwitterionic intermediates. Therefore, the mechanism of oxidation of thioketenes by singlet oxygen is speculated to be different from that of ketenes and ketenimines.

As a logical extension of the above studies, we have carried out the oxidation of α,β-unsaturated thiones and the results are presented here. The reaction of singlet oxygen with alkenes has been studied extensively.[16] Despite this, there are relatively few examples of the successful oxidation of alkenes that are substituted with electron withdrawing groups. It has been established that the reactivity of α,β-unsaturated ketones toward singlet oxygen is strongly dependent on the conformation of the unsaturated system.[17] Those α,β-unsaturated carbonyl systems which prefer the s-*cis* conformation are rapidly oxidized by singlet oxygen, whereas those systems which prefer s-*trans* conformation react slowly or not at all.[18] In this connection, we thought that it would be interesting to compare the behaviour of α,β-unsaturated thiones with α,β-



unsaturated ketones. Further, very little is known about the excited state behaviour of α,β-unsaturated thiones due to their high ground state reactivity. Thiones 1–5 studied here are unusually stable and, thus, provided an opportunity to explore their ground and excited state behaviour.

RESULTS

Direct excitation of α,β-unsaturated thiones 1–5 in aerated solvents resulted in decolorization and formation of the corresponding ketones **11–15**, respectively (Table 1). Based on our earlier studies,[10,11] corresponding sulphines are also expected as one of the oxidation products. Failure to detect sulphine in these cases is neither due to their poor stability nor to their ready oxidizability as tested by independent experiments. α,β-Unsaturated sulphines are a poorly known class of compounds. However, they were found to be quite stable upon synthesis from the corresponding thiones using *m*-chloroperbenzoic acid. These sulphines are also oxidized by singlet oxygen and ozone to the corresponding ketones, but the rate of oxidation is appreciably slower than that of thiones 1–5. Therefore, the absence of sulphines **6–10** during photo-oxidation of **1–5** is real and mechanistically significant. Suppression of these oxidations in the presence of singlet oxygen quenchers, such as Dabco, 1,3-diphenylisobenzofuran and 2,3-dimethylbut-2-ene, and the formation of the corresponding singlet oxygenation products in the latter two cases suggested the involvement of singlet oxygen in these photo-oxidations. To substantiate this, oxidation of thiones by singlet oxygen, generated independently, was carried out. As expected, singlet oxygen, generated independently through dye sensitization and by thermal decomposition of triphenyl phosphite ozonide, readily reacted with **1–5** to yield the corresponding ketones in similar yields as upon direct excitation (Table 1). Efforts to characterize the reactive intermediates through trapping studies using alcoholic solvents, diphenyl sulphide and diphenyl sulphoxide were unsuccessful. In addition to ketone, sulphur and sulphur dioxide were identified among the reaction products. Sulphur dioxide evolved during the oxidation was estimated gravimetrically[19] and, on the basis of this, the expected yield of ketone was estimated and is shown in Table 1 for thiones **1–3**. The rates of singlet oxygen quenching as measured by the inhibition of the self-sensitized rubrene photo-oxidation method[20] are given in Table 1. Based on the results obtained with thioketones,[10,11] the excited triplet state of thione is expected to be the reactive species. No quenching and sensitization studies were carried out with **1–5**. However, spectroscopic measurements suggested **1–5** to have a unit quantum yield of intersystem crossing from S_1 to T_1.[21] They also exhibited intense phosphorescence at 77 K and were found to have triplet energy in the range 40–45 kcal/mol. Thus, triplet thiones having sufficient energy to generate singlet oxygen are expected to be the active species. Interaction between singlet oxygen and thione can be expected to lead to a superoxide anion which, in turn, could be the real oxidizing species. In this regard, oxidation of thiones **1** and **4** with potassium superoxide was conducted (Table 1). During our studies on dialkyl and arylalkylthiones,[11] a similarity in behaviour between oxidation with ozone and singlet oxygen was

