The Mechanism of Benzophenone-sensitised Oxidation of 9-Phenylxanthene with Oxygen

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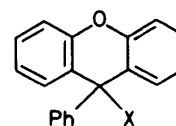
From an investigation of the effect of inhibitors, quenchers, and the failure of a singlet sensitiser to effect the oxidation, it is proposed that the benzophenone-sensitised oxidation of 9-phenylxanthene with oxygen is a type I process. Further support for this conclusion is afforded by spectroscopic considerations. Evidence is also presented that the oxidation is a non-chain process, and the effect of acid on the product distribution is discussed.

Recently[1] we reported that 9-hydroperoxy-9-phenylxanthene (**1a**) can be synthesized by irradiating an oxygen-saturated benzene solution of 9-phenylxanthene (**1b**) containing benzophenone or xanthone, through a soda-glass filter. This paper describes our studies that were directed towards determining the role of benzophenone in the photo-oxidation reaction.
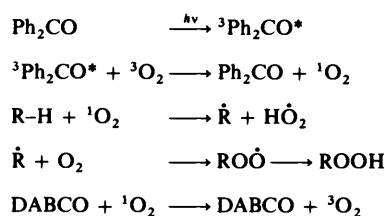
Upon excitation, benzophenone rapidly intersystem-crosses to the T_1 (n,π^*) state,[2a] which is diradical in nature, and whose reactions are similar to those of alkoxyl radicals.[3] In their studies of the photo-oxidation of propan-2-ol in the presence of benzophenone, Pitts *et al.*[4] found that the acetone yield is independent of oxygen concentration, while oxygen impedes benzopinacol formation. Hence they concluded that the 1-hydroxy-1,1-diphenylmethyl radical, formed when excited benzophenone abstracts a hydrogen atom, is reconverted into benzophenone upon reaction with oxygen with concomitant formation of hydrogen peroxide. However it has been established[5] that the triplet state of benzophenone is effectively quenched by ground-state oxygen, which is then converted into singlet oxygen.

In order to determine whether the photo-oxidation of 9-phenylxanthene (**1b**) is initiated by singlet oxygen (Scheme 1), an oxygen-saturated solution of 9-phenylxanthene which also contained Rose Bengal, a well established singlet-oxygen sensitiser,[6] was irradiated. In contrast to a control experiment in which 1,5-diphenylisobenzofuran, which is known to be susceptible to singlet-oxygen oxidation,[7] was rapidly consumed, 9-phenylxanthene was recovered unchanged. This result affords compelling evidence that the photo-oxidation of 9-phenyl-xanthene in the presence of benzophenone is not due to singlet oxygen. It was also found that 1,4-diazabicyclo[2.2.2]octane (DABCO), a well established singlet-oxygen quencher[8] retarded the benzophenone-sensitised photo-oxidation of 9-phenylxanthene. However, this result is not unambiguous since DABCO is known to interact with benzophenone to form a charge-transfer complex[9] and this could inhibit the role of benzophenone in not only singlet-oxygen generation, but in other processes as well.
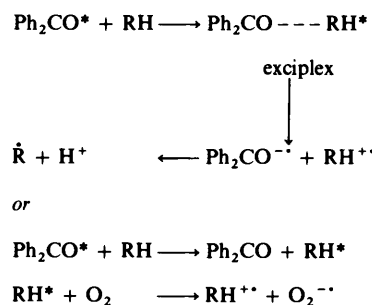
Another way in which excited benzophenone could effect the oxidation is by energy transfer to 9-phenylxanthene (Scheme 2). This energy transfer could take place *via* an exciplex in which charge transfer would lead to the substrate radical cation and hence the 9-phenylxanthenyl radical after deprotonation. Alternatively, direct energy transfer could generate excited 9-phenylxanthene which could undergo charge-transfer inter-action with oxygen leading to a superoxide ion and the 9-phenylxanthene radical cation. Exciplex formation does not occur since the emission spectrum of the mixture was recorded and displayed no new or shifted absorption bands. It was

(1)

a; X = O$_2$H
b; X = H
c; X = OH

$$Ph_2CO \xrightarrow{hv} {}^3Ph_2CO^*$$

$${}^3Ph_2CO^* + {}^3O_2 \longrightarrow Ph_2CO + {}^1O_2$$

$$R-H + {}^1O_2 \longrightarrow \dot{R} + H\dot{O}_2$$

$$\dot{R} + O_2 \longrightarrow R\dot{O} \longrightarrow ROOH$$

$$DABCO + {}^1O_2 \longrightarrow DABCO + {}^3O_2$$

Scheme 1.

