J. Org. Chem. 1984, *49*, 615–621

Oxidation of Thioketenes by Singlet Oxygen

V. Jayathirtha Rao and V. Ramamurthy*

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India

E. Schaumann and H. Nimmesgern

Institut fur Organische Chemie and Biochemie der Universitat Hamburg, Hamburg, West Germany

Received October 26, 1983

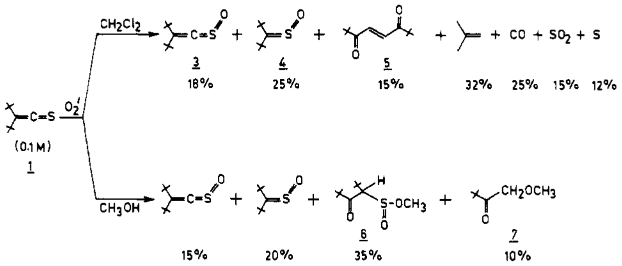
Oxidation of di-*tert*-butylthioketene (1) and 1,1,3,3-tetramethyl-2-(thiocarbonyl)cyclohexane (2) by singlet oxygen has been investigated and has been found to exhibit a unique behavior different from that of ketenes and ketenimines. Oxidation of 1 in methylene chloride yielded the corresponding thioketene *S*-oxide (3), thioketone *S*-oxide (4), and *trans*-2,2,7,7-tetramethyl-4-octene-3,6-dione (5), and that in methanol gave 3, 4, methyl 1-*tert*-butyl-3,3-dimethyl-2-oxobutanesulfinate (6), and 1-methoxy-3,3-dimethylbutanone (7). Similar oxidation of 2 in methylene chloride gave 1,1,3,3-tetramethyl-2-(thiocarbonyl)cyclohexane *S*-oxide (8), 2,2,6,6-tetramethylcyclohexanethione *S*-oxide (9), and 2,2,6,6-tetramethylcyclohexanone (10), and in methanol methyl 3,3,7,7-tetramethyl-2-oxocycloheptanesulfinate (11) and 10 were formed. Formation of the above products has been rationalized to arise through the involvement of zwitterionic intermediates (12) resulting from the attack of singlet oxygen on the sulfur lone pair of the thioketene functionality. The difference in behavior between 1 and 2 is suggested to be due to the difference in the nature of cleavage of the suspected intermediate α-peroxy thiolactone. Reasons for the variation in the product distribution with respect to temperature and solvent are yet to be understood.

The physical and chemical properties of singlet oxygen is a subject of enduring interest.[1] Among the reactions of singlet oxygen with organic substrates, addition to carbon–carbon double bond is certainly most intensely investigated one. Depsite this, the mechanism of these additions has proven to be enigmatic. In addition to many other chromophores allenes,[2] ketenes[3] and ketenimines[4] have been demonstrated to give dioxetanes similar to olefins, thus revealing that the presence of an additional chromophore (ketone in ketenes and imines in the case of ketenimines) plays a minor role in the product distribution. Surprisingly, oxidation of closely analogous system, namely, thioketenes, by singlet oxygen and ozone have escaped investigation. As a continuation of our interest in the reactions of singlet oxygen with thiocarbonyl chromophore,[5] we have investigated the oxidation of two stable thioketenes, namely, di-*tert*-butylthioketene (1) and 1,1,3,3-tetramethyl-2-(thiocarbonyl)cyclohexane (2). Results presented here clearly establish that thioketenes are distinct in their behavior toward singlet oxygen and that it cannot be extrapolated from that of the related heterocumulene systems.

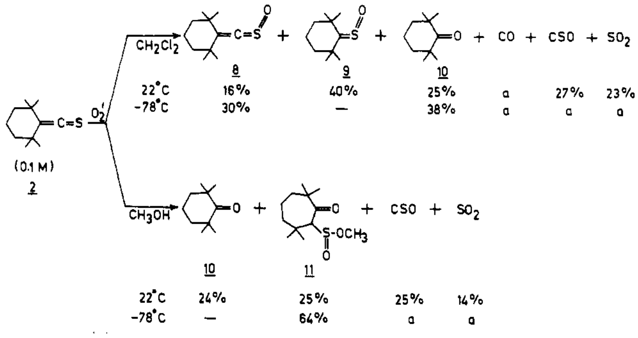
Results

Singlet oxygen generated by dye sensitization (rose bengal, eosin, crystal violet, rhodamin B, and methylene blue) readily reacted with thioketenes 1 and 2 to give products shown in Schemes I and II. Oxidation of 1 in methylene chloride, chloroform, and carbon tetrachloride gave the corresponding thioketene *S*-oxide (3), thioketone S-oxide (4) and an unexpected olefin, namely, *trans*-2,2,7,7-tetramethyl-4-octene-3,6-dione (5). The former two products were identified by comparison with authentic samples. Spectral characteristics of the trans isomer (5) and the cis isomer obtained upon photolysis of 5 were in complete agreement with literature reports.[6] Oxidation of 1 in methanol gave 3 and 4 along with a structurally challenging and novel product, 6, and a mechanistically important product, 7. On the basis of spectral data (UV, IR, ^{1}H NMR, ^{13}C NMR, and mass spectra) 6 is believed to be methyl 1-*tert*-butyl-3,3-dimethyl-2-oxobutanesulfinate. Confirmatory evidence came from the X-ray

Scheme I. Oxidation of Di-*tert*-butylthioketene



Scheme II. Oxidation of 1,1,3,3-Tetramethyl-2-(thiocarbonyl)cyclohexane (2)



^{a} Not estimated.

---

(1) Wasserman, H. H.; Murray, R. W. "Singlet Oxygen"; Academic Press: New York, 1979.

(2) Greibrokk, T. *Tetrahedron Lett.* **1973**, 1663.

(3) Bollyky, L. J. *J. Am. Chem. Soc.* **1970** *92*, 3230. Turro, N. J.; Ito, Y.; Chow, M. F.; Adam, W.; Rodriquez, O.; Yany, F. *Ibid.* **1977**, *99*, 5836. Turro, N. J.; Chow, M. F.; Ito, Y. *Ibid.* **1978**, *100*, 5580.

