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Photooxygenation of α,α'-Dimethylstilbenes Sensitised by Photochromic Compounds

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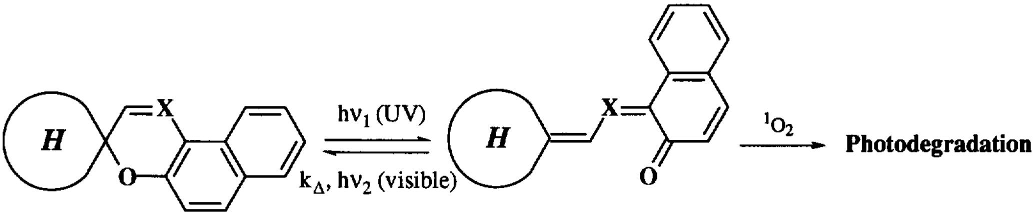
Abstract *: A convincing evidence of the ability of the coloured open forms or photomerocyanines of photochromic compounds to act as sensitiser of singlet oxygen is provided by photosensitised oxidation of reference olefins, cis- and trans-α,α'-dimethylstilbenes, to a hydroperoxide.* Copyright © 1996 Published by Elsevier Science Ltd

INTRODUCTION

The chemistry of spiro compounds has recently become particularly important in connection with the rapid development of optical materials.[1] However, the resistance of these photochromic compounds to photochemically induced degradation had to be improved.[1-3] Currently a great deal of interest is being shown in the development of mechanistic investigations on the photodegradation processes particularly of the species represented in scheme 1.[4-8]

In previous studies, we have identified the main photoproducts[4] generated under continuous irradiation of some photochromic compounds in acetonitrile solution (Figure 1) and proposed possible mechanisms for the oxidation reactions, one of these involving singlet oxygen.[9,10] Here we report experimental evidence for this pathway.



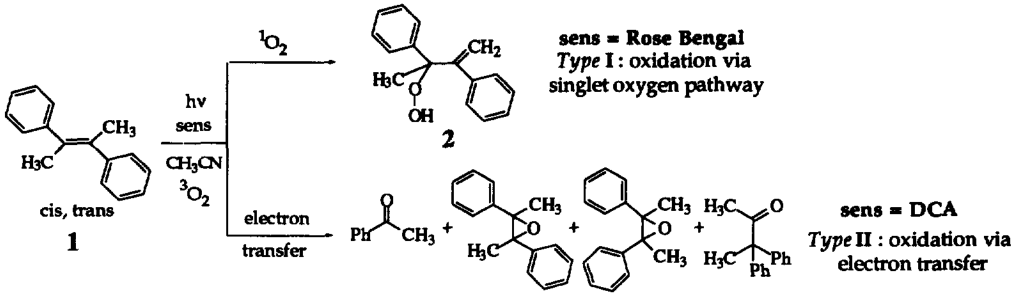
CF
Colourless Closed Form

PM
Coloured Open Form or
Photomerocyanine

X = CH Spiropyrans (I) or [2H]-Chromenes (III)
X= N Spirooxazines (II)
H = heterocycle or aromatic groups

Scheme 1 : Photochromic equilibrium between the closed and open forms.

The key to our approach is the photosensitised oxidation of a mixture of cis- and trans-α,α'-dimethylstilbenes[11,12] **1** by a photochromic compound. Recently, it was reported that the irradiation of these olefins in acetonitrile in the presence of both oxygen and a suitable sensitiser as Rose Bengal[13,14] gave only compound **2** when the sensitiser can produce specifically singlet oxygen via a *Type I* reaction, while, if the sensitiser can give a *Type II* process, a completely different product mixture was obtained (scheme 2).



Scheme 2 : Photooxidation of a mixture of cis- and trans-α,α'-dimethylstilbenes **1** in 2-hydroperoxy-2,3-diphenylbut-3-ene **2** sensitised by Rose Bengal (type I) or by 9,10-Dicyanoanthracene DCA (Type II).

EXPERIMENTAL

A thermostated (+13.0 ± 0.1°C) and aerated acetonitrile solution (5mL) containing a mixture of cis- and trans-α,α'-dimethylstilbenes **1** (5×10^{-4}M) and Rose Bengal or a photochromic compound (1.5×10^{-4}M) was irradiated by using a 250W xenon arc lamp (XBO Osram) with a filter WG360 Schott cutting off at 345nm. The reaction mixtures were analysed regularly by high performance liquid chromatography (figure 1).

According to the ^{13}C-NMR spectra of the original product mixtures, the ene-product **2** is the sole observable product by photooxygenation of **1** exclusively *via* the singlet oxygen pathway (^{13}C-NMR (62.5MHz, $CDCl_3$) : δ (in ppm from TMS) : 25.02 (q, C_1) ; 88.52 (s, C_2) ; 117.72 (t, C_4) ; 142.20 (s, C_3)). Reduction of **2** by $LiAlH_4$ yields the corresponding alcohol : ^{13}C-NMR (62.5MHz, $CDCl_3$) : δ (in ppm from TMS) : 29.53 (q, C_1) ; 75.84 (s, C_2) ; 113.19 (t, C_4) ; 141.36 (s, C_3)). Diazabicyclo[2.2.2]octane, a known quencher of singlet oxygen, was found to inhibit the formation of **2**.

These experiments were realised with three representative photochromic compounds, 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,2'-[3H]-naphth[2,1-b]pyran] **I**[15,16], 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]-naphth[2,1-b][1,4]oxazine] **II**[15, 17] and 3,3-diphenyl-[3H]-naphth[2,1-b] pyran **III**.[18]

The HPLC separations were carried out with a Beckman Gold system equipped with a 168 UV-visible diode array detector (scan range 200-450nm, 1Hz). The column consisted of a reversed phase ultrasphere C18 25cm*4,6mm 5μm. The separations were performed with a mobile phase : CH_3CN/H_2O 30/70 for 10min, then 100% of CH_3CN within 30min. The flow rate was fixed at $1mL.min^{-1}$.