$$Ph_2CO^* + RH \longrightarrow Ph_2CO --- RH^*$$

exciplex

$$\dot{R} + H^+ \longleftarrow Ph_2CO^{-\cdot} + RH^{+\cdot}$$

or

$$Ph_2CO^* + RH \longrightarrow Ph_2CO + RH^*$$

$$RH^* + O_2 \longrightarrow RH^{+\cdot} + O_2^{-\cdot}$$

Scheme 2.

established that irradiation of a mixture of benzophenone and 9-phenylxanthene in benzene in the absence of oxygen produced a complex mixture which contained benzopinacol. Hence it is concluded that excited benzophenone abstracts a hydrogen atom rather than transferring its energy to 9-phenylxanthene. Since 9-phenylxanthene absorbs light in the same region as benzophenone, the generation of superoxide ion by charge transfer from 9-phenylxanthene, which is excited either by energy transfer from excited benzophenone or by direct excitation, seems unlikely. Another factor which militates against such a process is the observation of an induction period
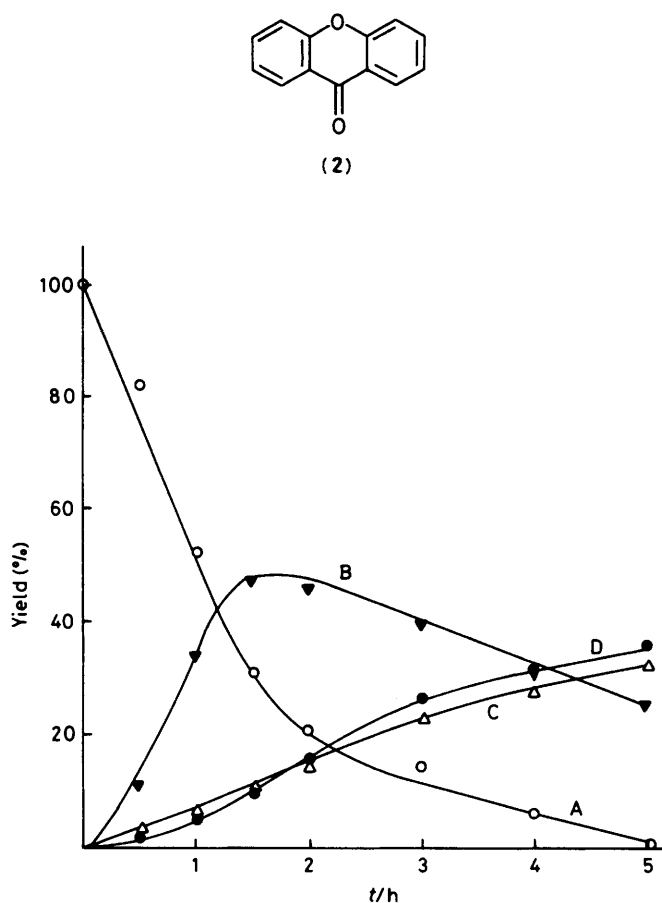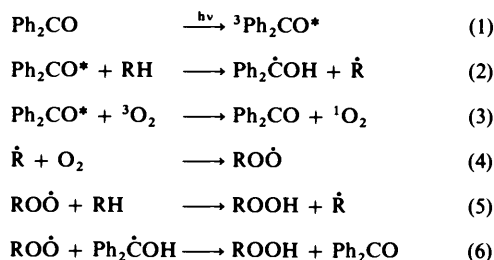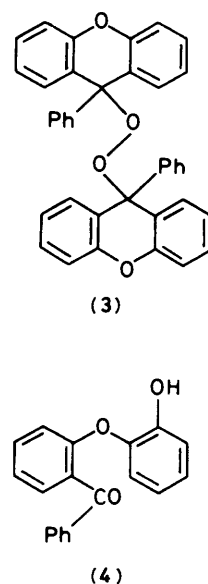
(2)

Figure 1. Effect of excess of potassium superoxide on the photo-oxidation of 9-phenylxanthene (A) and formation of 9-hydroperoxy-9-phenyl-xanthene (B), 9-hydroxy-9-phenylxanthene (C), and xanthone (D)

(3)