(4) Adam, W.; De Lucchi, O; Quast, H.; Recktenwald, R.; Yany, F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 788. Ito, Y.; Mutsuura, T.; Kondo, H. *J. Am. Chem. Soc.* **1979**, *101*, 7105. Ito, Y.; Yokoya, H.; Kyono, K.; Yamamura, S.; Yamada, Y.; Matsuura, T. *J. Chem. Soc., Chem. Commun.* **1980**, 898.

(5) Jayathirtha Rao, V.; Muthuramu, K.; Ramamurthy, V. *J. Org. Chem.* **1982**, *47*, 127. Ramnath, N.; Ramesh, V.; Ramamurthy, V. *Ibid.* **1983**, *48*, 214. Jayathirtha Rao, V.; Ramamurthy, V. *J. Chem. Soc., Chem. Commun.* **1981**, 638.

(6) Brown, W. H.; Wright, G. F. *Can. J. Chem.* **1957**, *35*, 236.

0022-3263/84/1949-0615$01.50/0

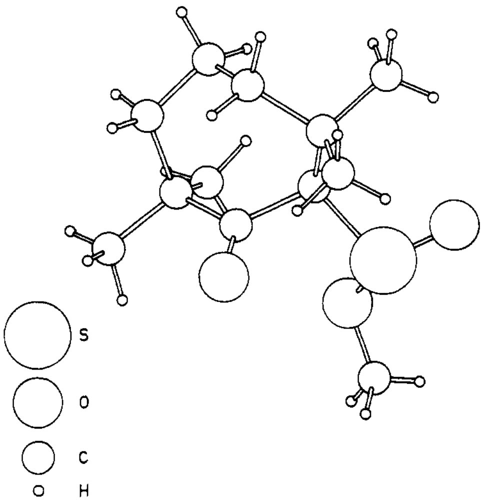


Figure 1. ORTEP diagram for **11**.

crystal structure analysis of the similar product from **2**. However, di-*tert*-butyl ketone was absent in the product mixture both in methanol and methylene chloride. Dye-sensitized oxidation of **2** in methylene chloride, chloroform, and carbon tetrachloride gave the corresponding thioketene *S*-oxide (**8**), thioketone *S*-oxide (**9**), and 2,2,6,6-tetramethylcyclohexanone, whose structures were confirmed by comparison with authentic samples. Similar oxidation in methanol gave the ketone **10** along with a novel product, **11**. Spectral data of **11** are closely similar to those of **6** derived from **1**. X-ray structural analysis of **11** independently carried out by Trotter and Ponnuswamy[7] confirmed the proposed structure. An ORTEP diagram for **11** is presented in Figure 1. During the oxidations of **1** and **2** some polymeric material which was not characterized was also obtained. Spectral properties of **1**–**11** are tabulated in Table III. Oxidation of **2** by singlet oxygen was much more rapid (0.1 M, 2 h) than that of **1** (0.1 M, 20 h). The rates of singlet oxygen quenching by **1** and **2** as measured by the self-sensitized rubrene photooxidation method[8] are 1.2×10^7 and 9.9×10^7 M^{-1} s^{-1}, respectively.

In addition to the products mentioned above, the gaseous products were identified qualitatively and quantitatively estimated by standard procedures. As shown in Scheme I, isobutylene, carbon monoxide, and sulfur dioxide were obtained during the oxidation of **1**, and the estimated yields presented in Scheme I are mechanstically significant. Oxidation of **2** gave carbon monoxide, carbonyl sulfide, and sulfur dioxide. Owing to the difficulty in estimating carbon monoxide in the presence of carbonyl sulfide, the former could be detected only qualitatively. Since triphenyl phosphite ozonide reacted directly with thioketenes even at lower temperatures, this could not be used as the source of singlet oxygen. However, as several dyes were found to be effective and gave the same product distribution, it is believed that singlet oxygen alone is involved in the oxidation, and the observed products do not arise from any other processes. Consistent with this, Dabco, a known quencher of singlet oxygen, suppressed the course of oxidation.

Experiments designed to understand the mechanism of oxidation were carried out with **2** only, owing to the considerably slow oxidation of **1**. Dye-sensitized oxidation of **2** at −78 °C generated products which differed significantly from those of room-temperature oxidation. At −78 °C thioketene *S*-oxide **8** and 2,2,6,6-tetramethylcyclohexanone (**10**) were the only products. Thioketone *S*-oxide **9**, formed in significant yields at room temperature, was absent during the low-temperature oxidation of **2** in methylene chloride. Similar oxidation in methanol gave only the sulfinate ester **11**, the ketone **10** being totally absent. Unfortunately, we could not infer much regarding the reactive intermediates during these low-temperature oxidations.

Attempts, although unsuccessful, were made to trap intermediates such as α-peroxy thiolactone **15** and perepoxides **12** during the oxidation of **2**. In one set of experiments, oxidation was carried out at −78 °C in methylene chloride, and to the irradiated solution, presumably containing reactive intermediates and maintained at the same temperature, were added trapping agents such as diphenyl sulfide,[9] diphenyl sulfoxide,[10] and triphenyl phosphite.[11] However, no product derived from the trapping agents was formed, nor was the original product distribution affected. In another set of experiments, oxidation of **2** at −78 °C in the presence of the above-mentioned trapping agents was carried out, but the product distribution remained the same as in their absence. Interestingly, addition of methanol to the photooxidized solution of **2** at −78 °C (carried out in methylene chloride) produced the sulfinate ester **11**. This suggests that oxidation in methylene chloride generates a farily stable intermediate at −78 °C which is trapped by methanol to give **11**.

Thioketones are known to be oxidized upon direct excitation in aerated media.[5] Intrigued by our earlier observation with thioketones, an attempt was made to study the oxidation of **1** and **2** upon direct excitation. Oxidations of **1** and **2** upon direct excitation by using 500-W tungsten lamps were extremely slow. Typically 8 days of irradiation resulted in 30% conversion (0.1 M **1** or **2**). Direct excitation of **1** resulted in the same set of products both in methanol and chloroform as those obtained on dye-sensitized oxidation. However, the oxidation of **2** gave only polymeric material. Since the oxidation of **1** and **2** upon direct excitation was extremely slow, no further experiments were conducted.