DISCUSSION

In polar and non-polar solvents, energy transfer from triplet excited sensitisers such as anthracenes, xanthene dyes (e. g. rose bengal, erythrosin), chlorophyll, tetraphenylporphin, to molecular oxygen ($^3O_2$) yields singlet oxygen ($^1O_2$, in its $^1\Delta_g$ state).[19,20] In agreement with the photocoloration process of unsubstituted indolinospiropyrans and indolinospirooxazines which proceeds mainly via the singlet channel[21], we propose that $^1O_2$ is produced through the reaction between the photomerocyanine in its triplet state and ground state oxygen according to the following scheme (in acetonitrile).

$$CF \xrightarrow{h\nu} {}^1CF^* \quad \text{Excitation}$$
$${}^1CF^* \longrightarrow {}^1PM^* \quad \text{Photocoloration (singlet pathway)}$$
$${}^1PM^* \longrightarrow {}^3PM^* \quad \text{Intersystem Crossing}$$
$${}^3PM^* + {}^3O_2 \longrightarrow {}^1PM + {}^1O_2{}^* \quad \text{Photosensitisation}$$

Scheme 3 : Singlet oxygen production by $^3PM^*$ / $^3O_2$ interactions.

So this property is a function of the structure of the activated species generated under UV irradiation of the spiro compound.[9]

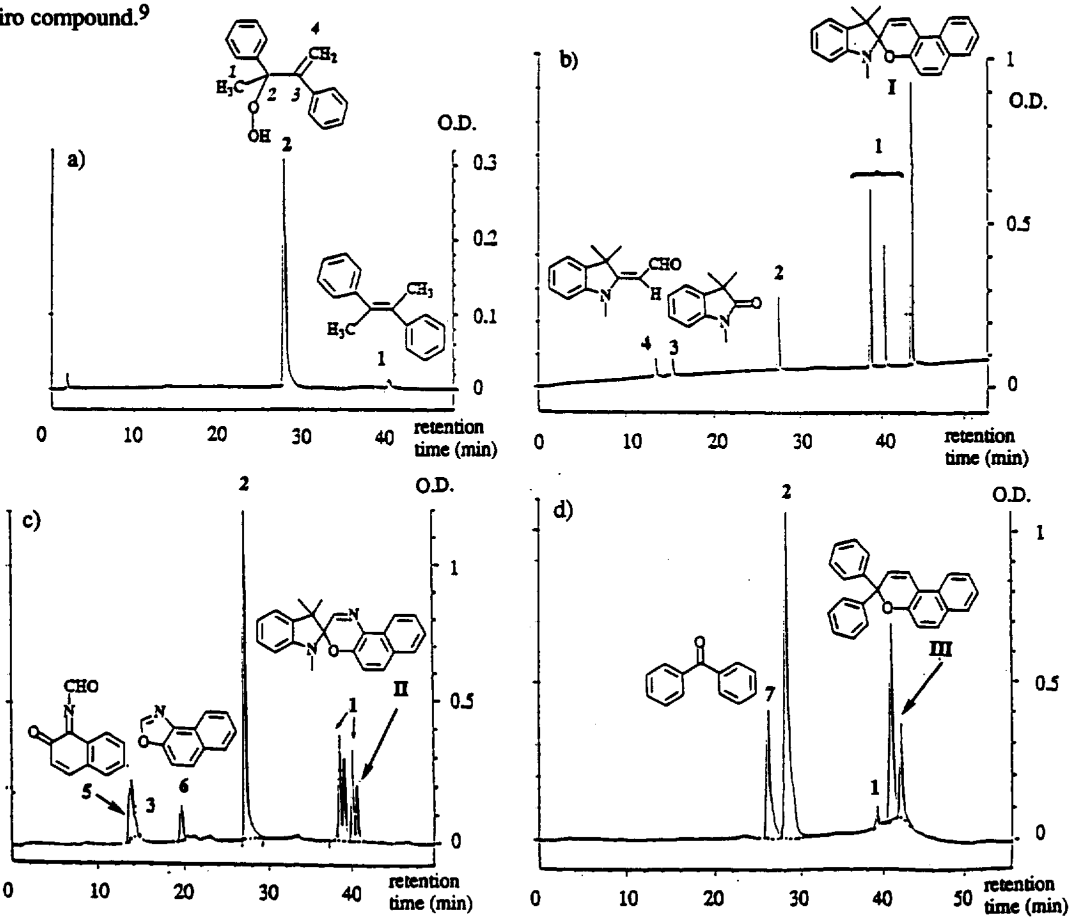


Figure 1 : Chromatographic separation (HPLC) of photosensitised oxidation of cis- and trans-α,α'-dimethylstilbenes **1** by sensitisers : (a) Rose Bengal, (b) **I**, (c) **II** and (d) **III**, (Detection at 240±5nm; Irradiation by a 250W xenon arc lamp (XBO Osram) with a filter WG360 Schott cutting off at 345 nm; CH_3CN; 13°C).

CONCLUSION

In conclusion, we have unambiguously described the ability of three important representative photochromic compounds (spiropyran, spirooxazine, [2H]-chromene) to act as photosensitiser of singlet oxygen.

Furthermore, the photomerocyanines derived from the spiro compounds could be used as efficient singlet oxygen sensitisers in photobiological experiments.

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