(4)

$$Ph_2CO \xrightarrow{hv} {}^3Ph_2CO* \qquad (1)$$

$$Ph_2CO* + RH \longrightarrow Ph_2\dot{C}OH + \dot{R} \qquad (2)$$

$$Ph_2CO* + {}^3O_2 \longrightarrow Ph_2CO + {}^1O_2 \qquad (3)$$

$$\dot{R} + O_2 \longrightarrow RO\dot{O} \qquad (4)$$

$$RO\dot{O} + RH \longrightarrow ROOH + \dot{R} \qquad (5)$$

$$RO\dot{O} + Ph_2\dot{C}OH \longrightarrow ROOH + Ph_2CO \qquad (6)$$

Scheme 3.

for the appearance of 9-hydroperoxy-9-phenylxanthene (1a) when 9-phenylxanthene (1b) is irradiated in the absence of added ketone. Generation of superoxide ion by energy transfer from excited benzophenone is unlikely since it has been established that fewer than 1% of the deactivating collisions of oxygen with the eosin triplet[10] generate superoxide ions. Nevertheless, the oxidation of 9-phenylxanthene in benzene with an excess of potassium superoxide in the presence of 18-crown-6-ether under a nitrogen atmosphere was carried out and found to generate rapidly the hydroperoxide (1a), which then decomposed to xanthone (2) and 9-hydroxy-9-phenylxanthene (1c) under the reaction conditions (Figure 1). The absence of dialkyl peroxide (3) and 2-(o-hydroxyphenoxy)benzophenone (4), which were found in the photo-oxidation reaction, lend some support to the conclusion that superoxide involvement is not the major pathway for hydroperoxide (1a) formation if it can be assumed that the basic reaction conditions are not responsible for the different product compositions. However, this experiment shows that the superoxide ion can be used to generate the hydroperoxide (1a) from 9-phenylxanthene (1b).

Hence it is concluded that benzophenone sensitises the photo-oxidation in a process where excited benzophenone abstracts a hydrogen from 9-phenylxanthene in competition with it being quenched by oxygen (Scheme 3). The photo-oxidation proceeds despite the diffusion-controlled quenching by oxygen because of its low concentration in benzene.[11] In support of this it was found that when naphthalene, which is an effective benzo-phenone triplet quencher,[12] is added to the benzophenone-

sensitised photo-oxidation of 9-phenylxanthene the reaction is retarded (Figure 2). 2,6-Di-t-butyl-4-methylphenol (DBPC), a well established anti-oxidant,[13] was only effective in retarding the reaction when the ratio of DBPC to benzophenone was 2:1 (Figure 3). A 1:1 ratio did not significantly retard the rate of disappearance of 9-phenylxanthene (1b), but did have an effect on the rate of formation of hydroperoxide (1a) (Figure 4). This experiment indicates that hydrogen abstraction from DBPC by excited benzophenone is unlikely to be the process whereby DBPC retards the oxidation, since all concentrations of DBPC would have been expected to be effective. No conclusions can be drawn from the difference in rates of hydroperoxide (1a) formation since the presence of DBPC could influence acid-catalysed decomposition processes of the hydroperoxide (1a). The retardation of photo-oxidation by DBPC is thus evidence only of radical intermediates.

The hydroperoxide (1a) could either be formed in a chain-propagation step [Scheme 3, equation (5)] or in a termination step [equation (6)]. Since lead tetra-acetate is known to be a good reagent for peroxyl radical generation from hydro-peroxides[14] its reaction with the hydroperoxide (1a) was investigated. After a short period the hydroperoxide (1a) was converted mainly into 9-hydroxy-9-phenylxanthene (1c). The reaction of 9-phenylxanthene (1b) with a catalytic amount of the hydroperoxide (1a) and lead tetra-acetate in the presence of oxygen led only to the decomposition of the hydroperoxide (1a) and no decrease in the amount of 9-phenylxanthene (1b).