Discussion

Oxidations of thioketenes by singlet oxygen, unlike ketenes and ketenimines, yield several products as illustrated in Schemes I and II (see Table I). Except for the formation of 2,2,6,6-tetramethylcyclohexanone (in the case of **2**), all other products are unexpected on the basis of the established behavior of ketenes[3] and ketenimines.[4] In addition to the general behavior exhibited by the two thioketenes, there is a significant difference in the product distribution between the two. One of the striking observations is the absence of di-*tert*-butylketone and the formation *trans*-2,2,7,7-tetramethyl-4-octene-3,6-dione (**5**) in lieu of the former during the oxidation of **1**. Although low-temperature studies and the trapping experiments have yielded interesting results, they have not provided any concrete evidence in favor of a single mechanism. An attempt has been made here to rationalize the formation of various products during the singlet oxygen oxidation of **1** and **2** (Scheme III).

---

[7] Full details on the X-ray structural investigation of **11** will be published independently by J. Trotter and M. N. Ponnuswamy.

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

[9] Wasserman, H. H.; Saito, I. *J. Am. Chem. Soc.* **1975**, *97*, 905. Saito, I.; Matsugo, S.; Matsuura, T. *Ibid.* **1979**, *101*, 4757.

[10] Campbell, B. S.; Denney, D. B.; Shih, L. S. *J. Am. Chem. Soc.* **1975**, *97*, 3850. Schaap, A. P.; Recher, S. G.; Faler, C. R.; Villasener, S. R. *Ibid.* **1983**, *105*, 1691.

[11] Bartlett, P. D.; Baumstark, A. L.; Landis, M. E.; *J. Am. Chem. Soc.* **1973**, *95*, 6486. Bartlett, P. D.; Baumstark, A. L.; Landis, M. E.; Lerman, C. L. *Ibid.* **1974**, *96*, 5267.

Table I. Product Distribution during the Oxidation of 1,1,3,3-Tetramethyl-2-(thiocarbonyl)cyclohexane (2)[a]

	distribution, %					
conditions[b]	thioketene *S*-oxide	thioketone *S*-oxide	ketone	11	SO_2	COS
methylene chloride, room temp	16	40	25		23	27
methylene chloride, −78 °C	30	0	38			
methylene chloride, −78 °C, diphenyl sulfide (0.5 M)	26	0	35			
methylene chloride, room temp, diphenyl sulfide (0.5 M)	15	40	27			
methanol, room temp	0	0	24	25	14	25
methanol, −78 °C	0	0	0	64		
methanol, −78 °C, diphenyl sulfide (0.5 M)	0	0	0	54		
methanol, room temp, diphenyl sulfide (0.5 M)	0	0	26	20		

[a] Product distribution based on TLC isolated yields; average of three independent runs (error limit ±5%). All gaseous products were estimated as described in the Experimental Section. [b] Solvent and temperature. Thioketene concentration: 0.1M; Methylene blue was used as the dye to generate singlet oxygen.

Table II. Concentration Dependent Product Distribution upon Oxidation of Thioketenes in Chloroform[a]

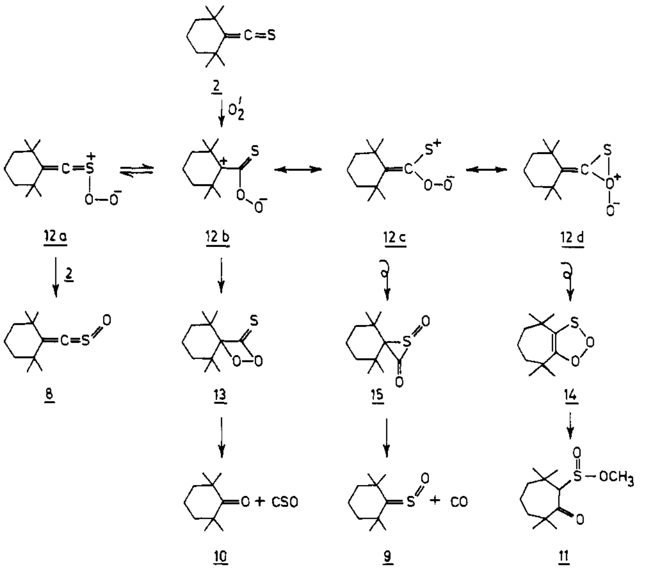
	distribution, %		
[thioketene], M	thioketene *S*-oxide	thioketone *S*-oxide	*trans*-2,2,7,7-tetramethyl-4-octene-3,6-dione[1] or 2,2,6,6-tetramethylcyclohexanone[2]
	Di-*tert*-butylthioketene (1)		
0.20	17	24	15
0.10	17	25	14
0.01	16	25	15
0.001	14	25	14
0.0005	10	26	14
0.001	9	29	14
	1,1,3,3-Tetramethyl-2-(thiocarbonyl)cyclohexane (2)		
0.01	16	40	24
0.02	15	41	24
0.0027	15	40	25
0.0005	11	44	28
0.0001	7	46	29

[a] Product yields based on TLC isolated yields; average of three independent runs; methylene blue sensitized oxidation; product distribution measured after complete conversion.

The structures of various intermediates suggested during this oxidation are yet to be substantiated. However, these represent a reasonable pathway for the formation of products 3–11. Thioketene *S*-oxides 3 and 8, we suggest, are formed from 12 through a bimolecular process. As shown in Table II, the yields of 3 and 8 decrease, although not drastically, upon lowering of the thioketene concentration. This is in contrast to our observation with thioketones where the product yields were independent of thioketone concentration. This implies that the thioketene is capable of removing the residual oxygen from the zwitterionic intermediate. However, it is important to note that diphenyl sulfide and diphenyl sulfoxide, known scavengers of perepoxides,[10,12] failed to alter the product yields.

