Thermal and Photochemical Decomposition of 9-Arylxanthen-9-yl Hydroperoxides and Peroxides

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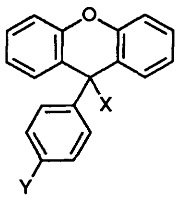
The thermolysis and photolysis of a series of 9-arylxanthenyl hydroperoxides and peroxides have been investigated by means of differential scanning calorimetry, electron paramagnetic spectroscopy and product studies. These relatively stable peroxidic compounds were found to rearrange smoothly on being heated at temperatures >120 °C and on photolysis, respectively, through concerted reaction pathways. Photolysis of 9-hydroperoxy-9-phenylxanthene and di(9-phenylxanthen-9-yl) peroxide, respectively, have been shown by EPR spectroscopy to generate 9-phenylxanthenyl radicals which dimerise at low temperatures and reform the free radicals at ambient temperature.

The thermal decomposition of hydroperoxides is generally accepted to proceed through homolytic cleavage of the peroxide O–O bond.[1] This process leads to alkoxyl and hydroxyl radicals which account for the multitude of products obtained in autoxidations[2] and is used for the initiation of radical-chain processes in polymerisation reactions.[3] The difference in product composition from acid-catalysed and thermal decompositions of hydroperoxides has been used as evidence for distinguishing between heterolytic and homolytic reaction pathways.[4]

9-Hydroperoxy-9-phenylxanthene (**1a**) is indefinitely stable at ambient temperature in the dark and could not be induced to explode either by friction or heat. The thermal stability of the hydroperoxide **1a** was investigated by heating nitrogen-saturated benzene solutions in sealed glass ampoules, for various periods at different temperatures. HPLC analysis of the reaction mixtures derived from **1a** (5% in benzene) showed that at 100 and 140 °C the half-life is 2 and 0.5 h, respectively. The major product from the reaction was 2-(*o*-hydroxyphenoxy)-benzophenone (**6a**) (Table 1) and comparable yields of xanthen-9-one (**5**) and phenol (**7a**). Since no hydroxylated derivatives of the xanthene moiety or solvents were detected, it seems unlikely that thermolysis of the hydroperoxide **1a** leads to homolysis of the peroxide O–O bond. This mode of fragmentation would have produced hydroxyl radicals, the addition of which to aromatics has been shown to be a facile process.[5] This rearrangement of **1a** probably occurs *via* a concerted process. However, if O–O bond cleavage occurs, it must be followed by rapid rearrangement of the radicals formed in the solvent cage to form **6a** as well as xanthone **5** and phenol.

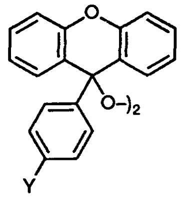
Our results are in accord with the observations and mechanistic proposals of Neckers *et al.*[6] for similar thermolytic and photolytic dismutations of di(triarylmethyl) peroxides for which they propose a concerted rearrangement with O–O bond homolysis or a short-life-time alkoxyl intermediate.



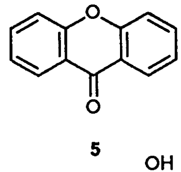
1a : X = OOH, Y = H
b : X = OOH, Y = CH_3
c : X = OOH, Y = OCH_3
d : X = OOH, Y = Cl
e : X = OOH, Y = CF_3

2a : X = OH, Y = H
b : X = OH, Y = CH_3
c : X = OH, Y = OCH_3
d : X = OH, Y = Cl
e : X = OH, Y = CF_3

3a : X = H, Y = H



4a : Y = H
b : Y = CH_3
c : Y = OCH_3
d : Y = Cl
e : Y = CF_3



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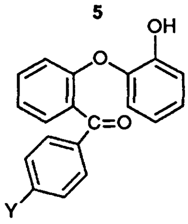
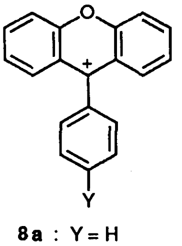
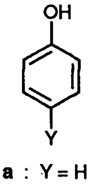


