q is null or negligible. Second, deviations from additivity are not random nor due to specific interactions but are explained by a substituent dependence of the reaction constant ρ, which is proportional to q. Finally, making the additivity assumption leads to average reaction constants which optimize the deviations and which, in this way, lose a large part of their mechanistic significance. A reaction system is therefore perfectly described only if the reaction constants *and* the cross-interaction constants q are known. Moreover, q, which measures the ρ sensitivity to structural effects, can be a valuable source of information regarding the factors which causes ρ to vary. For this reason, more work is in progress to determine the generality of the IFER for the MSEs and the significance of the cross-interaction constant.

Experimental Section

α-Methylstilbenes were prepared by dehydration of the corresponding tertiary alcohols by *p*-toluenesulfonic acid in benzene.

$$XC_6H_4C(OH)MeCH_2C_6H_4Y \rightarrow XC_6H_4CMe{=}CHC_6H_4Y$$

The alcohols were prepared by condensation of Y-substituted benzylmagnesium chlorides with X-substituted acetophenones.

α-Methylstilbenes were purified by preparative column chromatography on Al_2O_3 or preparative GLC and were identified by their NMR spectra.

Experimental rate constants were measured by potentiometry[27] and, for the methoxy derivatives, by couloamperometry[28] as described elsewhere.

Acknowledgment. We are indebted to Professor J. E. Dubois for helpful discussion and encouragement.

Registry No. (*E*)-**19**, 83816-17-5; (*E*)-**20**, 83830-92-6; (*E*)-**21**, 83816-18-6; (*E*)-**22**, 83816-19-7; (*E*)-**23**, 83816-20-0; (*E*)-**24**, 83816-21-1; (*E*)-**25**, 83816-22-2; (*E*)-**26**, 83816-23-3; (*E*)-**27**, 57058-24-9; (*E*)-**28**, 83816-24-4; (*E*)-**29**, 83816-25-5; (*E*)-**30**, 83816-26-6; (*E*)-**31**, 83816-27-7; (*E*)-**32**, 83816-28-8; (*E*)-**33**, 83816-29-9.

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Photochemical Oxidation of Thioketones: Steric and Electronic Aspects

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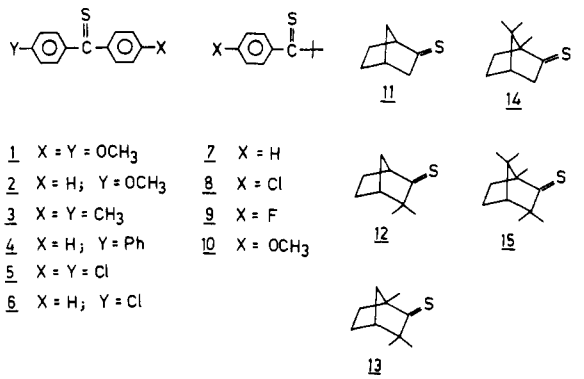
Oxidation of diaryl, aryl alkyl, and dialkyl thioketones by singlet oxygen generated via self-sensitization and other independent methods yielded the corresponding ketone and sulfine in varying amounts. A zwitterionic/diradical intermediate arising out of the primary interaction of singlet oxygen with the thiocarbonyl chromophore is believed to be the common intermediate for the ketone and sulfine. While closure of the zwitterion/diradical to give 1,2,3-dioxathietane would lead to the ketone, competing oxygen elimination is believed to lead to the sulfine. This partitioning is governed by steric and electronic factors operating on the zwitterionic/diradical intermediate.

Of known photochemical reactions oxidation has certainly been one of the most intensively investigated. However, most studies have been centered around the olefinic chromophore.[1] Oxidation of thiocarbonyl chromophores is of great concern to those interested in exploring their chemical behavior as oxidation contributes toward their instability. Since the initial report by Gattermann and Schulze,[2] the stability of several thioketones toward oxygen in the presence or absence of light has been investigated by several groups of workers. The reaction between thiobenzophenone and oxygen, in the dark, has been reported to yield the corresponding ketone and sulfine.[3] In contrast to this, oxidations in the presence of light of several dialkyl thioketones,[4] diaryl thioketones,[5] and *O*-alkyl thioesters[6] were reported to afford the corresponding carbonyl compounds in high yields together with elemental sulfur and sulfur dioxide. However, recently we[7] and Tamagaki and co-workers[8] noted that di-*tert*-butyl thioketone is an exception to this general behavior and yields the corresponding sulfine as the major product upon light-induced oxidation. Singlet oxygen generated by self-sensitization is believed to be the active species in all these cases. In spite of these scattered reports, no general picture has emerged on the oxidation of thiocarbonyls. Therefore, we have carried out a systematic investigation on the light-induced oxidation of a series of carefully chosen thioketones (Chart I), and the results are presented below.[9] The present study resulted from the surprising

Chart I. List of Thioketones Investigated



(1) Wassermann, H. H.; Murray, R. W., Eds. "Singlet Oxygen"; Academic Press: New York, 1979.
(2) Gattermann, L.; Schulze, H. *Ber.* **1896**, *29*, 2944.
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Table I. Product Distribution upon Oxidation of Diaryl Thioketones[a]

thioketone[b]	solvent	% yield for direct irrdn[c] (dye sens irrdn) ketone	sulfine
4,4'-dimethoxythiobenzophenone[e] (1)	cyclohexane	58	
	acetonitrile	57 (61)	
4-methoxythiobenzophenone (2)	cyclohexane	83	
	acetonitrile	87 (90)	
4,4'-dimethylthiobenzophenone (3)	cyclohexane	97	
	acetonitrile	97 (97)	
4-phenylthiobenzophenone (4)	cyclohexane	86	
	acetonitrile	85 (89)	
4,4'-dichlorothiobenzophenone (5)	cyclohexane	83	3
	acetonitrile	83 (67)	5 (6)
4-chlorothiobenzophenone (6)	cyclohexane	68	2
	acetonitrile	65 (70)	2 (2)