Thioketone *S*-oxides 4 and 9 are formed during the oxidation of 1 and 2, respectively. Although 4 is formed both in methanol and methylene chloride, 2,2,6,6-tetramethylcyclohexanethione *S*-oxide (9) is formed only in methylene chloride and is absent at lower temperatures during the oxidation of 2. The yield of thioketone *S*-oxides is independent of thioketene concentration (Table II), and this suggests that their formation does not involve a second molecule of thioketene. The immediate precursor for the thioketone *S*-oxides is believed to be α-thiolactone *S*-oxide 15. This is supported by the accompanying carbon monoxide formation both in the case of 1 and 2 and by its matching yield in the case of 1. Yet another piece of

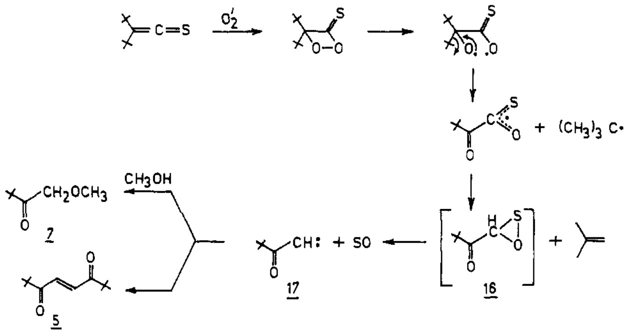
Scheme III. Comprehensive Mechanism for the Oxidation of 1,1,3,3-Tetramethyl-2-(thiocarbonyl)cyclohexane



---

(12) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795. Laver, H. S.; MacCallum, J. R. *Photochem. Photobiol.* **1978**, *28*, 91.

Scheme IV. Mechanism for the Oxidation of Di-*tert*-butylthioketene



evidence comes from the literasture report[13] in which the very same intermediate **15** has been proposed during the oxidation of 1,1,3,3-tetramethyl-2-(thiocarbonyl)cyclohexane *S*-oxide (**8**) by 2,2,4,4-tetramethylpyrroline *N*-oxide. Even here[13] **15** is found to be labile and to decompose to the corresponding thioketone *S*-oxide and carbon monoxide.

There is an important difference in the behavior of **1** and **2** toward singlet oxygen. While **2** gives the corresponding ketone 2,2,6,6-tetramethylcyclohexanone (**10**), the former does not give di-*tert*-butyl ketone, the expected product from the decomposition of α-peroxy thiolactone **13**. On the other hand, **1** gives a totally unexpected product, namely, *trans*-2,2,7,7-tetramethyl-4-octene 3,6-dione (**5**). Proposed mechanisms for formation of **10** and **5** are illustrated in Schemes III and IV, respectively. Support for the involvement of α-peroxy thiolactone as the precursor for **10** comes from the identification of carbonyl sulfide as one of the products. More importantly, the estimated yield of carbonyl sulfide both in methylene chloride and in methanol matches quite well with the isolated yields of 2,2,6,6-tetramethylcyclohexanone. Unfortunately, we could not isolate the suspected α-peroxy thiolactone, and our attempts to indirectly trap this intermediate using methanol, diphenyl sulfide, diphenyl sulfoxide, and triphenyl phosphite both at room and low temperatures were unsusccessful. Sulfur-substituted 1,2-dioxetanes have in fact been recently synthesized and demonstrated to have poor stability.[14]

Assuming that α-peroxy thiolactone is the precursor for ketone **10**, it is interesting to speculate on the reasons for the absence of di-*tert*-butyl ketone in the case of **1**. This could either be due to the lack of formation of the corresponding α-peroxy thiolactone or due to an unusual course of decomposition of the α-peroxy thiolactone formed. We suggest that *trans*-2,2,7,7-tetramethyl-4-octene-3,6-dione (**5**) is formed in place of di-*tert*-butyl ketone and is in fact derived through an unusual decomposition of α-peroxy thiolactone (Scheme IV). **5** is most likely the dimeric product of the carbene **17**. The same carbene generated independently has in fact been shown to dimerize and trimerize.[15] Further, when the oxidation of **1** is conducted in methanol, the methanol adduct of the above carbene, 1-methoxy-3,3-dimethylbutanone (**7**), has been isolated. Thus in the absence of any trapping agent, carbene **17** probably dimerizes. A likely pathway for the formation of the above carbene from the corresponding α-peroxy thiolactone is shown in Scheme IV. This mechanism requires that **5** be accompanied by sulfur dioxide and isobutylene, and this is indeed found to be so. Matching the yields of sulfur dioxide and isobutylene with the isolated yield of **5** provide major support for Scheme IV. Although Scheme IV provides a satisfactory rationale for the formation of **10**, there are some disquieting featues about this mechanism. First, one would expect the carbene **17** to react with oxygen under our experimental conditions, but no such products were isolated. Second, *tert*-butyl radical generated according to this mechanism might be expected to get oxidized to *tert*-butyl peroxide and *tert*-butyl alcohol, but these were not isolated.

Two probable modes of decomposition of α-peroxy thiolactone derived from **1** and **2** are shown in Schemes III and IV. In the case of **2**, a normal mode of decomposition occurs whereas in the case of **1** cleavage of the *tert*-butyl group occurs following that of the initial peroxide bond. This is due to the steric release arising from the loss of the *tert*-butyl group. This type of cleavage of the α bond following the dioxetane peroxide bond is known.[16] Absence of this type of cleavage in **2** is consistent with the relatively less steric crowding in this molecular framework.

Formation of sulfinate esters **6** and **11** is most interesting, and they suggest the involvement of zwitterionic intermediates during singlet oxygen oxidation of thioketenes. Of the various possibilities considered, the one shown in Scheme III appears to be the most reasonable. Sulfinate esters, we suggest, are the resultant products of the trapping of the intermediate **14**. Involvement of a reasonably stable intermediate in the formation of **6** and **11** is suggested by the following experiment. While the photooxidation of **2** was conducted at −80 °C in methylene chloride, only the thioketone *S*-oxide and the ketone **10** were formed. However, addition of methanol to the above photooxidized solution (conducted at −80 °C) maintained at −80 °C results in 6% sulfinate ester **11**; on the other hand, addition of methanol to the above photooxidized solution broght to room temperature did not result in **11**. The formation of **11**, therefore, is due to the trapping of a reasonably stable intermediate at −80 °C. One would not expect the zwitterionic intermediates to have such a long lifetime. As the above experiment suggests, the intermediate responsible for **11** is formed both in methylene chloride and in methanol. It is inferred that the suspected intermediate in the absence of trapping by alcohol decomposes to polymeric material.