6a : Y = H
b : Y = CH_3
c : Y = OCH_3
d : Y = Cl



8a : Y = H
b : Y = CH_3
c : Y = OCH_3
d : Y = Cl
e : Y = CF_3



7a : Y = H
b : Y = CH_3
c : Y = OCH_3
d : Y = Cl

Thermal treatment of 1% benzene solutions of **1a** (Table 2) showed no decomposition of **1a** at 80 °C, whereas at 100 °C a significant amount of decomposition occurred after 2 h and the major product was the dialkyl peroxide **4a**. Schönberg and Mustafa[7–9] have shown di(9-arylxanthen-9-yl) peroxides to decompose smoothly at elevated temperatures affording xanthone as the only isolable product. The difference in product composition in the 5 and 1% solutions of hydroperoxide **1a** is suggested to be due to acid-catalysed heterolytic processes in the more concentrated solution competing with the suggested homolytic pathway. Protonation of the hydroperoxide **1a** by another molecule of **1a** effects intramolecular rearrangement either to the benzophenone **6a** or to xanthone and phenol. This process which occurs to a lesser degree in dilute solution is reminiscent of the dismutation of **1a** in acetic acid.[10] Homolytic cleavage of the O–O bond of the hydroperoxide **1a** would have

Table 1 Thermal degradation of 9-hydroperoxy-9-phenylxanthene (**1a**) in benzene solution (5%) under various conditions

		Reaction components (%)[a,b]						
T/°C	*t*/h	**1a**	**2a**	**3a**	**4a**[c]	**5**	**6a**	**7a**
140	0.5	1	7	1	2	18	62	13
	1.0	0	6	1	1	21	66	15
	2.0	0	4	1	1	22	59	25
	3.0	0	2	1	1	20	58	9
120	0.5	20	1	1	6	8	48	7
	1.0	1	3	1	5	10	66	8
	2.0	2	4	1	3	8	53	2
	3.0	0	4	1	3	12	70	11
110	0.5	79	1	1	4	3	1	2
	1.0	37	1	1	5	3	31	1
	2.0	7	2	1	4	5	62	0
	3.0	3	4	1	5	6	61	7
100	0.5	98	1	1	2	1	1	1
	1.0	83	1	1	3	1	1	1
	2.0	50	1	1	5	2	14	1
	3.0	29	<1	1	4	6	42	1

[a] Determined by HPLC (μ-Porasil). [b] Based on 9-hydroperoxy-9-phenylxanthene (**1a**). [c] Yields based of 2 mol **1a** reacting to form 1 mol **4a**.

Table 2 Thermal decomposition of 9-hydroperoxy-9-phenylxanthene (**1a**) in benzene under various conditions (1% solutions)

		Reaction components (%)[a,b]						
T/°C	*t*/h	**1a**	**2a**	**3a**	**4a**[c]	**5**	**6a**	**7a**
80	0.25	99	0	<1	0	<1	0	0
	0.50	99	0	<1	<1	<1	0	0
	1.0	99	0	<1	2	<1	0	0
	2.0	99	0	<1	<1	<1	0	0
	3.0	99	0	<1	<1	<1	0	0
100	0.25	98	1	<1	2	<1	<1	0
	0.50	97	<1	<1	2	<1	0	0
	1.0	96	0	<1	3	<1	0	0
	2.0	54	0	<1	35	5	2	0
	3.0	62	0	<1	28	1	1	0

[a] Determined by HPLC (μ-Porasil). [b] Based on 9-hydroperoxy-9-phenylxanthene (**1a**). [c] Yields based on 2 mol **1a** reacting to form 1 mol **4a**.

been expected to produce relatively high yields of the alcohol **2a**, hydroxylated aromatics, biphenyl or bibenzyl in benzene and toluene, respectively. Since the yields of **2a** in the 5% solution in benzene were negligible and radical coupling products could not be detected, the formation of the dialkyl peroxide **4a** by coupling of two alkoxyl radicals is unlikely. Hence it is proposed that the dialkyl peroxide **4a** in the dilute solution is formed by coupling of the xanthylium cation **8a**, generated by heterolysis of the C_9–OOH bond, and the hydroperoxide **1a**.