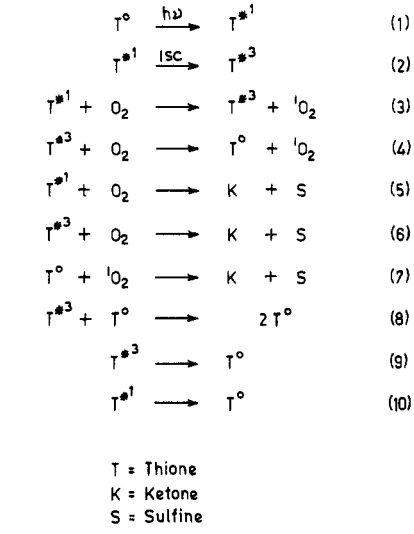
[a] Product distribution based on TLC isolated yields; average of three independent runs; error limit ±5%. [b] [Thioketone] = 0.02 M. [c] Direct excitation conducted by using a 500-W tungsten lamp. [d] Methylene blue and rose bengal were used as dyes. [e] The yield of evolved sulfur dioxide estimated gravimetrically for direct as well as dye-sensitized irradiations was 31% and 30%, respectively (error limit ±5%).

features exhibited by the highly hindered di-*tert*-butyl thioketone and the similar but less hindered 2,2,4,4-tetramethylcyclobutyl thioketone during the oxidation by singlet oxygen.[10]

Results

Direct excitation of diaryl (1–6), aryl alkyl (7–10), and dialkyl (11–15) thioketones in aerated solvents resulted in decolorization and formation of the corresponding sulfine and/or ketone as shown in Tables I–III. In all cases (1–15), the corresponding sulfine and/or ketone were the only oxidation products. However, the isolated product yields, especially for 11–15, are low. This resulted from the difficulty in the isolation procedures and was not due to any side products. Due to the volatility of ketones corresponding to 11–15, yields less than 50% are common in our case. However, sulfines were less volatile, and the yields represented in Tables II and III are true values. Therefore, mechanistic discussions based on these yields, especially on sulfine yields, are meaningful. Diaryl and aryl alkyl thioketones (0.02 M solutions) required approximately 12 h for complete reaction, whereas the dialkyl series (11–15), having poor absorption in the visible region, required more than 48 h under the same conditions. 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 last two cases suggested the involvement of singlet oxygen in these oxidations. To substantiate this, we made an attempt to correlate the quantum yields of oxidation of these thioketones with the lifetime of singlet oxygen in various solvents, the results of which are shown in Table IV. Expectedly, singlet oxygen, generated independently through dye sensitization and by thermal decomposition of triphenyl phosphite ozonide, readily reacted with all these thioketones (1–15) to yield ketone and sulfine in similar yields as upon direct excitation (Tables I–III).

Scheme I. General Kinetic Scheme for the Oxidation of Thioketones



The product distribution upon dye-sensitized oxidation was independent of the concentration of the thioketone (0.2–0.001 M; Table V). No marked effect on the product distribution due to increased polarity of the solvents was observed (Tables I–III). In methanol, however, other than an increase in the rate of oxidation, 10–13 showed nearly a threefold increase in the percentage of sulfine; these thioketones showed little or no sulfine in nonhydroxylic solvents. Efforts to characterize the reactive intermediates through trapping studies (using alcoholic solvents, tetracyanoethylene, and other thioketones) were unsuccessful. However, indirect evidence in favor of one of the suspected intermediates, 1,2,3-dioxathietane was available through identification of sulfur and sulfur dioxide as additional products during dye-sensitized and direct exposed oxidation. Sulfur dioxide evolved during the oxidation was estimated gravimetrically,[11] and the yields are represented in Tables I–III.

To gain insight into the mechanism of the above oxidation, we measured the rates of singlet oxygen quenching by these thioketones and the efficiencies of singlet oxygen production upon direct excitation by following the established procedures,[12] and the results are presented in Tables VI and VII.[13] To identify the excited state of thioketone involved in the generation of singlet oxygen, we carried out sensitization and quenching studies. The oxidation was sensitized by triplet sensitizers such as 1,4-dibromonaphthalene and 4,4'-dibromodiphenyl and quenched by the triplet quencher alloocimene.

Discussion

Thioketones, in general, upon direct excitation are oxidized to the ketone and/or sulfine (Tables I–III). Such an oxidation can be visualized to occur through the kinetic scheme represented in Scheme I. Accordingly, formation of sulfine and ketone can arise through two pathways (in the absence of dark oxidation): one wherein singlet oxygen, generated through an energy-transfer process, oxidizes the

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(13) Results on these aspects (efficiency of singlet oxygen production and rate of singlet oxygen quenching) have been elaborated in the following papers: Ramesh, V.; Ramnath, N.; Ramamurthy, V. *J. Photochem.* **1982**, *18*, 293. Ramesh, V.; Ramnath, N.; Jayathirtha Rao, V.; Ramamurthy, V. *Ibid.* **1982**, *18*, 109.

Table II. Product Distribution (in Percent) upon Oxidation of Aryl Alkyl Thioketones[a]

		mode of oxidation					
		direct excitation[c]			dye-sensitized excitation[d]		
thioketone[b]	solvent	ketone	sulfine	SO_2[e]	ketone	sulfine	SO_2
thiopivalophenone (7)	cyclohexane	50	14				
	acetonitrile	63	16		60	12	
	methanol	59	17		57	17	
p-chlorothiopivalophenone (8)	cyclohexane	63	20				
	acetonitrile	52	25	26	51	25	25
	methanol	65	24		63	23	
p-fluorothiopivalophenone (9)	cyclohexane	43	18				
	acetonitrile	43	21		38	20	
	methanol	48	20				
p-methoxythiopivalophenone (10)	cyclohexane	77	2				
	acetonitrile	80	2	41	75	2	35
	methanol	82	10		85	9	

[a] Product distribution based on TLC isolated yields; average of three independent runs; error limit ±5%. [b] [Thioketone] = 0.02 M. [c] Direct excitation conducted using 500-W tungsten lamp. [d] Methylene blue and rose bengal were used as dyes to generate singlet oxygen. [e] Sulfur dioxide estimated gravimetrically; average of three independent runs; error limit ±5%.

Table III. Product Distribution (in Percent) upon Oxidation of Bicyclo[2.2.1]heptane Thioketones 11-15[a]

		dye-sensitized excitation[c]		
thioketone[b]	solvent	ketone	sulfine	SO_2[d]
thionorcamphor[e] (11)	chloroform	62		
	methanol	63		
thiocamphenilone (12)	carbon tetrachloride	67		
	chloroform	59		29
	acetonitrile	32	4	
	methanol	18	12	
thiofenchone (13)	chloroform	44		
	acetonitrile	44	2	
	methanol	34	7	
thiocamphor (14)	carbon tetrachloride	35	14	
	chloroform	30	14	16
	acetonitrile	32	15	
	methanol	22	19	
3,3-dimethylthiocamphor (15)	chloroform	64	20	30

[a] Product distribution is based on TLC isolated yields; average of three individual runs; error limit ±10%. [b] [Thioketone] = 0.04 M; direct excitation could not be conducted owing to their poor absorption in the visible region. [c] Methylene blue, rose bengal, and rhodamin B were used as dyes. [d] Sulfur dioxide estimated gravimetrically; error limit ±5%; average of three independent runs. [e] The sulfine of thionorcamphor prepared independently was found to be unstable.

