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Photochemistry of some 2,5-substituted tropone mesogens

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Abstract

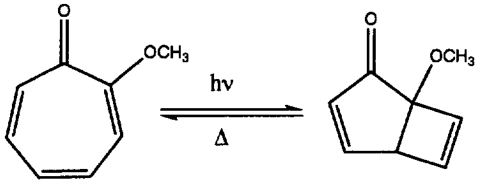
The photoreactivity of three 2-acyloxy-5-alkoxytropone derivatives, two of which are known to show thermotropic liquid crystalline phases, has been studied with the aim of finding photoresponsive mesogenic materials. The irradiation of solutions of these compounds in CH_3CN under air atmosphere brings to endoperoxides which do not show mesomorphism and are not fully reversible to their respective precursors neither photochemically nor thermally. From the chemical point of view, the facile and relatively neat formation of endoperoxides open synthetic routes to new functionalized tropone derivatives.

Keywords: Tropone derivatives; Endoperoxides; Oxygen addition; Photooxygenation; Liquid crystals

1. Introduction

In recent years, 2-acyloxy-5-alkoxytropone derivatives showing liquid crystalline phases have been synthesized [1–3]. The formation of mesophases depends on the nature of the groups bound to the tropone core. It seems clear that the occurrence of a (1,9) sigmatropic rearrangement, typical of simple 2-acyloxytropones [4], is deeply implied in the mesogenic aptitude, so that it is considered as a structural prerequisite for the mesomorphism of these compounds.

Besides their unconventional nature, additional interest in these mesogens derives from the rich photochemistry usually shown by troponoids. In particular, it is worth remembering the valence isomerization of many monosubstituted troponoids to bicyclo[3.2.0]hepta-3,6-dien-2-one derivatives. The first example of this reaction was reported by Chapman and Pasto [5–7], who studied the photorearrangement of 2-methoxytropone to 1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (see Scheme 1). This photoreaction could render the 2-acyloxy-5-alkoxytropone derivatives photoresponsive systems. In addition, the thermal reversion to the precursor shown by bicyclo[3.2.0]hepta-3,6-dien-2-ones could be used to reset the system. Essentially we could have the possibility of directly change, or destroy, the mesomorphism of our mesogenic troponoids inducing the photoisomerisation of the irradiated specimen with near-UV light. It must be noticed that in these compounds photochemical and mesomorphic properties are coupled *in a unique molecular system*, while photochromic molecules, especially tailored to contain long alkyl chains, are often dissolved in a liquid crystal in order to photoregulate its mesomorphism [8]. This prospect justifies our study on the photochemistry in solution of compounds 2-(4′-dodecyloxybenzoyloxy)-5-hexyloxytropone (**1**), 5-dodecyloxy-2-tridecanoyloxytropone (**2**) and 2-acetyloxy-5-hexyloxytropone (**3**), shown in Scheme 2, and on the thermochemistry of their photoproducts. Of course, one must be aware that the photochemistry in solution may differ, even considerably, from the photochemistry of a compound in its neat liquid cristalline phase; this will not be attempted here.



Scheme 1.

Compounds **1** and **2** are mesogenic [9,10], while **3** is not mesogenic and can be considered as a reference compound for the reactivity of this class of molecules.

The described Chapman isomerization (Scheme 1) revealed to be no longer the most important photoreaction of **1**, **2**, and **3**. In fact, photoaddition of molecular oxygen resulted in a much easier reaction leading to endoperoxides. This is a typical reaction of dienes and of polynuclear condensed aromatics. Some endoperoxides obtained from rigid polycyclic aromatic hydrocarbons, as anthracene, are photo-

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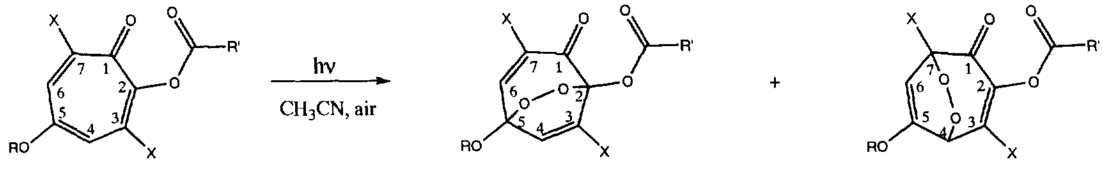


1: R = C_6H_{13}, R' = $C_6H_4OC_{12}H_{25}$, X = H
1a: R = C_6H_{13}, R' = $C_6H_4OC_{12}H_{25}$, X = D
2: R = $C_{12}H_{25}$, R' = $C_{12}H_{25}$, X = H
3: R = C_6H_{13}, R' = CH_3, X = H

5: R = C_6H_{13}, R' = $C_6H_4OC_{12}H_{25}$, X = H
5a: R = C_6H_{13}, R' = $C_6H_4OC_{12}H_{25}$, X = D
7: R = $C_{12}H_{25}$, R' = $C_{12}H_{25}$, X = H
9: R = C_6H_{13}, R' = CH_3, X = H