Hence it is concluded that the peroxyl radical does not generate the hydroperoxide in a chain-propagating step. In support of this it was found that if the lamp was switched off during the photo-oxidation of 9-phenylxanthene, no reaction
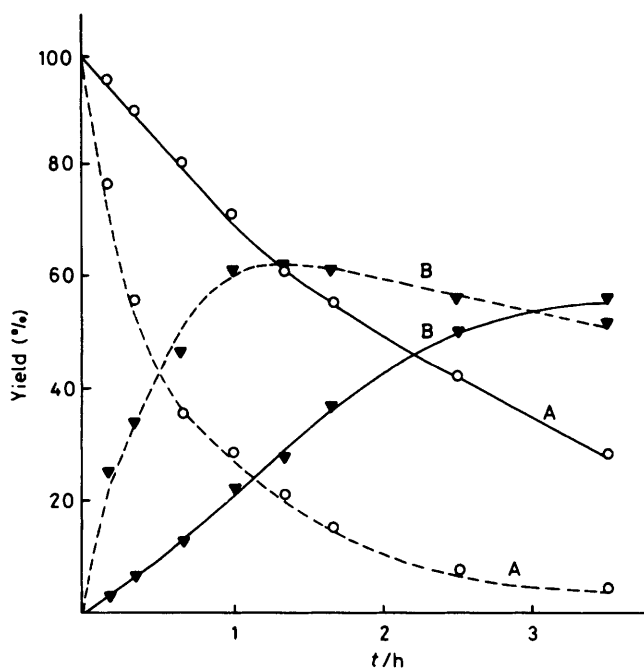
Figure 2. Effect of naphthalene on the photo-oxidation of 9-phenyl-xanthene (A) and formation of 9-hydroperoxy-9-phenylxanthene (B); —— naphthalene present and - - - naphthalene absent

Figure 4. Effect of DBPC in a 1:1 ratio to benzophenone on the photo-oxidation of 9-phenylxanthene (A) and formation of 9-hydroperoxy-9-phenylxanthene (B); —— DBPC present and - - - DBPC absent
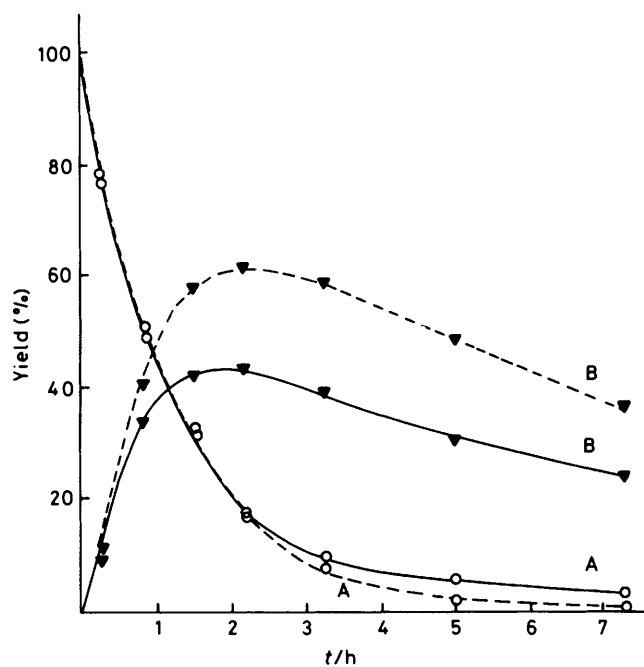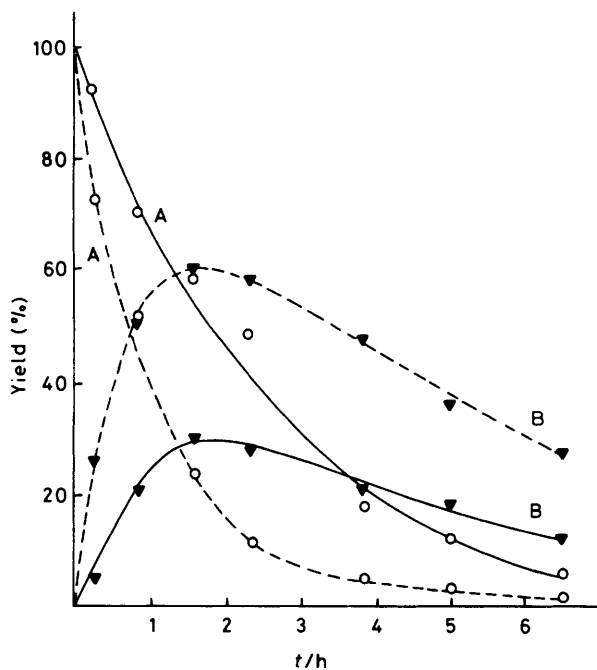