9-Aryl-9-hydroperoxyxanthenes (**1a–e**) and the di(9-arylxanthen-9-yl) peroxides (**4a–e**) all have sharp melting points, but since large discrepancies in the melting points of some of these compounds have been reported,[7–9] this property as a criterion for purity or identification should be applied with caution. It was found that the hydroperoxides (**1a**, **b**, **d**, **e**) melted with decomposition and resolidification and remelted at temperatures corresponding to the melting points of the dialkyl peroxides (**4a**, **b**, **d**, **e**). Differential scanning calorimetry (DSC) of the hydroperoxides (**1a**, **b**, **d**, **e**) first showed an endothermic decomposition which corresponded closely to the melting point of the hydroperoxide (Fig. 1). At higher temperatures an exothermic change corresponded with the melting point of the dialkyl peroxide (Fig. 2). In contrast with the hydroperoxides (**1a**, **b**, **d**, **e**), 9-hydroperoxy-9-(*p*-methoxyphenyl)xanthene (**1c**) decomposed when allowed to stand in the dark at ambient temperature, to form the dialkyl peroxide **4c**. This behaviour of the electron-rich 9-(*p*-methoxyphenyl) substituent further supports the proposal that in the xanthenyl hydroperoxides

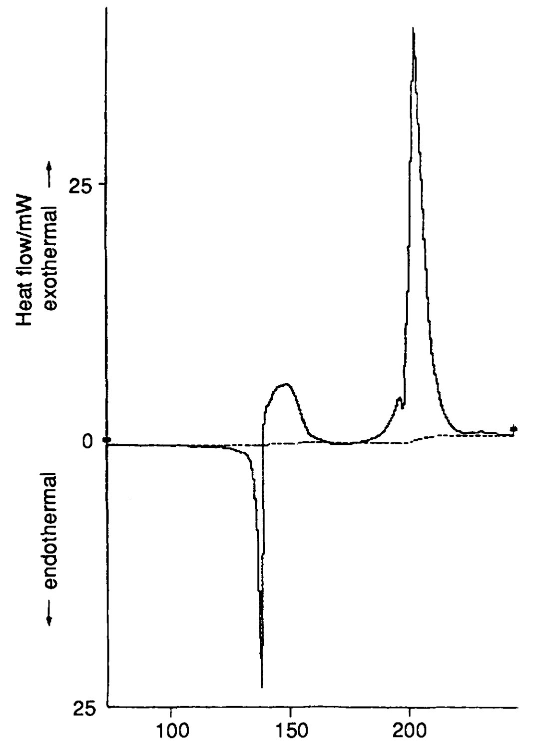


Fig. 1 DSC Thermogram of the decomposition of 9-hydroperoxy-9-(*p*-trifluoromethylphenyl)xanthene (**1e**) in the solid state

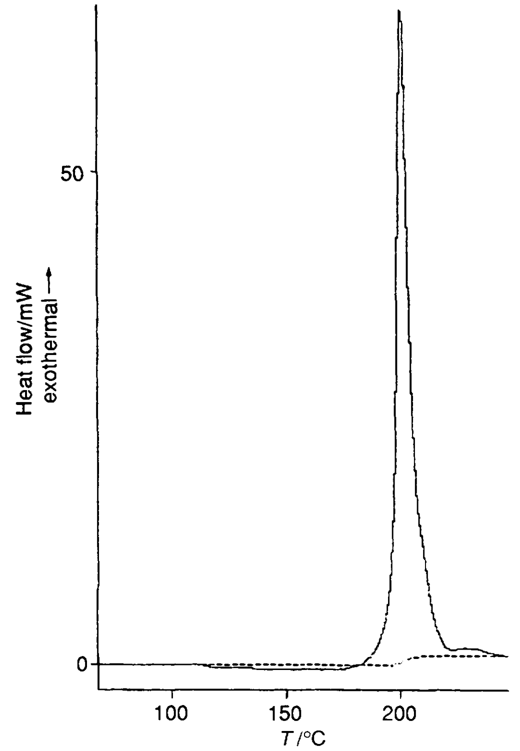
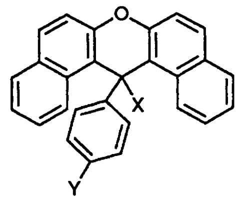
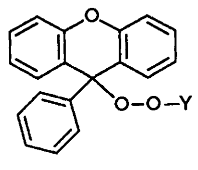


Fig. 2 DSC Trace of the thermal dismutation of di(9-*p*-trifluoromethylphenyl)xanthen-9-yl peroxide (**4e**) in the solid state