Table 1. Oxidation of α,β-unsaturated thiones

		Direct excitation		Dye-sensitized oxidation[c]		Triphenyl phosphite ozonide oxidation[d]		Ozonolysis		Reaction with KO_2[e]		
Thione[a]	Solvent	Ketone (%)	Reaction time (hr)	Ketone (%)	Reaction time (hr)	Ketone (%)	Reaction time (hr)	Ketone (%)	Reaction time (hr)	Ketone (%)	Reaction time (hr)	Rate of quenching of $^1O_2$ by thione k_q (M^{-1} s^{-1})
1	$CHCl_3$	65 (58.5)[b]	14	70	5	62	0.10	70	0.08	50	0.5	6.1×10^5
	MeOH	60	14									
2	$CHCl_3$	77 (70)[b]	8	90	4	72	0.15	73	0.08	—	—	5.616×10^5
	MeOH	75	4.5									
3	$CHCl_3$	76 (75)[b]	30	80	20	80	0.10	87	0.08	—	—	4.3×10^5
	MeOH	70	30									
4	$CHCl_3$	100	50	100	40	84	0.10	85	0.08	42	1.0	6.65×10^5
	MeOH	83	45									
5	$CHCl_3$	60	4	65	2	57	0.15	52	0.08	—	—	2.3×10^6
	MeOH											

[a] Thione = 0.02 M.

[b] Estimated yield of ketone based on sulphur dioxide evolved which was estimated gravimetrically; error limit, ±5%.

[c] Methylene chloride as the solvent and methylene blue as the dye sensitizer.

[d] Methylene chloride as the solvent at 0°.

[e] Dry acetonitrile as the solvent.

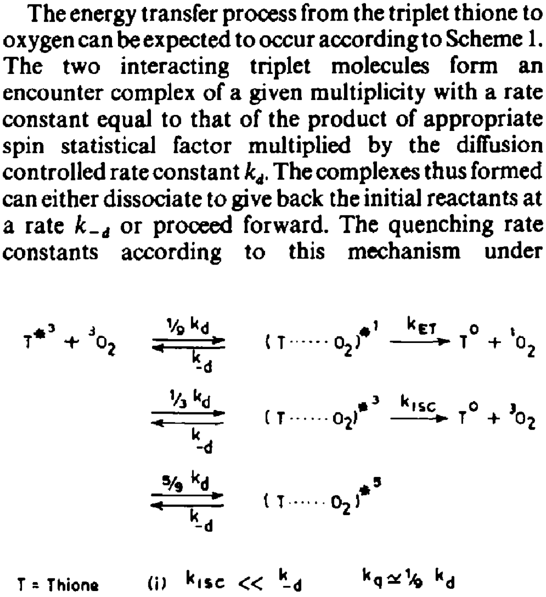
observed providing an important mechanistic analogy.[22] Ozonolysis of thiones 1–5 gave only the corresponding ketone and, at no stage of oxidation, did sulphine appear as the product.

DISCUSSION

α,β-Unsaturated thiones 1–5, in general, upon direct excitation are oxidized to the corresponding ketones. Formation of ketone can arise through two pathways: one where singlet oxygen generated through an energy transfer process oxidizes the ground state thione and the other where the ground state oxygen oxidizes the excited state thione. In the present system the involvement of the singlet oxygen pathway is suggested by the following observations. The rate of oxidation is completely suppressed by singlet oxygen quenchers, such as Dabco, 1,3-diphenylisobenzofuran and 2,3-dimethylbut-2-ene, and, at the same time the chemical quenchers of singlet oxygen yield the corresponding oxidized products. Further, the product obtained during oxidation by singlet oxygen, generated by dye sensitization and by thermal decomposition of triphenyl phosphite ozonide was the same as that during direct excited oxidation. Thus, we generalize that the singlet oxygen pathway is the major mode of oxidation upon direct excitation of thioketones and α,β-unsaturated thiones.