Table IV. Quantum Yields of Oxidation of Thioketones[a] and Their Relation to $^1O_2$ Lifetime[b]

	solvent ($10^6 \tau^1O_2$, s)				
thioketone	carbon tetrachloride (700)	chloroform (60)	acetonitrile (30)	benzene (24)	cyclohexane (17)
4,4'-dimethoxythiobenzophenone (1)	1.00	1.00	0.77	0.54	0.54
4-methoxythiobenzophenone (2)	1.00	0.93	0.56	0.43	0.15
4,4'-dimethylthiobenzophenone (3)	1.00	0.90	0.75	0.21	0.10
4-phenylthiobenzophenone (4)	1.00	0.75	0.47	0.25	0.18
4,4'-dichlorothiobenzophenone (5)	0.54	0.36	0.22	0.17	0.15
4-chlorothiobenzophenone (6)	0.86	0.61	0.34	0.21	0.10
thiopivalophenone (7)	0.46	0.19	0.32	0.31	0.30
4-chlorothiopivalophenone (8)		0.16	0.28	0.27	0.22
4-fluorothiopivalophenone (9)	0.45	0.20	0.33	0.20	0.26
4-methoxythiopivalophenone (10)	0.67	0.54	0.64	0.32	0.54

[a] Disappearance of the thione was followed by UV-visible absorption. [b] Wasserman, H. H.; Murray, R. W., Eds. ((Singlet Oxygen"; Academic Press: New York, 1979; p 120.

ground-state thioketone (eq 7) and the other wherein the ground-state oxygen oxidizes the excited-state thioketone (eq 5 and 6, Scheme I). Involvement of the singlet oxygen pathway to a major extent is suggested by the following observations.

(1) The rate of oxidation is completely suppressed in all these cases by singlet oxygen quenchers (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 (1,3-diphenylisobenzofuran gave *o*-dibenzoylbenzene, and 2,3-dimethylbut-2-ene gave 2,3-dimethyl-3-hydroperoxybut-1-ene).

(2) Perusal of Table IV reveals an interesting relationship between the quantum yield of oxidation upon direct excitation and the lifetime of singlet oxygen.

(3) Comparison of the relative quantum yields of oxidation of diaryl and aryl alkyl thioketones upon direct excitation (Table IV) indicates that the oxidation is favored by electron-donating substituents and retarded by elec-

Table V. Concentration-Independent Product Distribution (in Percent) upon Oxidation of Thioketones[a,b]

thioketone	concn, M	acetonitrile		methanol	
		ketone	sulfine	ketone	sulfine
thiopivalophenone (7)	0.2	55	18	58	23
	0.002	60	17	50	21
p-fluorothiopivalophenone (9)	0.1	38	17		
	0.001	32	16		
thiocamphor (14)	0.2	33	16	36	17
	0.002	34	17	35	15

[a] Product distribution based on TLC isolated yields; average of three independent runs; error limit ±10%. [b] Methylene blue sensitized oxidation.

Table VI. Rate of Quenching ($k_q{}^1O_2$) and Efficiency of Singlet Oxygen Production (Φ^1O_2) by Dialkyl Thioketones[a]

thioketone	rate of $^1O_2$ quenching by thioketones, $\times 10^{-4}$ M^{-1} s^{-1}	ionization potential,[b] eV		efficiency of $^1O_2$ generation upon direct excitation (Φ)	
		n	π	Φ^1O_2[c]	Φ^1O_2 (0.01 M)[d]
thionorcamphor (11)	18	8.32	9.94	1.00	0.56
thiocamphenilone (12)	10	8.15		1.00	0.59
thiofenchone (13)	51	8.10	9.6	1.00	0.83
thiocamphor (14)	8.1	8.17		1.00	0.87
3,3-dimethyl-thiocamphor (15)	5.8	8.01		1.00	0.91

[a] For a full discussion on these aspects see: Ramesh, V.; Ramnath, N.; Jayathirtha Rao, V.; Ramamurthy, V. *J. Photochem.*, 1982, *18*, 109. Ramesh, V.; Ramnath, N.; Ramamurthy, V. *Ibid.* 1982, *18*, 293. [b] Ionization potential values provided by R. Gleiter. [c] Quantum yield of $^1O_2$ production at zero concentration of thioketone. [d] Quantum yield of $^1O_2$ production at 0.01 M thioketone concentration.

Table VII. Rate of Quenching ($k_q{}^1O_2$) and Efficiency of Singlet Oxygen Production (Φ^1O_2) by Diaryl and Aryl Alkyl Thioketones[a]

thioketone	rate of $^1O_2$ quenching by thioketones, $\times 10^{-5}$ M^{-1} s^{-1}	σ	σ^+[b]	efficiency of $^1O_2$ generation upon direct excitation	
				Φ^1O_2[c]	Φ^1O_2 (0.01 M)[d]
4,4'-dimethoxy-thiobenzophenone	96	−0.27	−0.65	1.00	0.83
4-methoxy-thiobenzophenone	54	−0.27	−0.65		
4,4'-dimethyl-thiobenzophenone	37	−0.129	−0.26		
4-phenyl-thiobenzophenone	31	−0.01	−0.08	1.00	0.56
4,4'-dichloro-thiobenzophenone	2	+0.23	+0.04		
4-chloro-thiobenzophenone	11	+0.23	+0.04		
thiopivalophenone	4.3	0.00	0.00	1.0	0.94
4-chloro-thiopivalophenone	2.0	+0.23	+0.04		
4-fluoro-thiopivalophenone	3.6	+0.06	−0.25		
4-methoxy-thiopivalophenone	9.2	−0.27	−0.65	1.00	0.86

[a] For a full discussion on these aspects see: Ramesh, V.; Ramnath, N.; Ramamurthy, V. *J. Photochem.*, 1982, *18*, 293. Ramesh, V.; Ramnath, N.; Jayathirtha Rao, V.; Ramamurthy, V. *Ibid.* 1982, *18*, 109. [b] Values taken from: Swain, C. G.; Lupton, E. C., Jr. *J. Am. Chem. Soc.* 1968, *90*, 4328. [c] Quantum yield of $^1O_2$ production at zero concentration of thioketone. [d] Quantum yield of $^1O_2$ production at 0.01 M concentration of thioketone.

tron-withdrawing substituents, indicating that the oxidizing species is electrophilic in nature.