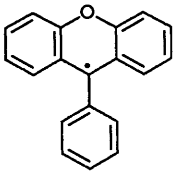


9a : X = OOH, Y = H
b : X = OOH, Y = OCH_3

10a : X = OH, Y = H
b : X = OH, Y = OCH_3



12a : Y = Bu^t
b : Y = Ph_3C



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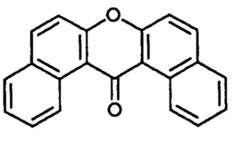

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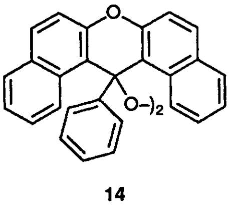

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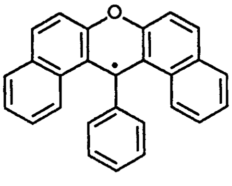

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(**1a**, **b**, **d**, **e**), thermal heterolysis of the C–O bond of the hydroperoxide which generates the stabilised carbenium ions (**8a–e**) requires less energy than peroxide O–O bond cleavage.

The relatively high thermal stability of the 14-aryl-14-hydroperoxydibenzo[*a,j*]xanthenes (**9a**, **b**) is manifested in the single exothermic decomposition peaks observed in the DSC thermograms at the relatively high melting points of these hydroperoxides.

The unsymmetrical peroxides, 9-(*tert*-butylperoxy)-9-phenylxanthene (**12a**) and 9-(triphenylmethylperoxy)-9-phenylxanthene (**12b**) were shown to be less stable than the dialkyl peroxides (**4a–e**), decomposing exothermally at temperatures above their melting points.

Benzophenone-sensitised,[10] as well as unsensitised[11] autoxidation studies have shown that 9-phenylxanthene (**3a**) produces the hydroperoxide **1a**, which on prolonged irradiation is converted into the dialkyl peroxide **4a**, xanthone (**5**), 9-phenylxanthen-9-ol (**2a**), the benzophenone **6a** and phenol (**7a**), respectively. Irradiation of **1a** with a 1000 W tungsten lamp through a Pyrex glass filter for an extended period at ambient temperature, resulted in an almost quantitative recovery of **1a**. In contrast, solar irradiation of a nitrogen-saturated benzene solution of **1a** through Pyrex glass for 20 h at ambient temperature gave, in addition to starting material, **1a** (7%), the dialkyl peroxide **4a** (70%), the benzophenone **6a** (2%), xanthone (**5**) (7%), the alcohol **2a** (2%) and phenol (12%) as degradation products. A similar result was obtained when **1a** was irradiated with UV light through quartz at ambient temperature for 20 h. Isolation of these reaction products by column chromatography yielded **4a** (60%), xanthone (15%), as well as the benzophenone **6a** (6%). These results are in accord with our previous results on the photo-oxidation of 9-phenylxanthene (**3a**), where it was established that the wavelength of the light sources used affected the yield of hydroperoxide (**1a**) formation, as well as its decomposition.[12] The relatively high yields of xanthone (**5**) with respect to 2-(*o*-hydroxyphenoxy)benzophenone (**6a**) in this case, as compared with the thermal and acid-catalysed rearrangements[13–15] of **1a** suggests a different mode of fragmentation in the photolysis reaction. The relatively high yield of phenol obtained (42% after 21 h) would suggest homolytic fission of the O–O linkage yielding alkoxyl and hydrolyl radicals. Hydroxylation of the solvent by the latter would have enhanced the yield of phenol obtained from **1a** in a concerted process. Similar photolysis of **1a** in chlorobenzene, however, gave no chlorophenols, whereas photolysis of the hydroperoxides **1b** and **1d** in benzene gave the corresponding dialkyl peroxides, **4b** and **4d** as well as xanthone as major products in both cases (Table 3). As only the corresponding *p*-substituted phenols could be detected in the latter reaction mixtures and no evidence for hydroxylation of the solvent (benzene) could be obtained, an intramolecular rearrangement mechanism is inferred. The relatively high yield of phenol obtained on UV irradiation of 14-hydroperoxy-14-phenyldibenzo[*a,j*]xanthene (**9a**) in benzene may be explained in terms of homolytic cleavage of the O–O bond and subsequent hydroxylation of the solvent. The alkoxyl radicals formed could abstract hydrogen atoms from **9a** or solvent to generate 14-phenyldibenzo[*a,j*]xanthen-14-ol (**10a**) and phenyl radicals, respectively. However, no biphenyl could be detected in these mixtures and intractable polymers were formed. Dimerisation of the corresponding alkoxyl radicals to generate the dialkyl peroxide **14** is inhibited by steric hindrance. Attempts to synthesise the peroxide **14** by an alternative route, were also unsuccessful.[16] Increased steric hindrance due to the additional fused benzene rings of 14-phenyldibenzo[*a,j*]xanthene in the transition state for hydrogen abstraction may explain why radical **15** was not observed upon UV irradiation of 14-phenyldibenzo[*a,j*]xanthene in the presence of di-*tert*-butyl peroxide in the cavity of an EPR spectrometer, and would also account for the slow rate of photosensitised oxidation of this hydrocarbon.[17] In contrast with 9-hydroperoxy-9-phenylxanthene (**1a**) and its analogues, 14-hydroperoxy-14-(*p*-methoxyphenyl)dibenzo[*a,j*]xanthene (**9b**) and hydroperoxide (**9a**) gave molecular ion peaks in their mass spectra. In addition **9a** and **9b** did not rearrange in acid media,[13] further demonstrating the higher relative stability of these dibenzoxanthenyl hydroperoxides.