The oxidizing species, namely singlet oxygen, can be expected to arise through the energy transfer process from the lowest excited singlet or triplet states of 1–5 ($E_{S_1} \sim 50$ kcal/mol and $E_{T_1} \sim 45$ kcal/mol). In general, thiones are established to have an efficient and high rate of intersystem crossing from S_1 to T_1 ($\Phi = 1$; $k_{isc} \sim 10^{11}$ s^{-1}).[23] Further, the small energy gap between S_1 and T_1 is insufficient to populate excited states of oxygen. These preclude the process involving the $n\pi^*$ excited singlet state. Therefore, singlet oxygen is believed to be generated via an energy transfer process from the $n\pi^*$ triplets of 1–5. Although, we did not measure the efficiency of singlet oxygen generation by 1–5, for other thiones this has been reported to be close to unity.[12]

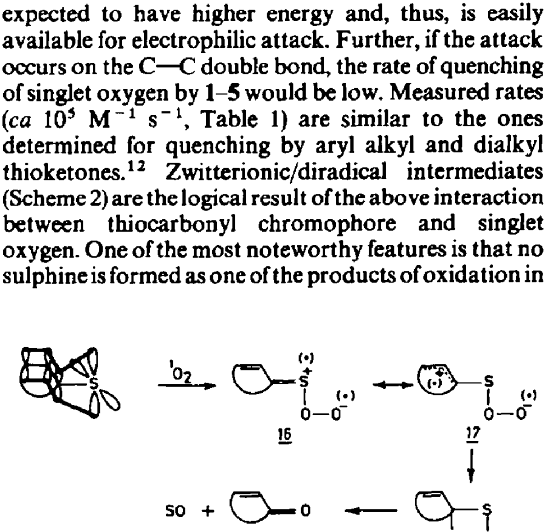
The energy transfer process from the triplet thione to oxygen can be expected to occur according to Scheme 1. The two interacting triplet molecules form an encounter complex of a given multiplicity with a rate constant equal to that of the product of appropriate spin statistical factor multiplied by the diffusion controlled rate constant k_d. The complexes thus formed can either dissociate to give back the initial reactants at a rate k_{-d} or proceed forward. The quenching rate constants according to this mechanism under conditions $k_{isc} \ll k_{-d}$ cannot exceed $1/9\ k_d$ and this is in agreement with experimental results for the oxygen quenching of aromatic hydrocarbon triplets.[24] Exceptions for which k_q approaches $1/3\ k_d$ include several stilbene derivatives[25] and carbonyl compounds.[26] Measurements of quantum efficiency of singlet oxygen production and rates of oxygen quenching of triplets of 1–5 and other thiones are underway (P. K. Das, C. V. Kumar, V. Pushkara Rao and V. Ramamurthy, unpublished results). However, for a few thiones, the quenching rates have been reported to be larger than $1/9\ k_d$.[27] On the basis of the data available at present it is not possible to identify the mechanism responsible for the high value of k_q.



Scheme 1.

Interaction between α,β-unsaturated thiones and singlet oxygen can result either in electron transfer or chemical bond formation. An electron transfer mechanism giving rise to a radical cation superoxide ion pair has been considered during the (2+2) cycloaddition of singlet oxygen to enamines and reactions with phenols, sulphides and azines.[16] If such an electron transfer prior to bond formation occurs in 1–5, the oxidizing species would be the superoxide anion. In this regard, oxidation of 1 and 4 with potassium superoxide in dry acetonitrile was conducted. Surprisingly, these were instantaneously oxidized to the corresponding ketones by superoxide. However, according to energetics, electron transfer from thiones to singlet oxygen is not expected. It has been suggested that an electron transfer reaction (from substrate to singlet oxygen) is possible only for substrates with oxidation potentials less than *ca* 0.5 V *vs* SCE.[28] In fact no evidence for electron transfer with olefins, having oxidation potentials up to *ca* 0.67 V was obtained.[29] Several diarylthioketones have been reported to have oxidation potentials in the range 0.93–1.70 V *vs* SCE.[30] Thiones 1–5 are also expected to have similar values based on the linear correlation that exists between E_{S_1} and the oxidation potential. Therefore, the electron transfer pathway is expected to be unimportant.