6: R = C_6H_{13}, R' = $C_6H_4OC_{12}H_{25}$, X = H
6a: R = C_6H_{13}, R' = $C_6H_4OC_{12}H_{25}$, X = D
8: R = $C_{12}H_{25}$, R' = $C_{12}H_{25}$, X = H
10: R = C_6H_{13}, R' = CH_3, X = H

Scheme 2.

chromic systems based on photoinduced detachment of O_2 [11]. In our case endoperoxides are not photochromic systems, at least in solution. Moreover, both their molecular geometry and electronic structure are so deeply altered with respect to starting troponoids that they are no more mesogens and they show very low light absorption in the 300–400 nm spectral region. Nevertheless, the endoperoxides obtained in the present work are interesting from a synthetic point of view since they can be useful precursors for the regio- and diastereoselective oxyfunctionalization of troponoids [12–14].

1.1. Photochemistry of 2,5-disubstituted tropones

Some information is reported in the literature on the photochemistry of 2,5-disubstituted tropones [15,16], even if, to the best of our knowledge, no data are present for tropones with an acyloxy group in position 2 and an alkoxy group in position 5. The irradiation with UV light gave bicyclo[3.2.0]hepta-3,6-dien-2-one derivatives which, in many cases, showed a strong thermal instability. In these cases the isolation of the photoproducts at room temperature resulted impossible and a spectroscopic characterization of the labile photoproducts in solution could be made only at very low temperature (about −80°C). The thermal instability of the bicycle depends mostly on the substituents and, in minor degree, on the solvent; for instance hydrocarbon solvents enhance the thermal reversion [15,16]. It was observed that the presence of an electron-donor or a H-bond acceptor group in position 2, and of an electron-withdrawing group in position 5 of the tropone ring helps the thermal conversion. However, these are not sufficient conditions. In fact, NO_2, Cl, Br, NO and azo groups in position 5 of the tropone ring give stable photo-derivatives, while a phenyl group in the same position ensures a facile thermal return to the precursor. In conclusion, we cannot make predictions on the photochemistry of 2-acyloxy-5-alkoxytropones nor on the thermochemistry of their eventual photoproducts, because in position 2 we have an electron-acceptor group and in position 5 an electron-donor group.

The simple approach, early proposed by Chapman and Pasto [5–7], of roughly representing the electron distribution in the photochemically active excited state, and try to deduce the photoreactivity of the different positions of the tropone ring under the influence of the stabilization/destabilization effects of the substituents does not allow us to draw conclusions regarding the photoreactivity of 2-acyloxy-5-alkoxytropone derivatives. In fact, for example, the alkoxy group in position 5 has a stabilizing effect, while a destabilizing effect is shown by the acyloxy group in position 2. Because of these conflicting effects the collapse of the tropone ring into a bicyclo[3.2.0]hepta-3,6-dien-2-one, by formation of a bond between the positions 2 and 5, is not immediately consequent.

Much more recently the importance of the nature of the lowest electronic excited state in defining the photochemistry of troponoids has been established both from the experimental and theoretical point of view [17,18]. Extensive quantum mechanical ab initio calculations on tropone showed the $n \rightarrow \pi^*$ nature of this state, which can be turned into a $\pi \rightarrow \pi^*$ state by protonation of the carbonyl oxygen. Experimentally, dramatic changes were observed in the photochemistry of tropone after reaction with Lewis or Broensted acids. Such a behaviour was also found for some mono-substituted troponoids; unfortunately accurate quantum mechanical calculations were not possible for them. Thus, it remains unclear if the presence of substituents on the tropone ring could alter the positions of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states with respect to the tropone excited states in a way similar to that observed for the complexation with acids.

2. Experimental details

2.1. Materials

Solvents used for irradiations, absorption measurements and HPLC operations were of HPLC grade. Samples of **1**, **1a**, an isotopomer of **1** deuteriated at C-3 and C-7 of the tropone ring, **2**, **3**, and **4** (2-acetyloxytropone) were synthesized as reported in Refs. [9,10].

2.2. Apparatus

The irradiations were performed using the near-UV emissions of an Argon laser (Coherent Innova 300/6) at $\lambda = 351$ and 364 nm, with intensities in a ratio of about 1:1 at 200 mW total emission. The fluence of the laser light was calibrated by means of a home-made calorimeter with a precision of $\pm 3\%$. The use of a laser as light source allowed us to obtain a perfect control of both the fluence and the energy density of the irradiating beam. In addition, irradiations could be performed even with small volumes of solutions, e.g., 3 ml, and very small amounts of substrate. The samples were contained in cylindrical vessels with a flat quartz window. The evolution of the photochemical reactions was monitored by high performance liquid chromatography (HPLC) using a Jasco 880 Pu pump equipped with a Jasco 875-UV or a Shimadzu SPD-10-A spectrophotometric detector. Unless otherwise stated, a reversed phase Spherisorb S5 ODS2 250×4.6 mm column with a RP 10×4.6 mm precolumn was employed. The Shimadzu SPD-10-A detector could measure Vis–UV absorption spectra at chromatographic peaks. Preparative separations of photoproducts from the reaction mixtures were obtained by HPLC using a RP C18 250×8 mm column.