(4) Further, the product distribution during oxidation by singlet oxygen, generated by dye sensitization and by thermal decomposition of triphenyl phosphite ozonide, is very similar to that during direct excited oxidation. Thus we suggest that singlet oxygen pathway is the major mode of oxidation upon direct excitation of all these thioketones. Although we could not completely rule out the existance of the pathway involving excited thioketone and triplet oxygen, our results suggest that its contribution is negligible.[14] Therefore, we discuss below the mechanism of oxidation of thioketones by singlet oxygen alone.

Singlet oxygen can be expected to arise through the energy transfer from the lowest excited singlet or triplet states of thioketones (eq 3 and 4, Scheme I). However, the small energy gap between S_1 and T_1 ($\Delta E \approx 7$ kcal/mol) precludes the process involving $n\pi^*$ excited singlet

(14) A pathway involving triplet oxygen and excited thioketone was also found to be involved during the oxidation of di-*tert*-butyl thioketone upon direct excitation. Tamagaki, S.; Akatsuka, R.; Nakamura, M.; Kozuka, S. *Tetrahedron Lett.* 1979, 3665. Jayathirtha Rao, V.; Ramamurthy, V. *Curr. Sci.* 1980, *49*, 199.

state.[15,16] Further, the sensitization and quenching studies support the contention that the triplet $n\pi^*$ thioketone is responsible for the production of singlet oxygen. In fact, the efficiency of singlet oxygen production by this process as measured by following the bleaching of 1,3-diphenylisobenzofuran in chloroform is close to unity in all cases (Tables VI and VII) and is limited only by self-quenching.[13] This is consistent with our postulate that the singlet oxygen pathway is the major mode of oxidation.

Perusal of Tables I–III reveals that the product distribution (ketone and sulfine) during direct excitation and upon oxidation by singlet oxygen is subjected to steric influence in the bicyclo[2.2.1]heptane series and to electronic influence in the case of diaryl and aryl alkyl series. The yields less than 100% are common with all the thioketones investigated due to the volatility of the ketones formed and not due to any other side products. The mechanistic discussion based on sulfine yields is valid as they all are found to be less volatile, and the variation in the yield of sulfine is a reflection of the inherent features of this ketones. Interestingly, sulfine formation is favored by the presence of methyl groups at the C_7 position of the bicyclo[2.2.1]heptane series and by the substitution of electron-withdrawing groups in the other two series. The rationale for this observation can be achieved with an insight into the nature of orbitals involved in the thiocarbonyl chromophore during the singlet oxygen attack.

Electrophillic singlet oxygen can be expected to interact either with the filled "π" or "n" orbitals of the thiocarbonyl chromophore. We believe that in all the three series investigated the interaction occurs with the "n" orbital of the thiocarbonyl. This is supported by the following observations.

(1) Rates of singlet oxygen quenching by dialkyl thioketones show a linear relationship with the "n" electron ionization potentials and not with that of the π electrons.[13]

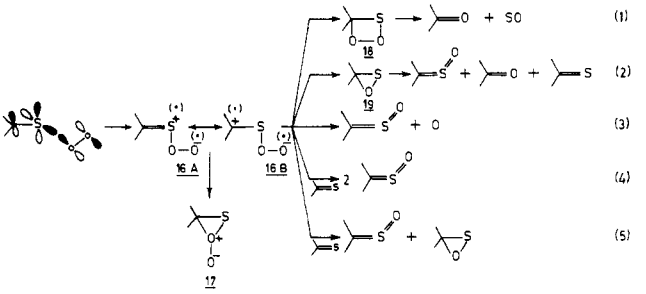
(2) Among the diaryl and aryl alkyl thioketones it is observed that the electron-donating groups enhance the rate while the electron-withdrawing groups retard it. The rate constants exhibit a linear free energy relationship (Hammett's plot), and a better correlation is obtained with σ than σ^+.[13] Definitive conclusions regarding the nature of the orbitals involved (n or π) during the quenching of singlet oxygen by these dialkyl and aryl alkyl thioketones could not be made owing to the lack of experimental data on the ionization potentials.

(3) The large energy gap between the "n" and "π" orbitals (~30 kcal/mol) as measured by the electronic spectra of the diaryl and aryl alkyl thioketones supports the contention that the "n" orbitals are more susceptible to electrophilic attack.[17]

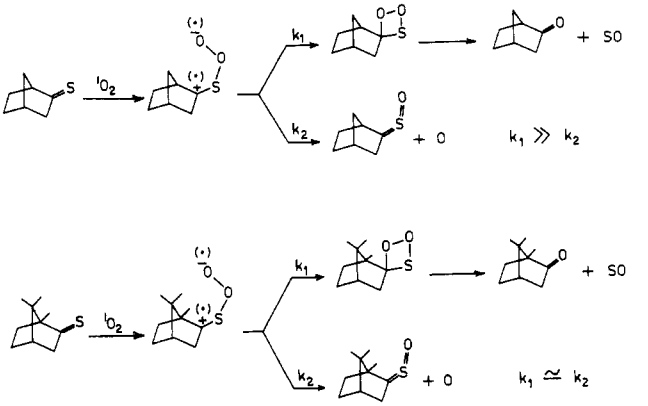
Linear relationships obtained in the dialkyl series with ionization potentials and in the diaryl and aryl alkyl series with σ values suggest that the nature and mechanism of attack do not vary within the series; i.e., substituents do not alter the nature of attack (n or π orbitals) although they influence the rate of attack by singlet oxygen.