Electrophilic singlet oxygen can be expected to interact either with the localized *n* orbital or delocalized π orbital of the enethione chromophore. We believe that singlet oxygen interacts with the *n* orbital since it is expected to have higher energy and, thus, is easily available for electrophilic attack. Further, if the attack occurs on the C—C double bond, the rate of quenching of singlet oxygen by 1–5 would be low. Measured rates (*ca* 10^5 M^{-1} s^{-1}, Table 1) are similar to the ones determined for quenching by aryl alkyl and dialkyl thioketones.[12] Zwitterionic/diradical intermediates (Scheme 2) are the logical result of the above interaction between thiocarbonyl chromophore and singlet oxygen. One of the most noteworthy features is that no sulphine is formed as one of the products of oxidation in



Scheme 2.

Table 2. Product distribution during the singlet oxygen oxidation and ozonolysis of thiopivalophenones

	$^1O_2$ oxidation[a]		Ozonolysis[b]	
Thioketone	Ketone (%)	Sulphine (%)	Ketone (%)	Sulphine (%)
4-Methoxythiopivalophenone	75	2	93	7
Thiopivalophenone	60	12	66	33
4-Chlorothiopivalophenone	51	25	5	95
4-Fluorothiopivalophenone	38	20	14	86

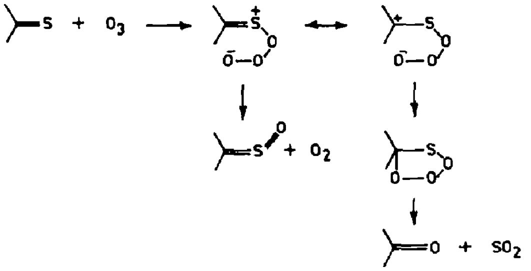
[a] Methylene blue sensitized oxidation in acetonitrile.
[b] Ozonolysis in acetonitrile.

the cases of 1–5. Based on the results on dialkyl thioketones,[10,11] 4 may be expected to yield a sulphine as the major product but even this did not give any sulphine. However, through independent experiments it has been established that sulphines 6–10, expected products of oxidation, are stable under our experimental conditions. Formation of 11–15 appears to be preceded by a 1,2,3-dioxathietane intermediate as the sulphur and sulphur dioxide products of its decomposition have been isolated in all the thiones investigated. Furthermore, the estimated yield of sulphur dioxide corresponds with the isolated yield of ketone (Table 1). However, direct evidence for dioxathietane intermediate, which is highly desirable, has not been obtained.

Oxidation of 1–5, we believe, follows the general mechanism proposed for the oxidation of thiones.[10] Similarity in behaviour between diaryl, aryl alkyl and α,β-unsaturated thiones is striking. Product distribution in 1–5 can be understood in terms of electronic factors operating on the zwitterionic/diradical intermediate. Resonance forms 16 and 17 contribute toward the structure of the suggested intermediate. While 17 can undergo facile ring closure to 1,2,3-dioxathietane, bonding constraints retard the closure of 16. Since the presence of an additional double bond adjacent to the thiocarbonyl chromophore favours the form 17, general preference for ketone formation is expected and is observed.

A similar substituent-dependent product distribution has also been observed during the ozonolysis of thiones. Distribution of products during the oxidation of thiopivalophenones by singlet oxygen and ozone is shown in Table 2. It is obvious that similarity exists in the ketone–sulphine ratio during the above two oxidations. Similar to singlet oxygen oxidation, ozonolysis of 1–5 gave only the corresponding ketones even under controlled conditions. We believe that these observations can once again be rationalized in terms of the electronic effect of the substituents on the intermediate that is formed by the attack of ozone on the thiocarbonyl chromophore (Scheme 3).

Efforts are being directed toward providing evidence for the proposed intermediates and achieving spectroscopic identification of the 1,2,3-dioxathietane. Studies so far, carried out on three systems, namely thioketones, α,β-unsaturated thiones and thioketenes, have revealed that there exists a similarity in their mechanisms of oxidation. Further, it has been demonstrated through studies on thioketenes and α,β-unsaturated thiones that the thiocarbonyl chromophore is the site of attack by singlet oxygen in these systems and the C—C double bond is inert under these conditions. Whereas α,β-unsaturated ketones are poorly reactive, α,β-unsaturated thiones are highly reactive toward singlet oxygen.