Figure 3. Effect of DBPC in a 2:1 ratio to benzophenone on the photo-oxidation of 9-phenylxanthene (A) and formation of 9-hydroperoxy-9-phenylxanthene (B); —— DBPC present and - - - DBPC absent
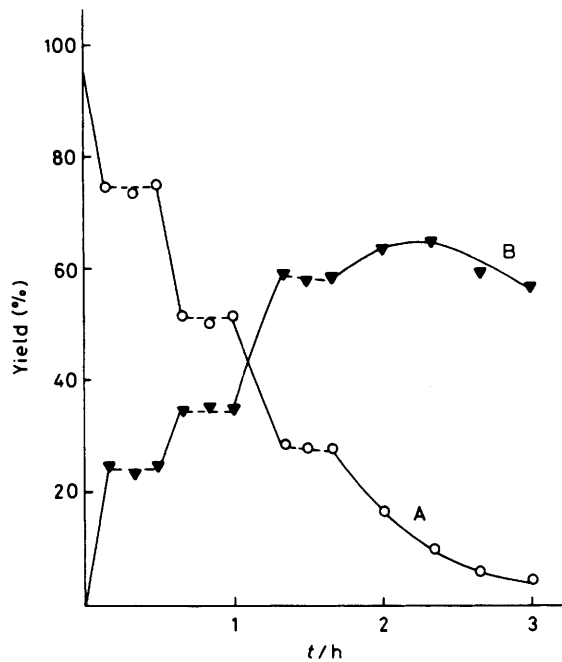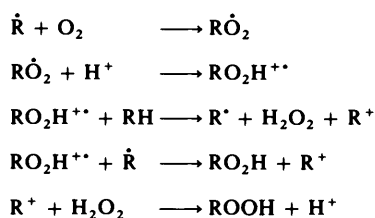

Figure 5. Effect of light on the photo-oxidation of 9-phenylxanthene (A) and formation of 9-hydroperoxy-9-phenylxanthene (B); —— light on and - - - light off

occurred in the dark (Figure 5). Furthermore, following on the experiments of Bartlett and Landis,[15] who showed that addition of carbon tetrahalides promoted chain propagation, it was found that addition of carbon tetrachloride to the photo-oxidation reaction mixture had no effect on the rate of disappearance of 9-phenylxanthene. These results thus lead to the conclusion that the hydroperoxide (1a) is formed by the 9-

phenylxanthene-9-peroxyl radical abstracting hydrogen from the 1-hydroxy-1,1-diphenylmethyl radical. This result is in accord with the results of Pitts et al.[4]

Ter Borg et al.[16] have suggested that autoxidation processes are acid catalysed (Scheme 4). In order to test the effect of acid, the benzophenone-sensitised photo-oxidation of 9-phenyl-xanthene (1b) in chloroform was carried out in the presence of

$$\dot{R} + O_2 \longrightarrow R\dot{O}_2$$

$$R\dot{O}_2 + H^+ \longrightarrow RO_2H^{+\cdot}$$

$$RO_2H^{+\cdot} + RH \longrightarrow R^{\cdot} + H_2O_2 + R^+$$

$$RO_2H^{+\cdot} + \dot{R} \longrightarrow RO_2H + R^+$$

$$R^+ + H_2O_2 \longrightarrow ROOH + H^+$$

Scheme 4.

added benzenesulphonic acid and compared with a photo-oxidation reaction carried out in the absence of added acid. Benzenesulphonic acid slightly increased the rate of disappearance of 9-phenylxanthene and led to the formation of 2-(o-hydroxyphenoxy)benzophenone (4). Treatment of the hydroperoxide (1a) with benzenesulphonic acid in the dark effected quantitative conversion into 2-(o-hydroxyphenoxy)benzophenone. These results demonstrate that acid not only weakly catalyses the photosensitised oxidation of 9-phenylxanthene, but also rapidly promotes the decomposition of the hydroperoxide (1a) to 2-(o-hydroxyphenoxy)benzophenone. The formation of 2-(o-hydroxyphenoxy)benzophenone together with the peroxide (3) in the photo-oxidation carried out in the absence of added acid is thus attributed to acid impurities in the solvent.

Experimental

Melting points were determined on a Kofler hot-stage and are uncorrected. The infrared spectra were recorded with a Perkin-Elmer infrared spectrophotometer, Model 297 and n.m.r. spectra with a 60 MHz Perkin-Elmer R12A spectrometer with Me_4Si as an internal reference.