Zwitterionic/diradical intermediate **16** is the logical resultant of the interaction between singlet oxygen and the thiocarbonyl chromophore, involving π^* and n orbitals, respectively.[18] This intermediate can be expected to decompose to ketone and sulfine through the paths illustrated in Scheme II. Ketone formation appears to be preceded by a 1,2,3-dioxathietane intermediate as the sulfur and sulfur dioxide expected from the decomposition have been isolated in all the thioketones investigated. More importantly, the estimated yield of sulfur dioxide corresponds with the isolated yield of ketone (Tables I–III), probably suggesting that this is the only pathway by which ketone is formed, and oxathiirene (**19**) might not be involved in its production (Scheme II, eq 2 and 5). On the basis of the fact that the ratio of sulfine to ketone is independent of the concentration of the thioketone (Table V), we conclude that the zwitterionic/diradical intermediate unimolecularly decomposes to sulfine (and oxygen) or closes to 1,2,3-dioxathietane, and the biomolecular pathways (Scheme II, eq 4 and 5) are absent. This conclusion is consistent with our earlier observations on di-*tert*-butyl thioketone and 2,2,4,4-tetramethylcyclobutyl thioketone.[10]

Scheme II. General Mechanism for the Oxidation of Thioketones



Scheme III. Steric Control during the Oxidation of [2.2.1]Bicycloheptane Thioketones



The variation in the product distribution may be viewed upon by considering two groups of thioketones. The first group is constituted of the diaryl and aryl alkyl thioketones **1–10**, while the second group is constituted of the bicyclo[2.2.1]heptyl thioketones **11–15**. We postulate that electronic factors govern the product distribution in the former while steric factors operate in the latter. The suggested intermediate, zwitterionic/diradical **16**, could decompose to the sulfine or close to give a 1,2,3-dioxathietane intermediate as suggested above. The ease of closure of the intermediate, however, will depend on the substituents at the C_7 carbon atom in bicyclo[2.2.1]heptane series, and the *gem*-dimethyl groups at C_7 hinder the closure (Scheme III). The absence of C_7 dimethyl groups in **11–13** favors the closure of the intermediate to 1,2,3-dioxathietane, and, consequently, the ketone is obtained

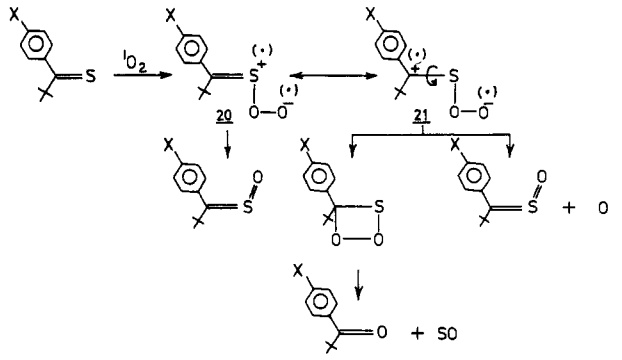
(15) Although we have not measured the energies of S_1 and T_1 for all these thioketones, a general trend having a small $E(S_1 - T_1)$ has been noted for a variety of thioketones: Blackwell, D. S. L.; Liao, C. C.; Loutfy, R. O.; de Mayo, P.; Paszyc, S. *Mol. Photochem.* **1972**, *4*, 171.

(16) Stevens, B.; Ors, J. A. *J. Phys. Chem.* **1976**, *80*, 2164. Gunnovich, G. P.; Salokhiddinov, K. I. *Chem. Phys. Lett.* **1982**, *85*, 9.

(17) Attempts are underway to establish a colloboration to obtain UV PES data for diaryl and aryl alkyl thioketones.

(18) Carlsen, L. *J. Chem. Soc., Perkin Trans. 2* **1980**, 188.

Scheme IV. Electronic Control during the Oxidation of Diaryl and Aryl Alkyl Thioketones



as the major product. On the other hand, in the case of **14** and **15** the C_7 methyl groups hinder the closure, as a result sulfine formation competes, and its yield is increased compared to **11–13**.

The variation in the product distribution in the diaryl and aryl alkyl series effected by substituents, we suggest, can be understood in terms of the electronic factors operating on the zwitterionic/diradical intermediate. The suggested intermediate **16** can exist in resonance forms **20** and **21** (Scheme IV). In the case of diaryl and aryl alkyl thioketones, electron-withdrawing ring substituents, which favor the sulfine formation, will shift the equillibrium to **20** at the expense of **21** whereas electron-donating substituents stabilize **21** with respect to **20**. While **21** can undergo facile ring closure to 1,2,3-dioxathietane, bonding constraints retard the closure of **20**, thus allowing competing oxygen elimination to occur. Since ring closure is more facile, the ketone formation still predominates. Thus electron-donating substituents which favor **21** produce ketone and the electron-withdrawing substituents which favor form **20** produce sulfine in addition to ketone. As the stabilization of **21** is larger in the case of diaryl thioketones due to delocalization into the aryl rings, it probably explains the general preference for ketone formation. A similar approach has been utilized to understand the variation in the ^{13}C NMR chemical shifts of thiocarbonyl upon protonation.[19]

The mechanism proposed here to understand the oxidation of thioketones by singlet oxygen is simple, and many aspects of it are yet to be substantiated. However, the credibility derives from its simplicity and ability to rationalize many of the observations. Experimental support in favor of the proposed intermediates (zwitterionic/diradical) and spectroscopic data for 1,2,3-dioxathietane (at lower temperature)[20] are highly desirable. Attempts were made to trap the proposed zwitterionic/diradical intermediate in alcoholic solvents. The results are ambiguous. Although ^1H NMR shows the formation of a product with a methoxy peak when irradiation of thioketones was carried out in methanol, its isolation after repeated efforts could not be achieved, probably due to its instability.[21] It is noteworthy that those thioketones (**10–13**) that give very little or no sulfine in other solvents show a threefold rise in its yield in methanol (Tables I–III). This, we believe, arises out of hydrogen bonding of the zwitterionic/diradical intermediate with solvent methanol, thereby retarding its closure. That the other thioketones do not show such a large jump indicates a saturation limit of partitioning between ring closure and elimination.

An interesting, yet poorly understood aspect of this study is the fate of oxygen that is derived from the zwitterionic/diradical intermediate after the production of the sulfine. This oxygen atom can be trapped by the thioketone to produce either sulfine or oxathiirene.[22] However, under our experimental conditions (continuous bubbling of oxygen) ozone is a likely product. Yet another possibility is the reaction of sulfur monoxide with the zwitterionic/diradical intermediate to produce sulfine and sulfur dioxide.[23] However, if this is the major mode of formation of sulfines, the estimated yield of sulfur dioxide would not be expected to match the yield of the ketone (Tables II and III). This, being one among the many possibilities, cannot be ruled out at this stage. Efforts are being directed toward understanding these processes and isolating or identifying 1,2,3-dioxathietane.

In conclusion, the generality of the light-catalyzed oxidation of thioketones by oxygen has been demonstrated. Singlet oxygen has been identified to be the oxidizing species. The oxidation is suggested to involve some novel intermediates such as 1,2,3-dioxathietane and a zwitterionic/diradical peroxide. Operation of electronic and steric factors upon the latter intermediate is probably responsible for the variation in the yields of ketones and sulfines in diaryl, aryl alkyl, and dialkyl thioketones.