Scheme 3.

EXPERIMENTAL

Spectral data. UV-visible absorption spectra were recorded on a Shimadzu UV-180 double beam spectrophotometer. IR data were obtained using a Perkin–Elmer Model 730 IR spectrometer. Varian T-60 and Bruker HW-270 FT NMR spectrometers were used for recording ^{1}H-NMR spectra.

Preparation of ketones. Ketones were either obtained commercially or prepared by reported methods.[31]

Preparation of thiones. Thiones were prepared by following any one of the procedures described below. Spectral data, the method employed and yields for individual thiones are presented in Table 3.

Method A. Dry H_2S and HCl gases were simultaneously bubbled through an alcoholic soln (50 ml) of ketone (0.03 M) for 2 hr. The HCl supply was then cut off and H_2S gas alone passed through for a further 4 hr. The soln was then poured into 500 ml of ice-cold water and extracted with hexane. The organic extract was washed three times with water and dried over Na_2SO_4. Evaporation of the solvent and purification of the crude mixture by column chromatography (silica gel–hexane) gave the corresponding thione.

Method B. The ketone (4 g) was dissolved in dry pyridine (40 ml) and to this P_2S_5 (6 g) was added in portions. The mixture was gently refluxed for 2 hr and the product extracted with hexane, washed with water and dried over Na_2SO_4. Thiones thus obtained were purified by column chromatography (silica gel–hexane).

Preparation of sulphines. Based on the reported oxidation of thiones,[11] sulphines were expected as one of the products of oxidation of 1–5. Therefore, authentic samples of sulphines 6–10 were prepared and their stability under our oxidation conditions tested. α,β-Unsaturated sulphines were obtained in quantitative yield (95%) upon controlled oxidation of the corresponding α,β-unsaturated thiones with *m*-chloroperbenzoic acid. Use of more than 1 equivalent of peracid resulted in over oxidation and yielded only the ketone.

Table 3. Spectral data of α,β-unsaturated thiones

Thiones	Method	Yield (%)	IR ν_{max}^{neat} (cm^{-1})	^{1}H-NMR (CCl$_4$) (δ)
1	A	75	1600 1100	6.54 (1H, m), 2.60 (2H, s), 2.00 (2H, m), 1.80 (3H, d), 1.00 (6H, s)
2	A	50	1595 1090	6.35 (1H, m), 3.40 (1H, t), 2.10–2.80 (3H), 1.95 (3H, d), 1.50 (3H, s), 1.00 (6H, s)
3	B	50	1160	6.9–7.6 (6H), 1.65 (6H, s)
4	B	60	1160	7.0–7.40 (5H), 2.3 (3H, d), 1.6 (6H, s)
5	A	30	1140	6.8–7.7 (5H), 3.8 (3H, s), 2.9 (4H, s)

A soln of *m*-chloroperbenzoic acid (3 mM in 100 ml of CHCl$_3$) was added, with stirring, to a soln of thione (3 mM in 200 ml of CHCl$_3$) over 40 min at 0°. Stirring was continued for another 30 min during which time the soln became colourless. The mixture was then extracted with 250 ml of NaHCO$_3$ aq washed with water and dried over Na$_2$SO$_4$. Removal of the solvent afforded the sulphine as a mixture of *Z* and *E* isomers. Both the isomers were characterized by IR and ^{1}H-NMR (using shift reagent if necessary) spectra. Spectral details are given in Table 4.

Photo-oxidation of thiones. Aerated solns of **1**–**5** in CHCl$_3$ (0.02 M, 100 ml) were irradiated using two 500 W tungsten lamps at room temp. The progress of the reaction was monitored by TLC. Irradiation was continued until the thione colour had disappeared. Solvent was removed and the crude irradiation mixture was column chromatographed (silica gel–hexane–benzene). Ketone was obtained as the only product and was identified by comparison with an authentic sample.

Oxidation of thiones by singlet oxygen. (*a*) *Dye sensitization.* Aerated solns of thiones **1**–**5** (0.02 M) in 100 ml of CHCl$_3$ were irradiated with two 500 W tungsten lamps in the presence of methylene blue (10^{-4} M) as the sensitizer. After complete disappearance of the thione, as tested by TLC, the solvent was distilled off and the product ketone was isolated by preparative TLC.