Analytical separations were performed on a Waters Analytical h.p.l.c. (μPorasil column) using a Model 440 absorbance detector linked to a Waters data module. Solvent programs were controlled by a Waters Model 660 solvent programmer.

General Irradiation Procedure.—An oxygen-saturated solution of the compound in dry benzene was contained in a sealed Pyrex flask and placed in a Pyrex water-bath. The Philips HPLS 400 W street lamp from which the casing was removed was placed 2.5 cm below the apparatus. A soda-glass filter (2 mm) was located between the waterbath and lamp.

Irradiation of 9-Phenylxanthene in the Presence of Rose Bengal.—(*a*) 9-Phenylxanthene (0.2010 g, 0.778 mmol), 18-crown-6-ether (0.4035 g, 1.526 mmol), and Rose Bengal (0.0340 g, 0.033 mmol) were dissolved in dry benzene (40 ml) and irradiated at 25 °C except that a 1 000 W tungsten lamp was used. Analysis (h.p.l.c.) after 6.5 h indicated 9-phenylxanthene (99.2%).

(*b*) 1,3-Diphenylisobenzofuran (0.2083 g, 0.770 mmol), 18-crown-6 (0.4646 g, 1.757 mmol), and Rose Bengal (0.034 g, 0.034 mmol) were dissolved in dry benzene (40 ml) and irradiated as above. This showed that the substrate was rapidly consumed (3 and 0.2% remaining after 15 and 30 min, respectively).

Irradiation of 9-Phenylxanthene in the Presence and Absence of 1,4-*Diazabicyclo*[2.2.2]*octane* (*DABCO*).—9-Phenylxanthene (0.2982 g, 1.154 mmol) and benzophenone (0.1099 g, 0.603 mmol) were dissolved in dry benzene (60 ml). Two aliquots were removed (25 ml) and one (solution A) was treated with DABCO (0.0449 g, 0.401 mmol) and the other (solution B) served as the control.

Table 1. Irradiation of 9-phenylxanthene in the presence (solution A) and absence (solution B) of DABCO

Time (h)	Product yield (%)				
	(1b)	(3)	(2)	(1c)	(1a)
Solution A					
0.25		0.1	0.3	0.9	3.0
0.83	5.6	0.5	0.6	2.9	10.4
1.58	42.2	1.0	1.1	5.3	19.3
2.25	30.8	1.7	2.2	7.2	28.7
3.00	21.7	2.7	2.8	8.7	31.0
5.25	6.1	5.7	8.1	13.6	22.6
7.25	2.2	4.3	10.0	14.3	11.9
Solution B					
0.25	67.0	1.6	0.6	0.5	8.0
0.83	36.1	2.5	1.2	0.8	36.4
1.58	18.5	2.8	2.7	1.4	59.7
2.25	5.6	5.3	4.4	3.0	58.3
3.00	3.2	6.3	7.2	3.3	54.0
5.25	1.8	7.4	11.9	4.0	39.5
7.25	1.4	11.2	13.6	3.3	31.4

Table 2. Irradiation of 9-phenylxanthene in the presence (solution A) and absence (solution B) of benzenesulphonic acid

Time (h)	Product yield (%)					
	(1b)	(3)	(2)	(1c)	(4)	(1a)
Solution A						
0.17	51.7		0.3		6.8	
0.33	21.7		0.4		24.5	
0.67	6.8		0.4		44.8	
1.00	2.4		0.7		50.2	
1.33	1.5		0.9		52.3	
1.67	1.0		1.0		56.1	
2.50	0.4		1.1		58.5	
3.50			1.2		57.9	
Solution B						
0.17	56.1	1.8	0.8		3.9	21.2
0.33	31.6	2.9	1.6		10.9	22.7
0.67	13.6	3.3	2.7	0.6	20.5	17.9
1.00	6.4	2.7	3.6	1.0	25.3	14.2
1.33	4.2	1.9	4.2	1.0	27.9	12.3
1.67	2.9	1.6	4.7	0.8	28.6	10.4
2.50	1.8	1.6	6.1	0.7	30.6	8.7
3.50	0.8	1.4	7.2	0.5	28.1	6.9

Solutions A and B were irradiated simultaneously in the usual manner at 25 °C. The results are summarised in Table 1.