The IS-MS measurements were performed on a Perkin Elmer Sciex API III plus spectrometer. The UV–Vis spectra were recorded on a Varian Cary 219 spectrophotometer with a spectral bandwidth of 1.5 nm. The IR measurements were performed on a FT-IR Perkin Elmer 1600 spectrophotometer. The NMR spectra were recorded on $CDCl_3$ solutions using a Varian Gemini 200 spectrometer, working at 200 MHz for proton and at 50.3 MHz for carbon-13, respectively. The mesomorphism of photoproducts was investigated by polarizing optical microscopy using a Reichert–Jung Polyvar microscope equipped with a Mettler FP5 hotstage.

2.2.1. UV irradiations

Irradiations were performed with 0.01–0.02 g of substrate dissolved in 25–40 ml of solvent. The concentration of the substrate was chosen in order to obtain a sufficient amount of photoproducts for characterization and an optical density, at the irradiation wavelengths, sufficiently low to ensure a penetration depth longer than 1 mm and, consequently, an efficient stirring of the irradiated mixture. In the irradiations, conversions of the substrates higher than 50% were avoided. We employed an intensity of the laser light in the range between 30 and 200 mW; no 334 nm emission was present. In some experiments the laser beam was enlarged by means of a quartz spherical lens ($f = 20$ mm) in order to reduce the energy density by a factor ca 50. In other irradiations a quartz cylindrical lens ($f = 25$ mm) was used with the semicylindrical axis perpendicular to the flow of the stirred solution. With this apparatus no formation of deposits on the optical window were observed.

2.3. UV irradiation of **1** under air

A solution of 0.030 g (0.059 mmol) of **1** in 35 ml of CH_3CN was irradiated with light of 140 mW intensity, until 27% disappearance of **1**. The course of the reaction was monitored by HPLC (RP C18 column, eluent CH_3CN, flow 0.75 ml/min, $\lambda = 260$ nm). A mixture was obtained containing **1** (retention time $t_R = 22' \, 30''$) and two main photoproducts, **5** and **6**, with $t_R = 15' \, 15''$ and $t_R = 17' \, 50''$, respectively, and a negligible quantity of minor unidentified products. The quantum yield of phototransformation of **1** was $\Phi = 0.053$ mol/Einst and the quantum yields of formation of **5** and **6** were evaluated as 0.015 and 0.036 mol/Einst, respectively. The reaction mixture was concentrated by solvent evaporation and the products were isolated by preparative HPLC.

Data of compound **5**: **IS-MS** *m/z*: 560 $[M + NH_4]^+$, 565 $[M + Na]^+$. **IR** (KBr) ν (cm^{-1}): 3070, 2924, 2854, 1740, 1704, 1658, 1606, 1580, 1510, 1466, 1426, 1380, 1346, 1310, 1254, 1228, 1168, 1122, 1044, 1002, 908, 846, 762, 724, 692, 644, 506; **UV** (CH_3CN) λ_{max} (nm) (ε ($M^{-1}\,cm^{-1}$)): 212 (17 500), 265 (18 000), 333 (380). **^{1}H NMR** ($CDCl_3$) δ (ppm) J (Hz): 0.85–0.97 (6H, m, CH_3), 1.24–1.41 (24H, m, CH_2), 1.62–1.79 (4H, m, CH_2), 3.82 (2H, t, OCH_2, $J = 6.6$), 4.00 (2H, t, OCH_2, $J = 6.6$), 6.03 (1H, d, H-7, $J_{6,7} = 11.8$), 6.39 (1H, d, H-3, $J_{3,4} = 9.9$), 6.88 (1H, dd, H-6, $J_{4,6} = 0.8$), 6.91 (2H, d, aromatics, $J = 8.9$), 7.00 (1H, dd, H-4), 8.03 (2H, d, aromatics, $J = 8.9$). **^{13}C NMR** ($CDCl_3$) δ (ppm): 14.19 (CH_3), 22.64, 22.77, 25.50, 26.03, 29.13, 29.43,29.69, 30.17, 31.55, 31.99 (CH_2 of alkyl chains), 66.01 (OCH_2), 68.39 (OCH_2), 102.48 (C-1 or C-5), 104.07 (C-1 or C-5), 114.34 (aromatics), 120.29 (aromatic), 126.20 (C-3 or C-7), 127.18 (C-3 or C-7), 132.37 (aromatic), 132.61 (aromatic), 141.26 (C-4 or C-6), 144.14 (C-4 or C-6), 162.75 (OCO), 163.95 (aromatic), 188.88 (C-1). Structural assignment of **5** is supported by the **^{1}H NMR** spectrum of **5a** obtained irradiating **1a**, an isotopomer of **1** deuteriated at C-3 and C-7. The spectrum of **5a** shows lack of the resonances at 6.03 (H-7) and 6.39 (H-3) ppm while both dd at 6.88 (H-6) and 7.00 (H-4) ppm become d with $J_{4,6} = 0.8$ Hz. m.p. 61–63°C with decomposition. Found: C, 70.5; H, 8.0. $C_{32}H_{46}0_7$ requires: C, 70.81; H, 8.55.