The yields of UV degradation products obtained from the dialkyl peroxides **4b** and **4d** are contained in Table 4. The absence of biphenyl or other radical coupling products in these experiments support the results previously obtained for thermolysis and photolysis of di(9-phenylxanthen-9-yl) peroxide (**4a**).[9,10] UV irradiation of the dialkyl peroxide **4a** in solution afforded an EPR spectrum of the 9-phenylxanthyl radical **11** (Fig. 3). The spectrum correlated reasonably well with a computer-simulated spectrum of this radical, using the hyperfine splittings reported by Hori *et al.*[18] (Fig. 4). Identical EPR spectra were obtained on irradiation of the hydroperoxide **1a**, or of 9-phenylxanthene (**3a**) in the presence of di-*tert*-butyl peroxide.

Radical **11** was found to be highly persistent and was still observable 6 h after the UV source had been removed. Furthermore, the presence of dissolved dioxygen did not significantly affect the spectra. The intensity of the spectrum of **11** obtained from **4a** was found to decrease with a lowering in

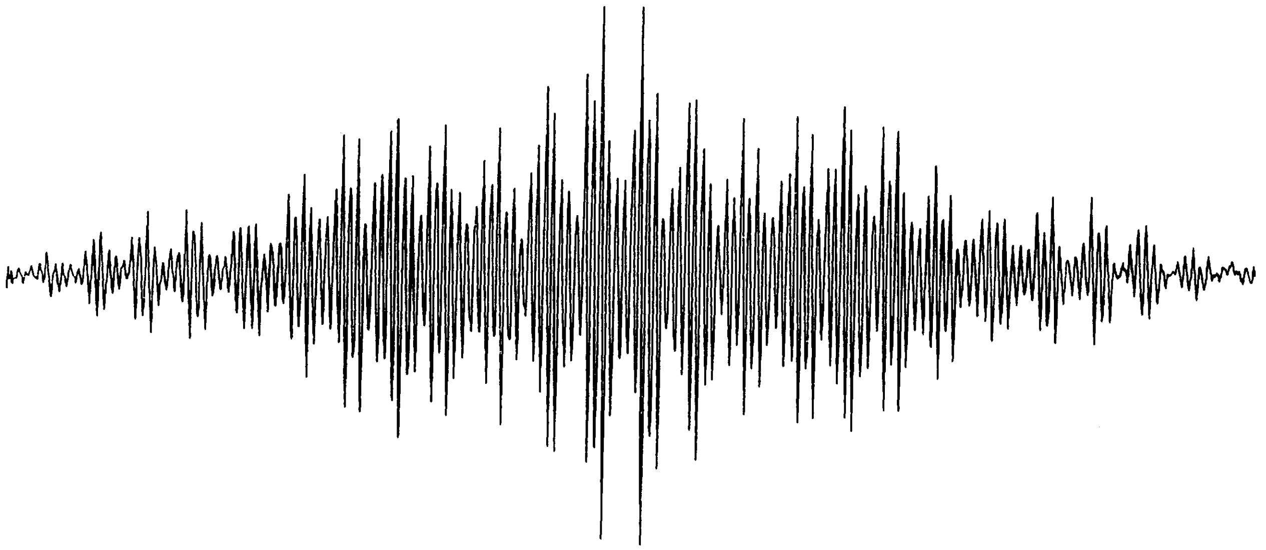

Fig. 3 EPR Spectrum of radical **11** at −60 °C on UV irradiation of dialkyl peroxide **4a**