Experimental Section

Preparation of Ketones. Ketones were either obtained commercially or prepared by reported methods.[24]

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

Method A.[25] Dry hydrogen sulfide and hydrogen chloride gases were simultaneously bubbled through an alcoholic solution of ketone (2 g/30 mL) at −5 to +10 °C for 24 h. The dark blue solution was concentrated, and the crystals were filtered out and recrystallized from hexane. In cases where the thioketone did not crystallize, it was extracted into hexane to give colored oil.

Method B.[26] The ketone (3 g) was dissolved in dry pyridine (40 mL) and to this was added phosphorus pentasulfide (1.5 equiv). The mixture was gently refluxed for 3 h, and the product was extracted with hexane, washed with water, and dried over anhydrous sodium sulfate. Thioketone thus obtained was purified by column chromatography (silica gel–hexane).

Method C.[27] To a solution of ketone (3 g) in diglyme (50 mL) was added 1.5 equiv of phosphorous pentasulfide, and the solution was heated to 110 °C. During a period of 1 h, 4 equiv of sodium hydrogen carbonate was added with stirring, and after complete addition the mixture was held at 110 °C for 1 h. The reaction mixture was cooled and poured into ice-cold water, and hexane was used for extraction. The thioketone thus obtained was purified by column chromatography.

(19) Yamabe, T.; Nagata, S.; Akagi, K.; Hashimoto, R.; Yamashita, K.; Fukui, K.; Ohno, A.; Nakamura, K. *J. Chem. Soc. Perkin Trans. 2* **1977**, 1516. Olah, G.; Nakajima, T.; Surya Prakash, G. K. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 810.

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(22) Such a process yielding sulfine may not be expected to show concentration dependence in the range studied (Table V). However, at very low concentrations such a process might be affected.

(23) We are grateful to one of the referees for pointing out this possibility.

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Table VIII. Method of Preparation and Spectral Data for Thioketones 1-15

thioketone	method	yield, %	IR, cm^{-1} (solvent)	UV (benzene) λ_{max}, nm (ϵ)	^1H NMR (CCl_4), δ	^{13}C NMR ($CDCl_3$), δ
4,4'-dimethoxy-thiobenzophenone (1)	A	90	1220 (Nujol)	591 (280), 354 (24 600)	3.8 (s), 6.7-7.8 (m, phenyl)	
4-methoxy-thiobenzophenone (2)	A	70	1240 (liquid film)	594 (153), 361 (9600)	3.8 (s), 6.7-7.9 (m, phenyl)	
4,4'-dimethyl-thiobenzophenone (3)	A	90	1220 (Nujol)	600 (223), 329 (22 800)	2.3 (s), 7-7.7 (m, phenyl)	
4-phenyl-thiobenzophenone (4)	A	90	1230 (Nujol)	604 (240), 353 (16 900)	7.3-7.7 (m, phenyl)	
4,4'-dichloro-thiobenzophenone (5)	A	60	1220 (Nujol)	605 (108), 328 (10 350)	7-7.8 (m, phenyl)	
4-chloro-thiobenzophenone (6)	A	60	1215 (liquid film)	603 (87), 322 (8950)	6.8-7.6 (m, phenyl)	
thiopivalophenone (7)	B	50	1100 (liquid film)	560 (70), 314 (1920)	1.4 (s), 7.15 (phenyl)	30.9 (q), 52.0 (s), 151.0 (s), 130.1, 124.0 (s), 265.9 (C=S)
4-chloro-thiopivalophenone (8)	B	50	1120, 1090 (liquid film)	560 (80)	1.4 (s), 7.1 (phenyl)	31.1 (q), 42.1 (s), 112, 132, 147, 164.5 (phenyl), 263.8 (C=S)
4-fluoro-thiopivalophenone (9)	B	50	1100, 1090 (liquid film)	560 (60), 263 (2500)	1.38 (s), 6.9-7.4 (m, phenyl)	31.2 (q), 52.0 (s), 114, 127, 147.2, 164.6 (phenyl), 263.8 (C=S)
4-methoxy-thiopivalophenone (10)	B	40	1090-1100 (liquid film)	560 (256), 310 (9400)	1.4 (s), 3.7 (s), 6.6-7.4 (m, phenyl)	31.6 (q), 51.3 (s), 55.3 (q), 112, 127, 160.5, 143.8 (phenyl), 263.6 (C=S)
thionorcamphor (11)	B	15	1200 (liquid film)	497 (6)	1.3-1.93 (m), 2.33, 2.73, 3.3	
thiocamphenilone (12)	B	40	1100, 1140, 1280 (Nujol)	494 (14)	1.16 (s), 1.2-3.35	18.0 (q), 23.3 (q), 37.2 (t), 26.0 (t), 28.4 (t), 47.9 (d), 58.36 (s), 65.0 (d), 277.8 (C=S)
thiofenchone (13)	C	20	1100-1200 (liquid film)	487 (9.0)	1.15, 1.16, 1.3 (s), 1.4-2.2	13.13 (q), 19.8, 19.6 (q), 31.8 (t), 34.0 (t), 31.8 (t), 41.3 (s), 45.3 (d), 55.6 (t), 69.2 (s), 271.4 (C=S)
thiocamphor (14)	C	40	1130 (Nujol)	498 (13)	0.8, 1.0, 1.2-2.2	13.0 (q), 19.8 (q), 27.2 (t), 34.0 (t), 45.7 (d), 48.8 (s), 55.0 (t), 69.2 (s), 271.5 (C=S)
3,3-dimethyl-thiocamphor (15)	A	30	1210 (liquid film)	490 (6)	0.83, 1.06, 1.23, 1.16-3.0	13.8 (q), 16.2 (q), 20.3 (q), 19.2 (q), 35.0 (t), 50.4 (d), 70.1 (s), 48.2 (s), 276.0 (C=S)