Data of compound **6**: **IS-MS** *m/z*: 560 $[M + NH_4]^+$, 565 $[M + Na]^+$. **IR** (KBr) ν (cm^{-1}): 3070, 2922, 2852, 1780 (vinyl ester C=O stretching), 1744, 1700, 1606, 1510, 1468, 1428, 1380, 1350, 1308, 1256, 1166, 1122, 1072, 1028, 972, 846, 810, 758, 724, 692, 638, 548, 510. **UV** (CH_3CN) λ_{max} (nm) (ε ($M^{-1}\,cm^{-1}$)): 210 (18 000), 263 (16 000), 325 (350). **^{1}H NMR** ($CDCl_3$) δ (ppm) J (Hz): 0.85–0.97 (6H, m, CH_3), 1.24–1.41 (24H, m, CH_2), 1.72–1.79 (4H, m, CH_2), 3.83 (2H, m, OCH_2), 4.00 (2H, t, OCH_2, $J = 6.6$), 5.03 (1H, ddd, H-4, $J_{3,4} = 8.7$, $J_{4,6} = 2.0$, $J_{4,7} = 0.7$), 5.09 (1H, dd, H-6, $J_{6,7} = 8.7$), 5.24 (1H, dd, H-7), 6.86 (1H, d, H-3), 6.92 (2H, d, aromatics, $J = 9.0$), 8.00 (2H, d, aromatics, $J = 9.0$). **^{13}C NMR** ($CDCl_3$) δ (ppm): 14.02 (CH_3), 14.15 (CH_3), 22.59, 22.75, 25.63, 26.05, 28.55, 29.16, 29.42, 29.65, 31.52, 32.00 (CH_2 of alkyl chains), 68.47 (OCH_2), 69.07 (OCH_2), 83.46 (C-4), 84.37 (C-7), 114.50 (aromatics), 120.43 (aromatic), 128.10 (C-3), 132.38 (aromatic), 148.00 (C-2), 163.79 (OCO), 163.79 (aromatic), 165.01 (C-5), 189.01 (C-1). As in the case of **5**, the structural assignment of compound **6** is supported by the spectrum of the isotopomer **6a**. This shows lack of both signals at 5.24

(H-7) and 6.86 (H-3) ppm, while ddd at 5.03 (H-4) and dd at 5.09 (H-6) ppm become d with $J_{4,6}=2.0$ Hz. m.p. 43–45°C. Found: C, 70.6; H, 8.2. $C_{32}H_{46}0_7$ requires: C, 70.81; H, 8.55.

2.3.1. UV irradiation, thermal and acid treatment of **5** and **6**

A solution of 0.002 g (0.004 mmol) of **6** in 2 ml of CH_3CN was irradiated with 40 mW of laser light until 66% phototransformation. During the photolysis of **6** ($t_R = 17' 50''$) HPLC analyses (RP C18 column, eluent CH_3CN, flux 0.75 ml/min, $\lambda = 260$ nm) revealed production of **5** ($t_R = 15' 15''$) as the main photoproduct accompanied by many other products, the most relevant giving peaks at 12′ 25″ and 10′ 50″. At the end of the reaction the ratio [**5** found]/[**6** disappeared] was 1:18. Taking into account that **5** and **6** have similar extinction coefficients at the laser emissions, this ratio represents the effect of photoproduction of **5** contrasting with photodestruction of **6** and **5**. The quantum yield of phototransformation of **6** at 16% decomposition was 0.39 mol/Einst. No photoreversion to precursor **1** was observed. An irradiation of **5**, performed in analogous conditions, led to many unidentified products containing the benzene ring, mostly already observed during the photolysis of **6**.

Solutions of **5** and **6** in CH_3CN [0.003 g (0.005 mmol) in 3 ml and 0.002 g (0.004 mmol) in 3 ml, respectively] were maintained in the dark in a water bath at 60°C and the course of the reactions was monitored by HPLC. **5** decomposes to unidentified products, whereas **6** gives a single product, **11**, with $t_R = 14' 40''$ (RP C18 column, eluent CH_3CN, flux 0.75 ml/min, $\lambda = 260$ nm). The conversions of **5** and **6** were both first-order with half-life times of 13.3 and 5.8 h, respectively. **11** has been isolated from the reaction mixture by semipreparative HPLC.

To solutions of **5** and **6** in CH_3CN (1 ml, both ca 0.0003 M) were added ca 10-fold stoichiometric amounts of HCl 0.01 N and the respective reactions were followed by HPLC. The disappearing of **5** and **6** resulted exponential with time; the half-life times were 10 and 21 h, respectively. No reversion to the precursor or interconversion between **5** and **6** was observed; both reactions resulted in formation of very low retention time products.