(*b*) *Thermal decomposition of triphenyl phosphite ozonide.* Triphenyl phosphite ozonide was prepared at −80° in methylene chloride by bubbling O$_3$ through a soln of triphenyl phosphite (100 mg in 50 ml).[32] The soln was warmed to −10° at which time the O$_2$ evolution was visible and at this stage thione (0.3 mM) was added. The mixture was left at room temp for 30 min by which time the oxidation was complete in all the cases. After evaporation of the solvent, the product ketone was isolated by column chromatography. Oxidation was almost instantaneous in all cases.

In order to check for the direct reaction between triphenyl phosphite ozonide and thiones, a pre-cooled methylene chloride soln of thiones was added to triphenyl phosphite ozonide at −80° and left at this temp for 2 hr. All thiones (**1**–**5**) reacted at that temp to yield the corresponding ketones. However, this reaction was at least an order of magnitude slower than room temp oxidation. Therefore, we believe that, at room temp oxidation occurs by reaction with singlet oxygen and at −80° by direct reaction with triphenyl phosphite ozonide.

Ozonolysis of thiones. O$_3$ (generated using Pennwalt type BA) was passed through a methylene chloride soln (20 ml) of thione (100 mg) at room temp for 15 min. During this time the thione colour disappeared. Solvent was removed and the product isolated by column chromatography to give ketone as the only product.

Oxidation with potassium superoxide. Reaction with KO$_2$ was carried out under dry N$_2$. Finely powdered KO$_2$ (1 mM) was suspended in 15 ml of dry MeCN. Thione (1 mM) and 18-crown-6 (Aldrich; 1 mM) in 15 ml of dry MeCN were added drop-wise to the KO$_2$ suspension. The mixture was stirred vigorously during the addition. After 1 hr the mixture was diluted with 20 ml of water to destroy the excess KO$_2$. HCl was added in excess to the product and extracted with ether. The ethereal extract was washed with NaHCO$_3$ aq followed by water and dried over Na$_2$SO$_4$. Crude product obtained after evaporation of the solvent was purified by TLC. Ketone was

Table 4. Spectral data of α,β-unsaturated sulphines

Sulphine	IR $\nu_{max}^{neat\,a}$ (cm^{-1})	^{1}H-NMR (CDCl$_3$) (δ)
6*E*	1610, 1110, 1045	6.15 (1H, m), 2.605 (2H, s), 2.0 (2H, m), 1.90 (3H, d), 0.96 (3H, s), 0.93 (3H, s)
6*Z*	—	7.0 (1H, m), 2.13 (2H, s), 2.0 (2H, m), 1.95 (3H, d), 0.96 (3H, s), 0.93 (3H, s)
7*E*	1590, 1110, 1050	6.95 (1H, m), 2.6–3.0 (3H), 2.2–2.4 (1H, m), 1.95 (3H, d), 1.49 (3H, s), 0.92 (3H, s)
7*Z*	—	6.15 (1H, m), 4.05 (1H, t), 2.6–3.0 (2H, m), 2.2–2.4 (1H, m), 1.92 (3H, d), 1.49 (3H, s), 0.92 (3H, s)
8*E*[b]	1150, 1090	7.0–7.4 (5H, m), 6.55 (1H, d), 1.63 (6H, s)
8*Z*[b]	—	7.0–7.4 (4H, m), 6.35 (2H, s), 1.93 (6H, s)
9*E*[c]	1150, 1090	6.9–7.3 (4H), 6.18 (1H, m), 2.26 (3H, d), 1.63 (6H, s)
9*Z*	—	6.9–7.3 (4H), 6.1 (1H, m), 2.02 (3H, d), 1.93 (6H, s)
10*E*	1140, 1030	6.9–7.4 (4H, m), 6.78 (1H, m), 3.76 (3H, s), 3.31 (2H, t), 2.91 (2H, t)
10*Z*	—	6.9–7.4 (5H, m), 3.76 (3H, s), 2.9 (4H, s)

[a] IR data refers to the mixture of isomers.
[b] Assignment of isomers is based on shift reagent study.
[c] *E* and *Z* isomers are separable by TLC.

obtained as the major product with the two thiones investigated.