Possibility of α-thiolactone *S*-oxide **15** being the precursor for sulfinate esters was considered especially since the thioketone-S-oxide was not produced in methanol (Scheme II), But, when α-thiolactone *S*-oxide was generated in methanol by following the literature method,[13] the sulfinate ester **11** was not formed. Therefore, **14** or an oxathiet derived from it is the precursor for sulfinate esters. Formation of **14** requires a migration of the carbon–carbon bond. Such a type of migration is expected to be facile in ionic systems. Therefore, we suggest that the migration of the *tert*-butyl group in **1** and the ring expansion in **2** occur through the zwitterionic intermediate **12d**. Similar ionic rearrangements during singlet oxygen oxidation of olefins have been observed.[17]

---

[13] Schaumann, E.; Behrens, U. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 722.

[14] Adam, W.; Arias, L. A.; Schautzow, D. *Tetrahedron Lett.* **1982**, *23*, 2835.

[15] Serratosa, F.; Quintana, J. *Tetrahedron Lett.* **1967**, 2245.

[16] Ando, W.; Saiki, T.; Migita, T. *J. Am. Chem. Soc.* **1975**, 1735. Wesserman, H. H.; Terao, S. *Tetrahedron Lett.* **1975**, 1735. Ando, W.; Suzuki, J.; Arai, T.; Migita, T. *Tetrahedron* **1973**, *29*, 1507. Ando, W.; Watanabe, K.; Migita, T. *Tetrahedron Lett.* **1975**, 4127.

[17] McCapra, F.; Beheshti, I. *Chem. Commun.* **1977**, 517. Rubottom, G. M.; Nieves, M. I. L. *Tetrahedron Lett.* **1972**, 2423. Friedric, E.; Lutuz, W. *Chem. Ber.* **1980**, *113*, 1245. Adam, W.; Fierro, J. D.; Quiroz, F.; Yany, F. *J. Am. Chem. Soc.* **1980**, *102*, 2127. Capdevielle, P.; Maumy, M. *Tetrahedron Lett.* **1980**, *21*, 2417. Wilson, S. L.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 679.

Table III. Spectral Data for Compounds 1-11

compd[a]	IR, cm^{-1}	^{1}H NMR ($CDCl_3$), δ	^{13}C NMR ($CDCl_3$), δ	mass spectrum, *m/e*
1	1750	1.26 (s)	30.4 (s), 31.0 (q), 100.5 (s), 272.0 (s)	
2	1740	1.20 (s, 12 H), 1.50-1.55 (br, 6 H)		
3[b]	1700, 1110	1.24 (s)	31.4 (q), 36.2 (s), 156.8 (s), 230.0 (s)	186 (M^+)
4[b]	1180, 1080	1.54 (s), 1.37 (s)	29.5 (q), 30.6 (q), 40.4 (s), 43.5 (s), 216.4 (s)	174 (M^+)
5[c]	1700	1.20 (s, 18 H), 7.35 (s, 2 H)	25.8 (q), 43.7 (s), 133.0 (q), 204.2 (s)	197 (M + 1) (CI)
6	1700, 1025	1.13 (s, 18 H), 3.60 (s, 3 H), 3.87 (s, 1 H)	27.5 (q), 28.9 (q), 34.8 (s), 43.6 (s), 56.2 (q), 82.2 (d), 212.2 (s)	235 (M + 1) (CI)
7	1650	1.13 (s, 9 H), 3.60 (s, 3 H), 3.80 (s, 2 H)	25.7 (q), 44.7 (s), 54.7 (q), 65.1 (t), 206.9 (s)	129 (M + 1) CI
8[b]	1700, 1090, 1050	1.23 (s, 6 H), 1.33 (s, 6 H), 1.56-1.64 (br, 6 H)		198 (M^+)
9[b]	1500, 1160, 1050	1.30 (s, 6 H), 1.50 (s, 6 H), 1.54-1.60 (br, 6 H)	18.1 (t), 27.6 (q), 40.2 (t), 44.3 (s), 220.4 (s)	186 (M^+)
10[b]	1720	1.12 (s, 12 H), 1.75-1.80 (br, 6 H)		
11[d]	1700, 1000	1.03 (s, 3 H), 1.08 (s, 3 H), 1.16 (s, 3 H), 1.22 (s, 3 H), 1.4-1.7 (br, 6 H), 3.66 (s, 3 H), 3.83 (s, 1 H)	19.7, 22.1, 24.9, 26.2, 27.6, 35.9, 38.2, 42.8, 47.2, 56.6 (q), 81.7 (d), 211.7 (s)	246.1 (M^+)

[a] For compound numbering, see Schemes I and II. [b] Structure confirmed by comparison with authentic samples. [c] Spectral data consistent with the literature: Brown, W. H.; Wright, G. F. *Can. J. Chem.* **1957**, *35*, 236. [d] Structure confirmed by X-ray crystal structure analysis.

Singlet oxygen, an electrophile, can be expected to attack the thioketene either on the sulfur lone pair or on the central carbon. In the case of thioketones, the attack of singlet oxygen was inferred to occur on the sulfur lone pair.[5] In order to gain some information regarding the point of attack by singlet oxygen, ozonolysis of **1** and **2** was conducted in methylene chloride at room temperature. We expected that since both singlet oxygen and ozone were electrophiles, their initial interaction with the thioketene chromophore might be the same. However, it is realized that the mechanism for the ozonolysis of thioketenes could be different. Ozonolysis of **1** and **2** gave the corresponding thioketene *S*-oxides **3** and **8**, respectively, as the primary products. However, prolonged ozonolysis resulted in polymeric material, and this is established to be due to the secondary ozonolysis of the product. Therefore, ozone, an electrophile, most likely is attacking the sulfur lone pair to give rise to thioketene *S*-oxide and oxygen. On the basis of this and the expected lower ionization potential for sulfur lone pair, we suggest that the initial attack of singlet oxygen occurs on the sulfur atom of thioketene. The primary interaction of singlet oxygen with a sulfur lone pair is known in sulfides.[12] This behavior is different from that of ketenes and ketenimines where the singlet oxygen is suggested to interact primarily with the central carbon.

The cause for the variation in the product formation upon lowering the temperature and upon varying the solvent is yet to be understood. The results presented above have clearly established that the behavior of thioketenes is indeed different from that of ketenes and ketenimines. The novel results discussed above justify the necessity of further work to understand the complicated photooxidation mechanism.