Data of compound **11**: **IS-MS** *m/z*: 560 $[M+NH_4]^+$, 565 $[M+Na]^+$. **UV** (CH_3CN) λ_{max} (nm): 217, 280. ^{1}**H NMR** ($CDCl_3$) δ (ppm) J (Hz): 0.85–0.97 (6H, m, CH_3), 1.24–1.41 (24H, m, CH_2), 1.83 (4H, m, OCH_2CH_2), 3.52 (2H, m, OCH_2), 4.05 (2H, t, OCH_2), 6.45 (1H, d, H-2, $J_{2,3}=5.5$), 6.49 (1H, d, H-7, $J_{6,7}=15.5$), 6.94 (2H, d, aromatics, $J=8.1$), 7.14 (1H, dd, H-6, $J_{6,7}=15.5$), 7.63 (1H, d, H-3, $J_{3,2}=5.5$), 8.04 (2H, d, aromatics, $J=8.1$).

2.3.2. UV irradiation of **1** under N_2

A solution of 0.022 g (0.043 mmol) of **1** in 38 ml of CH_3CN, repeatedly degassed under vacuum and sealed under nitrogen atmosphere, was irradiated with 200 mW light until 20% disappearance of **1**, and the course of the reaction was monitored by HPLC. Three main photoproducts were obtained: **5**, **6**, and **12** with $t_R = 20' 20''$ (RP C18 column, eluent CH_3CN, flux = 0.75 ml/min, $\lambda = 260$ nm); some 32% of disappeared **1** was lost in minor products. The quantum yield of actual phototransformation of **1** was 0.0042 mol/Einst while the photogeneration yields of **5**, **6** and **12** resulted 0.00058, 0.0010 and 0.0012 mol/Einst, respectively. The HPLC analysis revealed that formation of oxygenated products prevailed at the very beginning of the irradiation while, after consumption of O_2, only the concentration of **12** increased. An analogous behaviour was observed when Argon was used instead of N_2. **12** was separated from the reaction mixture by semipreparative HPLC.

Data of compound **12**: **IS-MS** *m/z*: 528 $[M+NH_4]^+$, 533 $[M+Na]^+$. **UV** (CH_3CN) λ_{max} (nm): 210 (sh), 263, 328, A(328)/A(263) = 1/35. ^{1}**H NMR** ($CDCl_3$) δ (ppm) J (Hz): 0.85–0.97 (6H, m, CH_3), 1.24–1.41 (24H, m, CH_2), 1.83 (4H, m, OCH_2CH_2), 3.62 (2H, m, OCH_2), 4.05 (2H, m, OCH_2), 6.90 (2H, d, aromatics, $J=8.9$), 8.12 (2H, d, aromatics, $J=8.9$), 6.16 (1H, d, H-3, $J_{3,4}=6.5$), 6.66 (1H, d, H-7, $J_{7,6}=2.6$), 7.00 (1H, d, H-6, $J_{6,7}=2.6$), 7.53 (1H, d, H-4, $J_{4,3}=6.5$). Found: C, 75.0; H, 9.0. $C_{32}H_{46}0_5$ requires: C, 75.24; H, 9.08.

2.3.3. UV irradiation of **1** under O_2

A solution of 0.007 g (0.014 mmol) of **1** in 24 ml of CH_3CN three times degassed under vacuum and saturated with O_2 at atmospheric pressure was irradiated with laser light (39 mW) until 15% conversion of **1**. As revealed by HPLC and UV analysis **5** and **6** were produced in a 1:2.4 ratio while no **12** was formed. The quantum yield of transformation of **1** was 0.018 mol/Einst, i.e., about 1/3 of the quantum yield estimated when the irradiation was performed under air.

2.4. UV irradiation of **2** under air

A solution of 0.010 g (0.020 mmol) of **2** in 25 ml of CH_3CN was irradiated with 38 mW UV light until 48% disappearance of **2**, and the course of the reaction was monitored by HPLC (Lichrosorb-CN 250×4.6 mm column, eluent *n*-hexane/isopropyl alcohol 98/2 v/v, flux 0.8 ml/min, $\lambda = 230$ nm). A mixture was obtained containing **2** ($t_R = 14' 10''$) and two main photoproducts, **7** and **8**, with $t_R = 6' 45''$ and $t_R = 15' 20''$, respectively. The quantum yield of phototransformation of **2** was $\Phi = 0.072$ mol/Einst at 22% conversion. With higher conversion levels this figure was observed to decrease rapidly ending to 0.027 mol/Einst, at 48% conversion. The mixture was concentrated by solvent evaporation and the products separated by preparative HPLC.