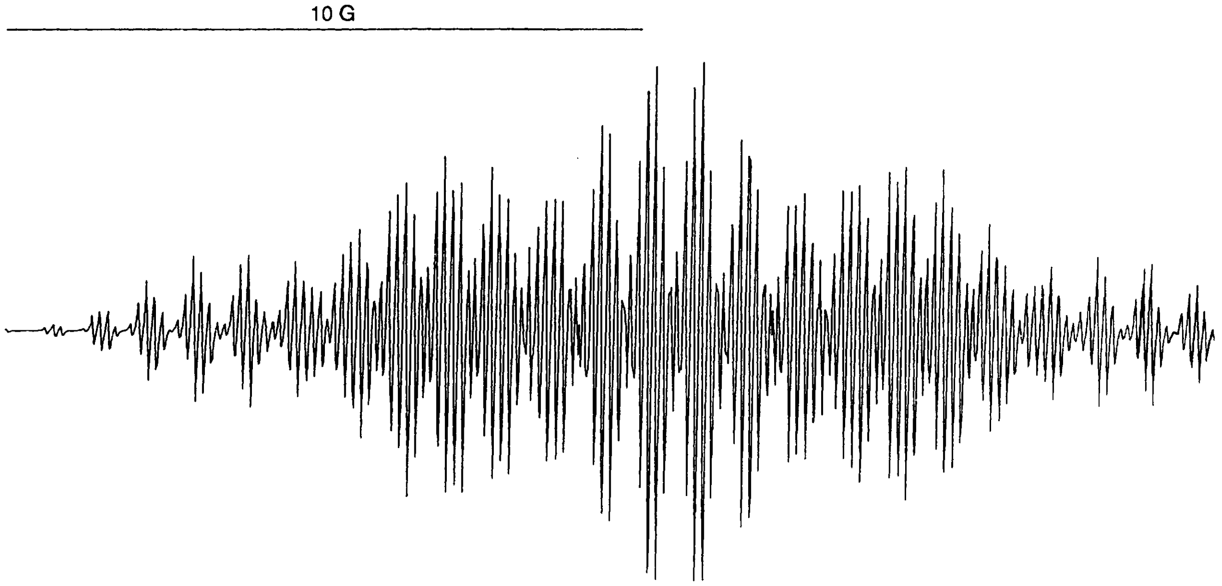

Fig. 4 Computer-simulated EPR spectrum of radical **11**

Table 3 Photodecomposition (UV) of 9-aryl-hydroperoxyxanthenes (**1**)

Substrate	[1]/mmol dm^{-3}	t/h	Reaction components (%)[a,b] 1	2	3	4	5	6	7
1b	0.69	22	0	6	55	0	27	2	29
1d	0.62	17.5	0	8	54	0	22	2	14

[a] Yields based on substrate **1**. [b] Yields determined by HPLC.

Table 4 Photochemical decomposition of di(9-arylxanthen-9-yl) peroxides

Peroxide	t/h	Reaction components (%)[a,b] 4	5
4b	48	8	53
4d	5	63	35

[a] Based on substrate **4**. [b] Traces (< 1%) of other rearrangement products detected.

temperature and then to increase again as the temperature was raised. This phenomenon may be explained in terms of C–O bond fission in the peroxide **4a**, followed by dimerisation of the 9-phenylxanthenyl radicals. Owing to the inherent steric strain, the dimer readily decomposes, thermally reforming radicals. This photolytic generation of the 9-phenylxanthenyl radical **11** from the dialkyl peroxide **4a** is unusual in that fission of the C–O bond is favoured over the O–O bond, which is most probably due to the relatively high stability of the alkyl radical **11** compared with the corresponding 9-alkoxyl radical.