Experimental Section

Synthesis of Thioketenes 1 and 2. Thioketnes **1** and **2** were prepared by following the published procedures[18] and were purified by column chromatography (silica gel, hexane). Spectral data for **1** and **2** are provided in Table III.

Dye-Sensitized Oxidations of 1 and 2. Dye-sensitized oxidations of **1** and **2** were conducted at room temperature (25 °C) in chloroform, carbon tetrachloride, methylene chloride, and methanol. Dyes commonly used were methylene blue, rose bengal, eosin, and rhodamin B. A general procedure adopted is described below.

Oxygenated chloroform, methylene chloride, or methanol solutions of thioketenes **1** and **2** (0.1 M) were irradiated at room temperature by using two 500-W tungsten lamps in the presence of the dyes (10^{-4} M). A continuous stream of oxygen was maintained during the irradiation, and the progress of the reaction was monitored by micro TLC. After complete conversion, the solvent was evaporated, and the products were isolated by column chromatography (silica gel, hexane/benzene/chloroform). In the case of **1**, total conversion took approximately 20 h whereas **2** required only 2 h. The products were identified by their spectral properties and by comparison with authentic samples in most of the cases.

Oxidation of **1** in chloroform or methylene chloride gave di-*tert*-butylthioketene *S*-oxide (**3**, 18%), di-*tert*-butylsulfine (**4**, 25%), and *trans*-2,2,7,7-tetramethyl-4-octene-3,6-dione (**5**, 15%) along with elemental sulfur (12%). Oxidation in methanol gave di-*tert*-butylthioketene *S*-oxide (15%), di-*tert*-butyl thioketone *S*-oxide (20%), methyl 1-*tert*-butyl-3,3-dimethyl-2-oxobutanesulfinate (**6**, 35%) and 1-methoxy-3,3-dimethylbutanone (**7**, 10%). Spectral data for these products are provided in Table III. Authentic samples of di-*tert*-butylthioketene *S*-oxide and di-*tert*-butylthioketone *S*-oxide were prepared by *m*-chloroperbenzoic acid oxidation of di-*tert*-butylthioketene and di-*tert*-butyl thioketone, respectively.[19] *trans*-2,2,7,7-Tetramethyl-4-octene-3,6-dione obtained here was compared with the literature report,[6] and the presence of a double bond was confirmed by reaction with dilute bromine and by photolytic conversion to the cis isomer. All spectral data are consistent with the proposed structure. Spectral data for **6** were closely similar to those of methyl 3,3,7,7-tetramethyl-2-oxocycloheptanesulfinate (**11**) whose structure has been confirmed by X-ray structural analysis.

Oxidation of **2** in chloroform or methylene chloride gave 2,2,6,6-tetramethylcyclohexanone (**10**, 25%), 1,1,3,3-tetra-

---

(18) Schaumann, E. *Chem. Ber.* **1982**, *115*, 2755.

(19) Schaumann, E.; Klein, W. R. *Tetrahedron Lett.* **1977**, 3457. Back, T. G.; Barton, D. H. R.; Britten-Kelly, M. R.; Guziec, F. S., Jr. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2079.

methyl-2-(thiocarbonyl)cyclohexane *S*-oxide (**8**, 16%), and 2,2,6,6-tetramethylcyclohexanethione *S*-oxide (**9**, 40%). Oxidation in methanol gave 2,2,6,6-tetramethylcyclohexanone (24%) and methyl 3,3,7,7-tetramethyl-2-oxocycloheptanesulfinate (**11**, 25%). Spectral data for all products are provided in Table III. Authentic samples of **8** were prepared by *m*-chloroperbenzoic acid oxidation of the corresponding thioketene.[19] 2,2,6,6-Tetramethylcyclohexanethione *S*-oxide (**9**) was prepared by the oxidation of the corresponding thioketene *S*-oxide **8** by 2,2,4,4-tetramethylpyrroline *N*-oxide as reported in the literature.[13] 2,2,6,6-Tetramethylcyclohexanone was prepared by the reported procedure.[20]

The structure of **11** was confirmed by X-ray structural investigation by Trotter and Ponnuswamy, and the results will be published separately.[7]

Dye-Sensitized Oxidation of 2 at -78 °C. Owing to the long time required in the case of **1**, oxidation at -78 °C was carried out only with **2**. A low temperature (-78 to -82 °C) was maintained by using a liquid nitrogen–methanol bath, and the procedure adopted for irradiation and isolation of products was similar to that of room temperature experiment. The time required for complete conversion of **2** (0.1 M) was only 2 h. Oxidation in methylene chloride gave 2,2,6,6-tetramethylcyclohexanone (38%) and 1,1,3,3-tetramethyl-2-(thiocarbonyl)cyclohexane *S*-oxide (30%). Surprisingly, 2,2,6,6-tetramethylcyclohexanethione *S*-oxide was absent. Oxidation in methanol gave methyl 3,3,7,7-tetramethyl-2-oxocycloheptanesulfinate only, and 2,2,6,6-tetramethylcyclohexanone was absent.

Dye-sensitized oxidations of **1** and **2** at room temperature were also conducted by varying the concentrations of thioketenes (0.1–0.0001 M), and the product yields were determined by isolation of products by preparative TLC. All experiments were repeated at least three times, and the average yields are provided in Table II. Interestingly, the yields of thioketene *S*-oxides decreased with the thioketene concentration.

Identification and Estimation of Gaseous Products: Sulfur Dioxide, Carbon Monoxide, Carbonyl Sulfide, and Isobutylene. During the oxidation of **1** by singlet oxygen, sulfur dioxide, carbon monoxide, and isobutylene were identified as gaseous products. Similar oxidations of **2** gave sulfur dioxide, carbon monoxide, and carbonyl sulfide. During the oxidation of **2**, since estimation of carbon monoxide interfered with that of carbonyl sulfide, only carbonyl sulfide and sulfur dioxide were estimated; however, formation of carbon monoxide was qualitatively identified.

(a) Oxidation of 1. By the method described below all three gases, namely, carbon monoxide, sulfur dioxide, and isobutylene, were estimated simultaneously without interference with each other.