Data of compound **7**: **IS-MS** *m/z*: 552 $[M+NH_4]^+$, 557 $[M+Na]^+$. **UV** (CH_3CN) λ_{max} (nm): 213, 225, 360, A(213)/A(360) = 26. ^{1}**H NMR** ($CDCl_3$) δ (ppm) J (Hz): 0.87 (6H, t, CH_3, $J=8.0$), 1.30 (36H, m, CH_2), 1.64 (4H, m, OCH_2CH2), 2.46 (2H, t, $OCOCH_2$, $J=7.3$), 3.80 (2H, t, OCH_2, $J=6.4$), 6.00 (1H, d, H-7, $J_{6,7}=11.8$), 6.22 (1H, d, H-3, $J_{3,4}=9.9$), 6.85 (1H, dd, H-6, $J_{4,6}=0.8$), 6.97 (1H, dd, H-4). ^{13}**C NMR** ($CDCl_3$) δ (ppm): 14.17 (CH_3), 22.74, 24.57, 28.94, 29.26, 29.34, 29.39, 29.67, 30.18, 31.96, 33.84 (CH_2 of alkyl chains), 65.97 (OCH_2), 125.86 (C-3 or C-7), 127.18 (C-3 or C-7), 141.65 (C-4 or C-6), 143.96 (C-4 or C-6). Found: C, 71.6; H, 10.0. $C_{32}H_{54}0_6$ requires: C, 71.86; H, 10.18.

Data of compound **8**: **IS-MS** *m/z*: 552 $[M+NH_4]^+$, 557 $[M+Na]^+$. **UV** (CH_3CN) λ_{max} (nm): 205, 250 (sh), 353, A(205)/A(353) = 43. ^{1}**H NMR** ($CDCl_3$) δ (ppm) J (Hz): 0.87 (6H, t, CH_3, $J=8.0$), 1.30 (36H, m, CH_2), 1.57 (2H, m, OCH_2CH_2), 1.66 (2H, m, OCH_2CH_2), 2.50 (2H, t, $OCOCH_2$, $J=7.2$), 3.80 (2H, t, OCH_2, $J=6.3$), 4.99 (1H, ddd, H-4, $J_{3,4}=8.7$, $J_{4,6}=2.0$, $J_{4,7}=0.7$), 5.06 (1H, dd, H-6, $J_{6,7}=8.7$), 5.21 (1H, dd, H-7), 6.73 (1H, d, H-3). ^{13}**C NMR** ($CDCl_3$) δ (ppm): 14.18 (CH_3), 22.74, 24.74, 25.90, 28.50, 29.00, 29.10, 29.29, 29.39, 29.48, 29.53, 29.67, 31.96, 33.63 (CH_2 of alkyl chains), 68.50 (OCH_2), 83.26 (C-4), 84.18 (C-7), 127.00. Found: C, 71.4; H, 10.1. $C_{32}H_{54}0_6$ requires: C, 71.86; H, 10.18.

2.4.1. Acid and thermal treatment of 7 and 8

To a mixture containing ca 0.001 g of **7** and 0.001 g of **8** in 250 μl of CH_3CN a drop of 0.01 N $HClO_4$ was added. After 15′ an HPLC analysis revealed formation of the precursor together with a decomposition product. After 1 h, the disappearing of **7** and **8** and of **2**, initially formed, was complete, with **8** disappearing more rapidly than **7**. An analogous solution of **7** and **8** was warmed up to 60°C for 2 min. A HPLC analysis revealed complete disappearing of **7**, partial of **8** and appearing of **2** and some unidentified byproducts.

2.5. UV irradiation of 3 under air

A solution of 0.011 g (0.037 mmol) of **3** in 25 ml of CH_3CN was irradiated for 30′ with 100 mW intensity light until 36% disappearance of **3**; the course of the reaction was monitored by HPLC (RP C18 column, eluent CH_3CN, flow 0.6 ml/min, $\lambda = 230$ nm). A mixture was obtained containing **3** ($t_R = 6'\ 25''$) and two main photoproducts, **9** and **10**, both with almost identical $t_R = 8'\ 00''$. Using CH_3CN/H_2O 80/20 v/v as eluent the separability of the photoproducts between them was impossible and that from the precursor was worst than before. The isolation of the photoproducts was not possible by TLC analysis on silica plates. In fact, in this case photoproducts converted back to the troponoidic precursor. The quantum yield of phototransformation of **3** was $\Phi = 0.040$ mol/Einst at 22% photoconversion. At 50% conversion of **3**, the photolysis rates of **9** and **10** were equal to those of their photoproduction. The NMR investigations were thus performed on a mixture of photoproducts. After NMR experiments, the $CDCl_3$ solution was found to contain about 30% of **3**.

The **UV** spectrum and the **IS-MS** data refer to the mixture of **9** + **10**. **IS-MS** *m/z*: 314 $[M+NH_4]^+$, 319 $[M+Na]^+$. **UV** (CH_3CN/H_2O 80/20 v/v) λ_{max} (nm): 225, 267 and 345, A(225)/A(267)/A(345) = 24/19/1.