Irradiation of 9-Phenylxanthene in the Presence and Absence of 2,6-*Di-t-butyl-4-methylphenol* (*DBPC*).—(*a*) 9-Phenylxanthene (0.3023 g, 1.171 mmol) and benzophenone (0.1043 g, 0.572 mmol) were dissolved in dry benzene (60 ml). Two aliquots (25 ml) were removed and one (solution A) treated with DBPC (0.0592 g, 0.268 mmol) and the other (solution B) served as the control.

Solutions A and B were irradiated in the usual manner at 25 °C. The results are summarised in Figure 4.

(*b*) Repeating the above experiment with DBPC (0.106 g, 0.481 mmol) gave results which are summarised in Figure 3.

Irradiation of 9-Phenylxanthene in the Presence and Absence of Benzenesulphonic Acid.—9-Phenylxanthene (0.5013 g, 1.941 mmol) and benzophenone (0.1670 g, 0.916 mmol) were dissolved in chloroform (100 ml). Two aliquots (40 ml) were

Table 3. Irradiation of 9-phenylxanthene in the presence (solution 1) and absence (solution B) of carbon-tetrachloride

	Product yield (%)					
Time (h)	(1b)	(3)	(2)	(1c)	(4)	(1a)
Solution A						
0.17	73.0	1.1	0.4	0.1	0.2	16.4
0.33	45.5	2.9	1.3	0.4	0.5	30.4
0.67	23.5	6.3	3.5	0.7	0.6	40.1
1.00	14.7	9.0	5.4	1.1	0.8	43.8
1.33	9.4	11.5	7.6	2.1	1.2	40.6
1.67	6.3	13.5	9.5	2.4	1.3	37.0
2.50	2.7	15.4	13.4	2.7	1.7	27.9
3.50	1.4	16.4	17.2	2.9	2.1	20.3
Solution B						
0.17	74.5	1.1	0.4		0.2	19.3
0.33	49.4	1.5	0.9	0.4	0.3	31.7
0.67	25.7	2.1	2.1	0.5	0.5	48.8
1.00	16.1	2.9	3.9	0.9	0.6	53.4
1.33	10.8	3.7	5.1	1.3	0.8	53.2
1.67	6.4	4.5	7.0	1.5	1.0	50.1
2.50	2.7	6.5	11.0	2.3	1.9	40.2
3.50	1.4	7.7	13.6	2.5	2.2	31.8

removed and one (solution A) treated with benzenesulphonic acid (0.6167 g, 3.898 mmol) and the other (solution B) served as the control.

Solutions A and B were irradiated simultaneously in the usual manner at 25 °C. The results are summarised in Table 2.

Irradiation of 9-Phenylxanthene in the Presence and Absence of Naphthalene.—9-Phenylxanthene (0.5001 g, 1.937 mmol) and benzophenone (0.1518 g, 0.833 mmol) were dissolved in dry benzene (100 ml). Two aliquots (40 ml) were removed and one (solution A) was treated with naphthalene (0.0544 g, 0.424 mmol) and the other (solution B) served as the control.

Solutions A and B were irradiated simultaneously in the usual manner at 25 °C. The results are summarised in Figure 2.

Irradiation of 9-Phenylxanthene in the Presence of Carbon Tetrachloride.—Benzophenone (0.1554 g, 0.853 mmol) was dissolved in a dry benzene solution (100 ml) containing 5% carbon tetrachloride. An aliquot (40 ml) was treated with 9-phenylxanthene (0.2005 g, 0.776 mmol) (solution A). Benzophenone (0.1554 g, 0.853 mmol) was dissolved in dry benzene (100 ml). An aliquot (40 ml) was treated with 9-phenylxanthene (0.2008 g, 0.777 mmol) (solution B).

Solutions A and B were irradiated simultaneously in the usual manner at 25 °C. The results are summarised in Table 3.

Interrupted Irradiation of 9-Phenylxanthene.—Benzophenone (0.1571 g, 0.862 mmol) was dissolved in dry benzene (100 ml). An aliquot (40 ml) was treated with 9-phenylxanthene (0.2017 g, 0.781 mmol) and irradiated in the usual manner at 25 °C except that at intervals the lamp was switched off and the mixture allowed to stand in the dark. The results are summarised in Figure 5.