A chloroform solution (20 mL) of **1** (330 mg) and methylene blue (5 mg) was placed in a Pyrex immersion well with a gas inlet and an outlet. The outlet was connected in series to four traps. The first two traps contained sodium hydroxide solution (0.3 M) to trap sulfur dioxide, the third trap contained aqueous neutral mercuric nitrate solution to absorb isobutylene, and the last trap was filled with aqueous palladous chloride solution (200 mg of palladous chloride in 80 mL of water) to trap carbon monoxide. The immersion well was irradiated with a 500-W tunsten lamp while oxygen was continuously bubbled through the inlet of the reaction vessel. The sulfur dioxide evolved was collected as sodium sulfite in the trap and was oxidized to sulfate by the addition of bromine. The sulfate was gravimetrically estimated by following the reported procedure.[21] Carbon monoxide was estimated by weighing the palladium precipitated in the aqueous palladous chloride trap.[22]

Estimation of isobutylene involved the following procedure.[23]

Mercuric oxide (10 g) was dissolved in aqueous nitric acid (70%, 20 mL). To this solution was added 1.5 g of sodium hydroxide in 2 mL of water dropwise until a faint white cloud of basic mercuric nitrate was formed. This solution was used as the trap for isobutylene. The orange-yellow precipitate collected in the aqueous neutral mercuric nitrate solution trap was transferred to a 250-mL beaker and heated on a water bath for 4 h for complete precipitation. The precipitate was filtered by using a G-4 cintered crucible and washed with water until it was free of mercuric ions. The precipitate was dissolved in 70% nitric acid (19 mL) and heated gently for complete dissolution. The solution was oxidized with potassium permanganate to convert mercurous to mercuric ions, and the excess potassium permanganate was destroyed by using oxalic acid. To the above solution was added 2 mL of saturated iron alum solution, and this was made up to 100 mL and titrated against standard potassium thiocyanate solution. A 1-mL sample of 0.1 N potassium thiocyanate is equivalent to 0.01003 g of mercury or 0.1601 mL of isobutylene at 0 °C and 760 mm pressure. Estimated yields of all three gases are provided in Scheme I along with the isolated yields of di-*tert*-butylsulfine, di-*tert*-butylthioketene *S*-oxide, and *trans*-2,2,7,7-tetramethyl-4-octene-3,6-dione.

(b) Oxidation of 2. Estimations of sulfur dioxide and carbonyl sulfide[24] during the oxidation of **2** were carried out by using a setup identical with that described for **1**. In the first two traps sodium hydroxide solution was kept to absorb sulfur dioxide, and the rest of the traps, maintained at 0 °C, contained ethanolic potassium hydroxide (10%) to absorb carbonyl sulfide. After complete reaction the contents of the traps containing 10% ethanolic potassium hydroxide (80 mL) were transferred to a conical flask, two drops of phenolpthalein were added, and the mixture was neutralized with acetic acid. During this process, xanthate in the solution was converted to xanthic acid, and the above solution was made up to 100 mL and titrated against iodine–ethanol by using soluble starch as an indicator. Estimated yields of sulfur dioxide and carbonyl sulfide along with the isolated products during the oxidation of **2** in chloroform and methanol are provided in Table I.

Determination of Rate Constants for Singlet Oxygen Quenching by 1 and 2. The rate of singlet oxygen quenching by **1** and **2** was measured by the inhibition of self-sensitized rubrene photooxidation method developed by Monroe.[8] The rate constants measured for **1** and **2** are 1.2×10^7 and 9.9×10^7 M^{-1} s^{-1}, respectively.

Oxidation of Thioketenes 1 and 2 upon Direct Excitation. Aerated solutions of **1** (0.1 M) in chloroform or methanol were irradiated with 500-W tungsten lamps, and the reaction was followed by micro TLC. After 8 days of irradiation approximately 20% conversion was obtained. Products were isolated by column chromatography and identified by their spectral data. All products obtained by dye-sensitized oxidation were also obtained here, but the oxidation was exceptionally slow.

Aerated solutions of **2** (0.1 M) in chloroform or methanol were irradiated with 500-W tungsten lamps for 10 days by which time only 30% conversion had occurred. However, only polymeric material could be isolated.

Attempted Experiments To Trap the Intermediates during the Dye-Sensitized Oxidation of 1 and 2. Diphenyl sulfide and diphenyl sulfoxide have been used quite recently to trap the zwitterionic intermediates[9,10] and triphenyl phosphite has been used to trap the dioxetanes.[11] We have attempted unsuccessfully to gain information regarding the mechanism of the oxidation by using diphenyl sulfide, diphenyl sulfoxide and triphenyl phosphite.

A methylene chloride solution of **1** and **2** (0.1 M), methylene blue (4 mg) and diphenyl sulfide, diphenyl sulfoxide or triphenyl phosphite (50 mg) was irradiated at room temperature using 500-W tungsten lamp. After complete conversion, the products were isolated, and the yields are presented in Table I. Similar irradiation was also conducted at -78 °C, and the product distributions are presented.

Control Experiments. (a) Stability of Thioketenes in the Dark. Thioketenes **1** and **2** are stable idefinitely in the dark in aerated media both as pure liquids and in organic solvents. Similarly, bubbling oxygen through these solutions in the dark for over 1 week did not bring about any change.

---

[20] Bohlmann, F.; Kieslich, K. *Chem. Ber.* **1954**, *87*, 1363.

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

[22] Kolthoff, I. M. "A Treatise on Analytical Chemistry"; Wiley-Interscience: New York, 1971; Part III, Vol. 2, p 61.

[23] Newton, A.; Buckler, E. J. *Ind. Eng. Chem., Anal. Ed.* **1940**, *12*, 251.

[24] Brewer, R. E.; Ghosh, J. K. *Ind. Eng. Chem.* **1949**, *41*, 2044.