In the ^{1}**H NMR** spectrum we can easily assign to **9** the following signals: δ (ppm) J (Hz): 0.91 (3H, t, CH_3, $J=8.0$), 1.33 (6H, m, CH_2), 1.60 (4H, m, OCH_2CH_2), 2.25 (3H, s, $OCOCH_3$), 3.81 (2H, t, OCH_2, $J=7.0$), 6.01 (1H, d, H-7, $J_{6,7}=11.8$), 6.22(1H, d, H-3, $J_{3,4}=10.3$), 6.86 (1H, d, H-6), 6.97 (1H, d, H-4). **10** shows: δ (ppm) J (Hz): 0.91 (3H, t, CH_3, $J=8.0$), 1.33 (6H, m, CH_2), 1.60 (4H, m, OCH_2CH_2), 2.25 (3H, s, $OCOCH_3$), 3.81 (2H, t, OCH_2, $J=7.0$), 5.00 (1H, dd, H-4, $J_{3,4}=8.6$, $J_{4,6}=1.7$), 5.07 (1H, dd, H-6, $J_{6,7}=8.6$), 5.22 (1H, d, H-7), 6.74 (1H, d, H-3).

2.5.1. Acid and thermal treatment of 9 and 10

To a mixture of photoproducts **9** and **10** in CH_3CN/H_2O 80/20 v/v (2 ml, ca 0.001 M) was added a drop of 0.1 N HCl. After 5 h at r.t. we found 90% transformation of photoproducts into one main unidentified demolition product together with a comparable quantity of the precursor and many other minor products.

An analogous sample of **9** and **10** was warmed up to 50°C and then analysed by HPLC. After 3 h the mixture was 40% converted into a mixture of products different from that observed after the acid treatment but containing the precursor **3**. The intensity of the HPLC peak corresponding to **9** and **10** decreased exponentially with time; the decay time was $\tau = 360'$.

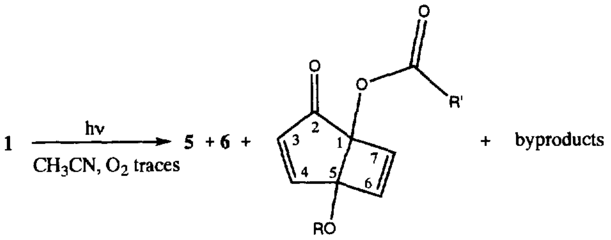
2.6. UV irradiation of 4 under air

A solution of 0.008 g (0.048 mmol) of **4** in 25 ml of cyclohexane was irradiated until 13% disappearance of **4** (100 mW for 100′), and the course of the reaction was monitored by HPLC (RP C18, eluent CH_3CN/H_2O 50/50 v/v, flux 0.5 ml/min, $\lambda = 330$ and 230 nm). The quantum yield of phototransformation of **4** ($t_R = 7'\ 25''$) was very low ($\Phi = 0.0041$ mol/Einst). Negligible amounts of many photoproducts were obtained. Irradiation of **4** in CH_3CN under air or N_2 atmosphere, or in 20% aqueous CH_3CN under air atmosphere, led to an even more reluctant photodestruction of **4**.

3. Results and discussion

3.1. UV irradiation of 1, 2, and 3

The irradiation of **1** in acetonitrile under air atmosphere brings mainly to **5** and **6** which are the only photoproducts observed when the irradiation is carried out under O_2 atmosphere (see Schemes 2 and 3). The UV–Vis analysis shows that these products do not contain the tropone ring anymore, the strong absorption at about 330 nm being not present in their spectra (see Fig. 1). On the other hand, the infrared and ultraviolet spectra indicate the presence of an α,β-unsaturated carbonyl group in both products. Moreover, the peaks characteristic of the cyclobutene moiety are not present in the IR spectra, indicating that **5** and **6** are not derivatives of the



12

R = C_6H_{13}, R' = $C_6H_4OC_{12}H_{25}$
Scheme 3.

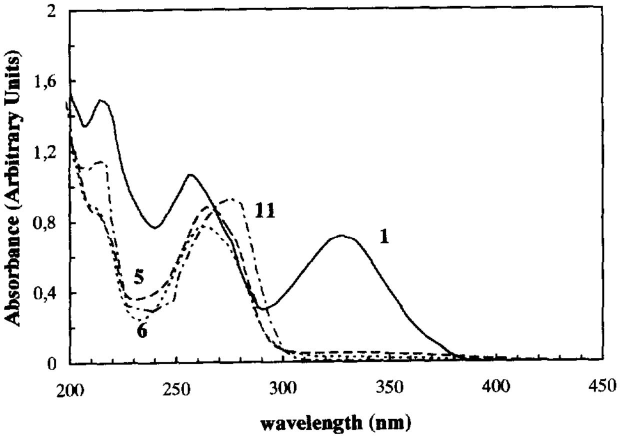


Fig. 1. UV–Vis spectra of compounds **1** (solid line), **5** (dashed line), **6** (dotted line) and **11** (dashed–dotted line).

bicyclo[3.2.0]hepta-3,6-dien-2-one. Mass spectrometry definitely confirms the hypothesis of O_2 addition. The structures of **5** and **6**, shown in Scheme 2, follow from the experimental data above described and from the analysis of the ^{1}H NMR and ^{13}C NMR spectra. Irradiation of the isotopomer of **1** deuteriated at C-3 and C-7 of the tropone ring, **1a**, gives photoproducts **5a** and **6a** whose spectra help in the structure assignment of **5** and **6**. The photoproducts are endoperoxides resulting from a [4+2] addition of an oxygen molecule to the tropone ring. Two of these reactions are possible for compound **1**, leading to **5** and **6**, respectively. Irradiation of **2** or **3** under the same experimental conditions (see Sections 2.4 and 2.5) brings to the couples of photoproducts **7** and **8**, or **9** and **10** (see Scheme 2), analogous to **5** and **6**, respectively. This is revealed by spectroscopic investigations (in Figs. 2 and 3 the UV–Vis spectra of **2** and **3** are compared with those of the respective photoproducts) and, in particular, by ^{1}H NMR.