Estimation of sulphur dioxide during photo-oxidation. A $CHCl_3$ soln (50 ml) of thione (200 mg) was placed in a Pyrex immersion well equipped with a gas inlet and an outlet. The outlet was connected in series to two traps containing NaOH soln (0.3 M). The immersion well was irradiated with two 500 W tungsten lamps while O_2 was continuously bubbled through. SO_2 evolved was collected as Na_2SO_3 in the traps and was oxidized to sulphate by the addition of Br. Sulphate was gravimetrically estimated by following the reported procedure.

Determination of rate constants for singlet oxygen quenching by thiones. The experimental procedure reported by Monroe[20] was adopted with slight modification to determine the rate of quenching of O_2 by thiones. A Hanovia 450 W medium pressure mercury lamp was used as the light source. By a suitable combination of filters the 480 ± 10 nm region was isolated for rubrene excitation. In all cases the excitation was effected in the region where the absorption by the thione was absent. After irradiation (10–20 min), the disappearance of rubrene was monitored by its electronic absorption and the rates were calculated by the reported procedure.

Control experiments. (*a*) *Dark reaction.* $CHCl_3$ solns of **1**–**4** kept in the dark in an aerated atmosphere were stable for several days. However, **5** decomposes within 1–2 days under these conditions.

(*b*) *Stability of thiones upon irradiation in an* N_2 *atmosphere.* Thiones **1**–**5** in $CHCl_3$ or benzene did not undergo any noticeable change upon irradiation (500 W tungsten lamps) in an N_2 atmosphere for 10 days.

(*c*) *Oxidation of sulphines* **6**–**10** *by singlet oxygen.* Triphenyl phosphite ozonide prepared as described earlier was warmed to -10°. During this time sulphine was added. The mixture was left at room temp for 2 hr by which time the oxidation was complete in all cases. After evaporation of the solvent, the product, ketone, was isolated by column chromatography. Although sulphines are also oxidized by singlet oxygen, the rate of oxidation is appreciably slow when compared to thione oxidation.

Aerated solns of sulphines in $CHCl_3$ (0.01 M, 50 ml) were irradiated using 500 W tungsten lamps in the presence of methylene blue (10^{-4} M). After complete disappearance of sulphine, the solvent was distilled off and the product ketone was isolated by preparative TLC. In the case of sulphines **6**, **7** and **10**, 60% conversion occurred in 24 hr, whereas 50 hr were required for 10% conversion in the cases of **8** and **9**.

Attempts to trap the intermediates. (*a*) *Oxidation in methanol.* Aerated solns of thiones in MeOH (0.02 M, 100 ml) were irradiated with two 500 W tungsten lamps. Irradiation was continued until the thione colour had disappeared. The decolorized irradiated mixture was found to contain only ketone. No MeOH addition products were observed.

(*b*) *Oxidation in the presence of phenyl sulphide.* Aerated solns of thiones in $CHCl_3$ (150 mg, 0.2 M) were irradiated with two 500 W tungsten lamps in the presence of phenylsulphide (1.0 g) at room temp. The progress of the reaction was monitored by TLC. Irradiation was continued until the thione colour had disappeared. Solvent was removed and the crude irradiated mixture was purified by preparative TLC. Ketone was isolated as the product of oxidation. Phenyl sulphide was recovered back. Neither diphenyl sulphoxide nor diphenyl sulphone was observed.

(*c*) *Oxidation in the presence of diphenyl sulphoxide.* Aerated solns of thiones in $CHCl_3$ (150 mg, 0.02 M) were irradiated with two 500 W tungsten lamps in the presence of diphenyl sulphoxide (930 mg). After complete decolorization, the irradiated mixture was concentrated and purified by preparative TLC. Ketone was isolated as the product. Diphenyl sulphoxide was recovered back. Diphenyl sulphone could not be observed.

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