(b) Stability of Thioketenes in a Nitrogen Atmosphere upon Irradiation. Thioketenes 1 and 2 did not undergo any noticeable change upon irradiation for 10 days with a 500-W tunsten lamp in a nitrogen atmosphere either in chloroform or in methanol. However, excitation to the higher excited singlet state by using a 450-W medium-pressure mercury lamp brought forth efficient reaction.[25]

(c) Stability of Sulfines. Both di-*tert*-butylthioketene *S*-oxide and 1,1,3,3-tetramethyl-2-(thiocarbonyl)cyclohexane *S*-oxide were found to decompose slowly to a polymeric material in about 10 days. However, both were found to be inert toward singlet oxygen. A chloroform or methanol solution of these thioketene *S*-oxides (100 mg) was irradiated in the presence of methylene blue (2 mg) in an aerated atmosphere for 2 days. The usual workup revealed no change. The thermal and photochemical behavior of thioketene *S*-oxides have been previously investigated.[26]

Di-*tert*-butylsulfine is stable in aerated media both in the absence and presence of visible light. But 2,2,6,6-tetramethylcyclohexanethione *S*-oxide decomposes over a period of 10 days even in dark. However, these two sulfines were found to be stable toward singlet oxygen (dye sensitization).

Acknowledgment. The Department of Science and Technology, Government of India, is thanked for financial support by V.R. and V.J.R. E.S. and H.H. gratefully acknowledge the financial support by Fonds der Chemischen Industrie, Frankfurt.

Registry No. **1**, 16797-75-4; **2**, 54440-00-5; **3**, 16797-76-5; **4**, 56956-25-3; **5**, 10507-31-0; **6**, 79265-24-0; **7**, 39195-77-2; **8**, 63702-87-4; **9**, 63702-89-6; **10**, 1195-93-3; **11**, 88131-22-0.

---

[25] Sharat, S.; Ramamurthy, V. *J. Org. Chem.*, in press.

[26] Carlsen, L.; Schaumann, E. *J. Chem. Soc., Faraday Trans 1* **1979**, *75*, 2624. Carsen, L.; Egsgard, H.; Schaumann, E.; Ehlers, J. *Chem. Ind. (London)* **1979**, 851.

Intramolecular Trapping of Alkyl- and Arylrhodium Hydride Intermediates in the Decarbonylation of Aldehydes by Chlorotris(triphenylphosphine)rhodium

J. A. Kampmeier,* S. H. Harris, and I. Mergelsberg

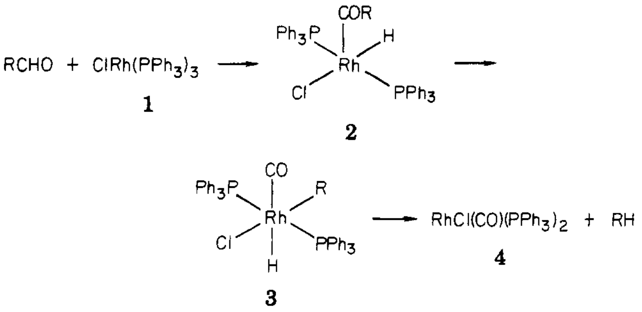
Department of Chemistry, University of Rochester, Rochester, New York 14627

Received July 26, 1983

The reaction of 5-hexenal with $RhCl(PPh_3)_3$ (1) or $[RhCl(PPh_3)_2]_2$ (5) gives some cyclopentane. The reaction of 2-allylbenzaldehyde with 5 gives a good yield of indan. These cyclization reactions to give cyclopentanes, and other reactions of Δ^4-enals to give cyclopropanes, reveal the presence of intermediate alkyl- and arylrhodium hydride complexes on the pathway for decarbonylation of aldehydes. The formation of nortricyclene from *endo*-5-norbornene-2-carboxaldehyde shows that the alkylrhodium hydride must be formed with retention of stereochemistry at the α-carbon of the aldehyde.

The standard mechanism for the decarbonylation of aldehydes by chlorotris(triphenylphosphine)rhodium (1) proceeds in stepwise fashion via intermediate acylrhodium hydride (2) and alkylrhodium hydride (3) complexes (Scheme I).[1,2] Since the rate-determining step in this sequence is the initial oxidative addition,[2-4] the intermediate complexes, 2 and 3, cannot be observed directly. In fact, the mechanism and the intermediacy of 2 and 3 were originally based, in part, on analogy to the decarbonylation of acid chlorides where the intermediate acyl and alkyl complexes can be isolated.[1] Miller provided the first solid evidence[5] for the role of complex 2 by trapping the acylrhodium hydride from 4-pentenal by addition of the Rh–H bond to the double bond to give a six-membered-ring rhodium complex which decomposes to cyclopentanone. Suggs first isolated the oxidative addition product of an aldehyde and complex 1 by using 8-quinolinecarboxaldehyde, a substrate with an intramolecular ligand to trap the 5-coordinate acylrhodium hydride.[6] Most recently, Milstein isolated a 6-coordinate acylrhodium hydride from the reaction of 4-pentenal with chlorotris(trimethylphosphine)rhodium.[7] Thus, there is good evidence for the intermediacy of 2 on the pathway for the decarbonylation of aldehydes by Rh(I) complexes. In contrast, there is little evidence for complex 3, the aryl- or alkylrhodium hydride intermediate. The stereochemistries of the formation and decomposition of the alkylrhodium hydride intermediate will determine the overall stereochemistry of the decarbonylation of a chiral aldehyde since these are the steps in which bonds are made and broken to the chiral center. In the absence of observations on complex 3, it is not possible to assign stereochemistry to the individual bond making and bond breaking steps from a single observation of the net stereochemistry of decarbonylation. This paper

Scheme I



---

[1] Ohno, K.; Tsuji, J. *J. Am. Chem. Soc.* **1968**, *90*, 99–107.

[2] Baird, M. C.; Nyman, C. J.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 348–351.

[3] Kampmeier, J. A.; Harris, S. H.; Wedegaertner, D. K. *J. Org. Chem.* **1980**, *45*, 315–318.

[4] Doughty, D. H.; Anderson, M. P.; Casalnuovo, A. L.; McGuiggan, M. F.; Tso, C. C.; Wang, H. H.; Pignolet, L. H. *Adv. Chem. Ser.* **1982**, *196*, 65–83.

[5] Lachow, C. F.; Miller, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 1281–1283.

[6] Suggs, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 640–641.

[7] Milstein, D. *J. Chem. Soc., Chem. Commun.* **1982**, 1357–1358.

0022-3263/84/1949-0621$01.50/0