Table IX. Physical and Spectral Characteristics of S-Oxides

S-oxide	mp, °C	UV ($CHCl_3$) λ_{max}, nm (ϵ)	IR ($CHCl_3$), cm^{-1}	^1H NMR (CCl_4), δ
p-chlorothiobenzophenone S-oxide[a]			1040–1260	7.2–7.7 (complex m)
p,p'-dichlorothiobenzophenone S-oxide[b]	78–79	269 (15 500), 336 (14 500)	1040–1260	7.3–7.8 (complex m, with loss of symmetry)
thiopivalophenone S-oxide[c]	66–67	265 (6900), 308 (sh, 2050)	1060, 1140	1.3 (s), 1.4 (s), 6.8–7.4 (phenyl)
p-methoxythiopivalophenone S-oxide[c]	87–89	263 (6100), 306 (sh, 2500)	1060, 1140	1.16 (s), 1.26 (s), 3.74 (s), 6.8–7.2 (phenyl)
p-chlorothiopivalophenone S-oxide[c]	94–96	263 (6600), 310 (sh, 2200)	1090, 1060, 1170	1.3 (s), 1.4 (s), 6.8–7.3 (phenyl)
p-fluorothiopivalophenone S-oxide	oil	263 (6500), 310 (sh, 2050)	1030, 1130	1.27 (s), 1.30 (s), 6.7–7.3 (phenyl)
thiocamphor S-oxide[c]	oil	270 (5150), 310 (sh, 500)	1050	0.91, 1.0, 1.15, 1.2–2.2
thiocamphenilone S-oxide[c]	88–89	273 (5700), 315 (sh, 600)	1060	1.28, 1.4, 1.45, 1.7–2.2, 3.1
thiofenchone S-oxide[c]	50–52	270 (5100), 310 (sh, 550)	1050	0.83, 0.96, 1.1, 1.2–2.2, 2.8
(3,3-dimethyl)thiocamphor S-oxide[b]	oil		1050	0.8, 1.0, 1.26, 1.3, 2.0

[a] Not sufficiently stable for elemental analysis. [b] The compound was not completely separable from the ketone. [c] Combustion analytical data for C and H were obtained.

Direct Excitation of Thioketones: Oxidation of Thioketones upon Direct Excitation. Direct excitation of diaryl, aryl alkyl, and dialkyl thioketones was conducted by using 500-W tungsten lamps. Under identical conditions dialkyl thioketones required more than 48 h for the oxidation whereas the other two series required only 12 h. This is attributed to the poor absorption of bicyclo[2.2.1]heptyl thioketones in the visible region ($\epsilon \approx 9$–13 at 480–560 nm). However, irradiation at a higher concentration did not bring about any improvement due to the well established self-quenching phenomenon.[28] The general procedure involved irradiation of aerated solutions of thioketones (0.02 M) in acetonitrile, chloroform, or methanol until decolorization as monitored by their absorption in the visible region. After complete decolorization (6–15 h, depending on the thioketone), the solvent was evaporated off, and the products were isolated either by column chromatography or thin-layer chromatography.

Dye-Sensitized Irradiations: Oxidation of Thioketones by Singlet Oxygen. Aerated solutions of thioketones **1–15** (0.04 M) were irradiated with 500-W tungsten lamps in the presence of dyes (10^{-4} M) such as methylene blue, rose bengal, and rhodamin B. After complete decolorization (as tested by micro-TLC) the solvent was boiled off, and the products were isolated by preparative TLC (silica gel, hexane/benzene). The products (ketone and sulfine) were identified by their spectral data and by comparison with authentic samples. Authentic samples of ketones were available from the above-described procedures, and sulfines were prepared either by the oxidation of thioketones by m-chloroperbenzoic acid or by the ozonolysis of thioketones.[29] Sulfines of diaryl thioketones were less stable compared to those derived from aryl alkyl and dialkyl thioketones. Spectral and elemental analysis data for sulfines are shown in Table IX.

Dye-sensitized irradiations were also carried out by varying the concentrations of thioketones (0.002–0.2 M) in the case of **7**, **9**, and **14**, and the product yields were determined as before (Table V). Since the three thioketones studied did not show any variation in the product distribution, studies on other thioketones were not carried out.

Oxidation of Thioketones by Singlet Oxygen Generated by the Decomposition of Triphenyl Phosphite Ozonide. Triphenyl phosphite ozonide was prepared at low temperature (−80 °C) in methylene chloride by bubbling ozone through a solution of triphenyl phosphite (100 mg in 50 mL of methylene chloride).[30] As the solution was warmed to room temperature, the thioketone (**1–15**) was added and the mixture left at room temperature for 2 h, by which time the thioketone color had completely faded. The oxidation was complete in all cases within 30 min. For the sake of uniformity all solutions were allowed to stand for 2 h. The products of oxidation were isolated by column chromatography and identified by their spectral data. Since the product separation posed problems due to the formation of triphenyl phosphate, this method was employed only to confirm the singlet oxygen pathway during direct exposed oxidation of thioketones and was not routinely employed.

Estimation of Sulfur Dioxide.[11] A chloroform solution (50 mL) of thioketone (250 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 two traps containing sodium hydroxide solution (0.3 M). The immersion well was irradiated with two 500-W tungsten lamps while oxygen was continuously bubbled through. The sulfur dioxide evolved was collected as sodium sulfite in the trap and was oxidized to sulfate by the addition of bromine. Sulfate was gravimetrically estimated by following the reported procedure. The ketone and sulfine products were estimated by preparative TLC as described above.

Determination of the Quantum Yield of Oxidation of Thioketones. A 0.006 M solution of the thioketone was made in organic solvents. A Hanovia 450-W medium-pressure mercury-vapor lamp was the source of irradiation. The 320–350-nm band was selected by use of a Corning glass filter (CS-7.60). Thioketone solutions (diaryl and aryl alkyl) were irradiated in a merry-go-round style until approximately 20% conversion had taken place. UV–visible absorption spectrophotometer was used to determine the amount of thioketone reacted. A potassium ferrioxalate actinometer was used to determine the light intensity.[31] The results obtained are shown in Table IV. All these irradiations were conducted by exciting the thioketones into the $\pi\pi^*$ state.

Quenching and Sensitization Studies. Aerated solutions of thioketones **1–10** in acetonitrile were irradiated in the presence of singlet oxygen quenchers (0.02–0.04 M; Dabco, 2,3-diphenylisobenzofuran, and 2,3-dimethylbut-2-ene were used). Oxidation in the presence of these quenchers was extremely slow. Virtually no conversion, during the period over which complete conversion takes place in the absence of these quenchers, was detectable.[32] However, products derived from the oxidation of the quenchers were isolated by preparative TLC: 2,3-diphenylisobenzofuran gave o-dibenzoylbenzene, and 2,3-dimethylbut-2-ene gave 2,3-dimethyl-3-hydroperoxybut-1-ene. These were identified by comparison with authentic samples.

Triplet-sensitized irradiation of thioketones **11–15** was conducted in acetonitrile by using 4,4'-dibromobiphenyl ($E_T \approx 62$

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(31) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

(32) Thioketones were found to react slowly with Dabco even in dark.

kcal/mol) and 1,4-dibromonaphthalene ($E_T \approx 66$ kcal/mol). Solutions of thioketones (0.05 M) were irradiated in the presence of the above sensitizers (0.001 M). Excitation of the sensitizer was effected by making use of a CS-7.60 Corning filter. Product yields were determined as before. Sensitization studies for thioketones 1–10 could not be carried out due to lack of filters to effect selective excitation.