In order to establish whether singlet oxygen is generated on decomposition of the peroxide **4a**, it was photolysed in a benzene solution containing 1,3-diphenylisobenzofuran, an established $^1O_2$ trap.[19] Only 6.8% *o*-benzoylbenzophenone could be detected after 24 h, whereas a control experiment conducted in the absence of the peroxide **4a**, gave *o*-benzoylbenzophenone in 1.5% yield. This apparently low yield of $^1O_2$ can be reconciled with the EPR observations if it is assumed that C–O fragmentation is a minor fragmentation pathway, competing with O–O bond cleavage. As the 9-phenylxanthen-9-oxyl radical cannot be detected in EPR experiments, the latter fragmentation mode cannot be entirely discounted in the photolytic reactions.

Experimental

Infrared spectra were recorded on a Perkin-Elmer spectrometer, Model 297. 60 MHz ^1H NMR spectra were obtained on a Perkin-Elmer R12A spectrometer with Me_4Si as an internal reference. High performance liquid chromatography (HPLC) was performed on a Waters Analytical instrument (μ-Porasil columns) using a Model 440 detector (254 nm) linked to a Waters data module and hexane–CH_2Cl_2–dioxane mixtures as mobile phases.

DSC thermograms were recorded on a Mettler DSC 20 standard cell, equipped with a TC 10 TA data processor in the temperature range 80–240 °C programmed at a rate of 10 °C min^{-1}.

Authentic standard compounds were synthesised as previously reported.[10,13,14,17] The previously unreported dialkyl peroxides **12a** and **12b** were also synthesised according to these procedures.

9-tert-Butylperoxy-9-phenylxanthene (**12a**). Crystallised from ethanol in 63% yield, m.p. 112–113 °C; $\nu_{max}(CDCl_3)/cm^{-1}$ 1615, 1585, 1484, 1455 and 1305; $\delta(CDCl_3)$ 0.88 (9 H, s) and 6.80–7.55 (13 H, m); *m*/*z* 273 (M – Bu^{t}O), 257 (9-phenylxanthylium cation, 100%), 77, 32 and 28 (Found: C, 79.9; H, 6.5. $C_{23}H_{22}O_3$ requires: C, 79.8; H, 6.4%).

9-Phenyl-9-(triphenylmethylperoxy)xanthene (**12b**). Crystallised in 90% yield from benzene–light petroleum (b.p. 40–60 °C), m.p. 188–189 °C; *m*/*z* 273 (M – PhCO), 257 (100%), 243 (Ph_3C^+), 77 and 32 (Found: C, 85.5; H, 5.4. $C_{38}H_{28}O_3$ requires C, 85.7; H, 5.3%).

Thermal Decomposition of 9-*Hydroperoxy*-9-*phenylxanthene* (**1a**).—(*a*) 9-Hydroperoxy-9-phenylxanthene (**1a**) (5.024 g, 0.1731 mol) was dissolved in anhydrous benzene contained in a 100 cm^3 volumetric flask and the volume adjusted to the mark. Aliquots (5.0 cm^3) were withdrawn and sealed in glass ampoules under nitrogen and placed in a constant-temperature oil bath at the appropriate temperature. Samples were withdrawn at regular intervals and the cooled solutions analysed by HPLC (Table 1).

(*b*) As in the above procedure, 1% benzene solutions of **1a** were decomposed and analysed (Table 2).

(*c*) 9-Hydroperoxy-9-phenylxanthene (**1a**) (330 mg, 1.14 mmol) in toluene (50 cm^3) was heated under reflux for 2 days and the cooled solution analysed (HPLC). In addition to starting material **1a** (2%), the mixture contained the dialkyl peroxide **3a** (4%), xanthone (61%), phenol (61%), the keto phenol **6a** (26%), as well as alcohol **2a** (4%). No bibenzyl or biphenyl was observed.

Photostability of 9-*Hydroperoxy*-9-*phenylxanthene* (**1a**).—(*a*) The hydroperoxide **1a** (500 mg, 1.72 mmol) in anhydrous benzene (10 cm^3) was irradiated through Pyrex glass with a 1000 W tungsten lamp at ambient temperature for 64 h. The solvent was distilled off under reduced pressure and the residue chromatographed (column chromatography on Al_2O_3–C_6H_6) to give starting material (98%).

(*b*) The hydroperoxide **1a** (500 mg, 1.72 mmol) in benzene (10 cm^3) was irradiated through quartz with a 125 W UV Hanovia medium-pressure lamp at ambient temperature for 20 h, during which time the dialkyl peroxide **4a** precipitated. The filtered solution was chromatographed (Al_2O_3/C_6H_6) as above to give the peroxide **4a** (140 mg); total yield of **4a**, 280 mg (60%). Elution of the column with chloroform gave xanthone (50 mg, 15%) and 2-(2-hydroxyphenoxy)benzophenone (30 mg, 6%).