Reaction of 9-Phenylxanthene with Potassium Superoxide.—9-Phenylxanthene (0.2016 g, 0.781 mmol) and 18-crown-6-ether (0.4602 g, 1.741 mmol) were dissolved in dry benzene (50 ml). The solution was flushed with nitrogen, treated with potassium

superoxide (0.2730 g, 3.830 mmol). and aliquots removed at regular intervals from the solution, which was stirred under nitrogen. The results are summarised in Figure 1.

Dark Reaction of 9-Hydroperoxy-9-phenylxanthene with Benzenesulphonic Acid.—9-Hydroperoxy-9-phenylxanthene (0.2530 g, 0.872 mmol) and benzophenone (0.1605 g, 0.881 mmol) were dissolved in chloroform (100 ml). Benzenesulphonic acid (0.1605 g, 1.014 mmol) was added to an aliquot (40 ml) and the mixture was stirred in the dark at room temperature. Analysis after 10 min indicated only 2-(o-hydroxyphenoxy)-benzophenone (98.2%).

Reaction of Lead Tetra-acetate with 9-Hydroperoxy-9-phenyl-xanthene in the Presence of 9-Phenylxanthene.—(a) Lead tetra-acetate (0.5422 g, 1.223 mmol) was added to 9-hydroperoxy-9-phenylxanthene (0.2240 g, 0.772 mmol) and sodium carbonate (1.01 g, 9.528 mmol) in dry benzene (40 ml). The solution was stirred at room temperature for 10 min. Analysis (h.p.l.c.) showed xanthone (0.6%), bis-(9-phenylxanthen-9-yl) peroxide (3.4%), and 9-hydroxy-9-phenylxanthene (74.4%), and no 9-hydroperoxy-9-phenylxanthene.

(b) A solution of 9-phenylxanthene (0.2122 g, 0.822 mmol), sodium carbonate (1.01 g, 9.528 mmol), and 9-hydroperoxy-9-phenylxanthene (0.0114 g, 0.039 mmol) in dry benzene (40 ml) was continuously saturated with oxygen at room temperature. Lead tetra-acetate (0.0226 g, 0.051 mmol) was added after 5 min and the resulting solution stirred for 30 min. Analysis (h.p.l.c.) showed 9-phenylxanthene (97.4%), 9-hydroxy-9-phenyl-xanthene (2.0%), xanthone (0.1%), and bis-(9-phenylxanthen-9-yl) peroxide (0.3%).

References
1 S. A. Glover, A. Goosen, C. W. McCleland, B. Taljaard, and F. R. Vogel, *S. Afr. J. Chem.*, 1984, in the press.
2 N. J. Turro, 'Modern Molecular Photochemistry,' Benjamin-Cummings, 1978, (a) p. 179; (b) p. 591.
3 C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, 1965, **87**, 3361.
4 J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *J. Am. Chem. Soc.*, 1959, **81**, 1068.
5 P. B. Merkel and D. Kearns, *J. Chem. Phys.*, 1973, **58**, 398.
6 R. S. Davidson and K. R. Trethewey, *J. Am. Chem. Soc.*, 1976, **98**, 4008.
7 J. A. Howard and G. D. Mendenhall, *Can. J. Chem.*, 1975, **33**, 2199.
8 C. Quannès and T. Wilson, *J. Am. Chem. Soc.*, 1968, **90**, 6527; R. H. Young and R. L. Martin, *ibid.*, 1972, **94**, 5183.
9 A. H. Parola and S. G. Cohen, *J. Photochem.*, 1980, **12**, 41.
10 A. Kepka and L. J. Grossweiner, *Photochem. Photobiol.*, 1972, **14**, 621; V. Kasche and L. Lindquist, *ibid.*, 1965, **4**, 923.
11 R. Livingston and K. E. Owen, *J. Am. Chem. Soc.*, 1956, **78**, 3301.
12 J. C. Sheehan and R. M. Wilson, *J. Am. Chem. Soc.*, 1964, **86**, 5277; J. C. Sheehan, R. M. Wilson, and A. W. Oxford, *ibid.*, 1971, **93**, 7222.
13 G. Scott, *S. Afr. J. Chem.*, 1979, **32**, 137.
14 P. D. Bartlett and P. Günther, *J. Am. Chem. Soc.*, 1966, **88**, 3288.
15 P. D. Bartlett and M. E. Landis, *J. Am. Chem. Soc.*, 1977, **99**, 3033.
16 A. P. ter Borg, H. R. Gersmann, and A. F. Bickel, *Recl. Trav. Chim. Pays-Bas*, 1966, **85**, 899.