A triplet quenching study was conducted by using alloocimine ($E_T \approx 47$ kcal/mol) as a triplet quencher of thioketones. This quenches the triplets of dialkyl thioketones and, less efficiently, that of aryl alkyl thioketone. However, owing to the lower triplet energy of diaryl thioketones alloocimene is found to be a poor quencher for these triplets. A typical experiment in the case of dialkyl and aryl alkyl thioketones is as follows. Four samples of 0.02 M solutions of thioketone with varying concentrations of the quencher (0.1–0.25 M) were irradiated (450-W medium-pressure mercury lamp with Corning glass filter CS-3.68). The amount of thioketone reacted was monitored by its visible absorption. In all the dialkyl thioketones (11–15) investigated, a linear Stern–Volmer plot was obtained. Quenching was observed in the case aryl alkyl thioketones but required high concentrations due to the poor quenching rate.

Control Experiments. (a) Stability of Thioketones in the Dark. Bicyclo[2.2.1]heptyl thioketones 11–15 kept in dark in organic solvents in an aerated atmosphere for over 1 week were found to be stable. Similarly, bubbling oxygen through these solutions in the dark for over 10 days did not bring about any reaction.

Aryl alkyl thioketones 7–10 were also stable to air and oxygen in the dark. However, thiopivalophenone polymerized in the dark at times, and the reasons for this are not clear. Rigorously purified thiopivalophenone was found to be indenfinitely stable.

Diaryl thioketones (1, 3, and 4) were stable compounds and could be stored. While (2, 5, and 6) were unstable and found to decompose over a period of 2–3 days in dark. Slow dark reaction for thioketones (1–6) was observed in chloroform, cyclohexane, benzene, carbon tetrachloride, and acetonitrile.

All the thioketones investigated revealed poor stability in dioxane and diglyme where rapid decolorization in dark occur.

(b) Stability of Thioketones in Nitrogen Atmosphere upon Irradiation. All thioketones 1–15 investigated did not undergo any noticeable change upon irradiation for 1 week with a 500-W tungsten lamp in a nitrogen atmosphere in organic solvents. However, excitation into the $\pi\pi^*$ band by using a 450-W medium-pressure mercury lamp resulted in decolorization; products of such photoreaction were not characterized. All these reactions were much slower compared to the oxidation.

(c) Stability of Sulfines to Singlet Oxygen Oxidation. Sulfines of 7–15 prepared independently were exposed to a 500-W tungsten lamp in the presence of methylene blue. But all these were found to be stable even after 2 days of irradiation in an oxygen atmosphere.

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Registry No. 1, 958-80-5; 2, 1141-07-7; 3, 1141-08-8; 4, 1450-32-4; 5, 3705-95-1; 5 *S*-oxide, 33240-29-8; 6, 2484-99-3; 6 *S*-oxide, 78132-56-6; 7, 40920-09-0; 7 *S*-oxide, 78132-53-3; 8, 78132-52-2; 8 *S*-oxide, 78132-55-5; 9, 82234-47-7; 9 *S*-oxide, 83816-83-5; 10, 41464-62-4; 10 *S*-oxide, 78132-54-4; 11, 51849-44-6; 12, 33312-98-0; 12 *S*-oxide, 83816-84-6; 13, 875-06-9; 13 *S*-oxide, 50404-36-9; 14, 7519-74-6; 14 *S*-oxide, 50404-35-8; 15, 81049-33-4; 15 *S*-oxide, 83816-85-7; triphenyl phosphite ozonide, 21294-88-2.

Configurationally Locked Retinoids: 13-*cis*-δ-Lactones of 12-Carboxyretinol and 12-(Hydroxymethyl)retinoic Acid

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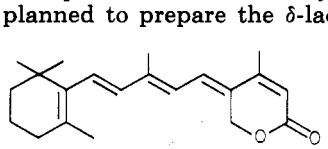
The synthesis of the δ-lactones of 13-*cis*-12-(hydroxymethyl)retinoic acid, 13-*cis*-12-carboxyretinol, 11-*cis*,13-*cis*-12-(hydroxymethyl)retinoic acid, and 11-*cis*,13-*cis*-12-carboxyretinol (1–4, respectively) from the half-esters 13-*cis*-12-carbomethoxyretinoic acid (8), methyl 13-*cis*-12-carboxyretinoate (9), 11-*cis*,13-*cis*-12-carbomethoxyretinoic acid (11), and methyl 11-*cis*,13-*cis*-12-carboxyretinoate (12) is described. The half-esters 8, 9, and 11 were prepared by methanolic saponification of 13-*cis*-12-carboxyretinoic anhydride (7); the half-ester 12 was obtained from partial methylation of 11-*cis*,13-*cis*-12-carboxyretinoic acid. The retinoids prepared were characterized primarily on the basis of their ^1H and ^{13}C NMR parameters. The relative propensity for interconversion between 13-cis and 11-cis,13-cis configurations in these systems is discussed.

As part of our interest in cyclic 13-*cis*-retinoids,[1] we had planned to prepare the δ-lactones 1–4. However, our observation that although 11-*cis*,13-*cis*-12-carboxyretinoic acid (5) was stable to isomerization, 11-*cis*,13-*cis*-12-carboxyretinoic anhydride (6) reverted to the 13-cis anhydride 7 in the dark[1] raised some doubts as to the feasibility of our goal.



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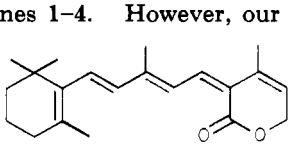

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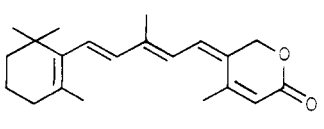
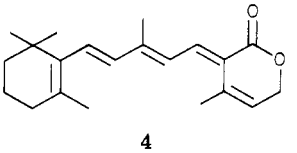


3



4

In earlier studies we had observed that treatment of 7 with methanolic base led to the production of half-esters.[1] Since selective reduction of these half-esters afforded a potential route to some of the δ-lactones 1–4, we undertook an investigation of the methanolic saponification of 7 and the reduction of the products obtained.

(1) Lewin, A. H.; Whaley, M. G.; Parker, S. R.; Carroll, F. I.; Moreland, C. G. *J. Org. Chem.* **1982**, *47*, 1799–1807.

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