(*c*) The above experiment was repeated with **1a** (500 mg, 1.72 mmol) in benzene (under N_2) at ambient temperature for 21 h. Analysis (HPLC) showed xanthone (25%) and phenol (42%).

(*d*) The hydroperoxide **1a** (500 mg, 1.72 mmol) in benzene (10 cm^3) contained in a Pyrex flask, the solution saturated with nitrogen and exposed to direct sunlight for 20 h (5 h per day). Analysis (HPLC) indicated the dialkyl peroxide **4a** (70%), starting material (**1a**, 7%), xanthone (7%), phenol (12%), the alcohol **2a** (2%), as well as the keto phenol **6a** (2%).

(*e*) Treatment of **1a** (1 g) in chlorobenzene (10 cm^3) as described in (*b*) above, and analysis (HPLC) showed only decomposition products of **1a** and no chlorophenols.

Photodegradation of Di(9-*phenylxanthen*-9-*yl*) *Peroxide* (**4a**).—(*a*) The dialkyl peroxide **4a** (500 mg, 0.92 mmol) in benzene (85 cm^3) was irradiated under nitrogen through quartz at ambient temperature with a 125 W UV lamp for 20 h. Analysis (HPLC) indicated starting material (**4a**, 30%) and xanthone (38%).

(*b*) Degradation as above using a Pyrex filter under solar irradiation for 20 h, gave starting material (**4a**, 44%) and xanthone (26%).

Photochemical Degradation of 9-*Aryl*-9-*hydroperoxyxanthenes*.—The hydroperoxide **1b** or **1d** (0.6 mmol) in benzene (10 cm^3) was irradiated with UV light (450 W) at 20 °C through Pyrex glass. HPLC analysis gave the results in Table 3.

Photochemical Degradation of Di(9-*arylxanthen*-9-*yl*) *Peroxides*.—The peroxide **4** in benzene (10 cm^3) was irradiated with UV light (450 W Hg lamp) at ambient temperature through Pyrex glass. Analysis (HPLC) gave the results depicted in Table 4.

Photochemical Stability of 14-*Hydroperoxy*-14-*phenyldibenzo*[a,j]*xanthene* (**9a**).—14-Hydroperoxy-14-phenyldibenzo-[*a*,*j*]xanthene (**9a**) (0.38 mmol) in benzene (10 cm^3) was irradiated with a 450 W UV lamp for 18 h. Analysis (HPLC) indicated starting material (**9a**, 1%), 14-phenyldibenzo-[*a*,*j*]xanthen-14-ol (**10a**) (29%), dibenzoxanthone (**13**) (23%) and phenol (**7a**) (44%).

EPR Studies.—EPR spectra were recorded with a Varian E-109c spectrometer equipped with 100 kHz modulation and an A-band klystron. Spectrum analysis was verified by simulation using a computer program kindly supplied by Dr. M. F. Chiu. Solutions of the appropriate substrate, *i.e.* **1a**, **4a** or **3a**/di-*tert*-butyl peroxide in hexane–dichloromethane were irradiated in the EPR cavity with an Oriel photolysis system equipped with a 1000 W high-pressure mercury–xenon lamp, over the temperature range –60 to 25 °C.

Flushing the solutions with nitrogen prior to irradiation was found to have a minimal effect on the EPR signal.

Attempted trapping of singlet oxygen possibly generated on UV irradiation of the peroxide (**4a**) indicated *o*-benzoylbenzophenone (6.8%). A similar reaction in the absence of **4a** gave *o*-benzoylbenzophenone (1.5%).

1,3-Diphenylisobenzofuran (250 mg, 0.925 mmol) in anhydrous benzene (80 cm^3), containing di(9-phenylxanthen-9-yl) peroxide (**4a**) (500 mg, 0.92 mmol), was irradiated at 25 °C with a 450 W Hanovia UV lamp for 24 h. HPLC quantification [μ-Porasil; n-hexane–CH_2Cl_2–dioxane (1200:50:40); 1.5 cm^3 min^{-1}] indicated *o*-benzoylbenzophenone (6.8%).

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