Photooxidations are reported in the literature for other troponoids [19–25]. In all cases a sensitiser (usually a dye) was needed in order to produce excited singlet oxygen ($^1O_2$) using visible light irradiation; $^1O_2$ adds to ground-state troponoids to give endoperoxides. However, in one case, namely in the UV irradiation of a benzotropone derivative reported by Forbes et al. [20,21], a self-sensitised reaction leading to derivatives of very unstable endoperoxides has been observed.

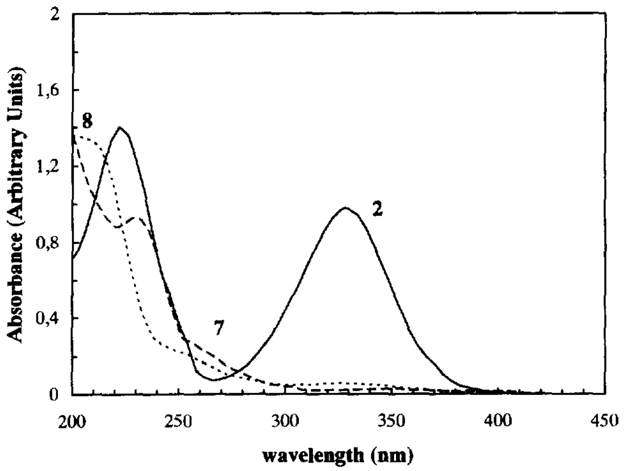


Fig. 2. UV–Vis spectra of compounds **2** (solid line), **7** (dashed line) and **8** (dotted line).

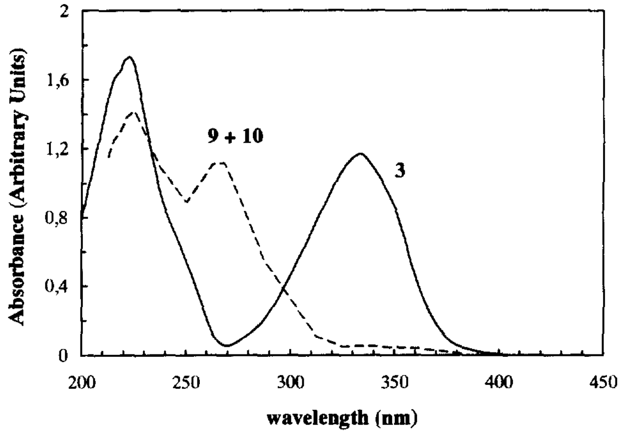


Fig. 3. UV–Vis spectra of compounds **3** (solid line), **9**+**10** (dashed line).

In the laser irradiation of 2-acyloxy-5-alkoxytropones here performed there was not need of a visible light sensitiser; the 364 and 351 nm laser lines directly excite the tropone chromophore. The behaviour of these substrates is remarkably different from that previously observed for other troponoids, for which the irradiation carried out under similar experimental conditions brought to Chapman photoisomerisation [5–7], dimer formation or other rearrangements. In fact, for the 2,5-substituted tropones here studied the above reactions are negligible with respect to the photoaddition of oxygen; this behaviour is obviously related to the relative quantum yields of the possible photoreactions. The electronic excited state of tropone is deeply influenced by the presence of an acyloxy group at C-2. We have found that the quantum yield for the photolysis of 2-acetyloxy tropone, **4**, is about 0.0041 mol/Einst, two orders of magnitude lower than that of tropolone (0.12 mol/Einst [26]). The introduction of an alkoxy group in position 5 of the tropone ring allows both photooxygenation and Chapman valence isomerisation reactions. However, the first process is more favoured, as revealed by the fact that the Chapman isomerization of **1** to the bicyclo[3.2.0]hepta-3,6-dien-2-one derivative **12** becomes important only when O_2 is not present (see Section 2.3.2).

Moreover, we have evaluated that the quantum yield of **12** in the absence of O_2 is about 0.002 mol/Einst, i.e., very small with respect to the quantum yields estimated for the isomerization of other 2-substituted tropones. In fact, quantum yields of 0.12 or 0.095 mol/Einst have been found when the substituents are $-OH$ or $-OCH_3$, respectively, and a quantum yield of 0.22 mol/Einst has been found for the photoisomerization of 2-hydroxy-4-isopropyl-tropone [26].

No sound affirmations can be made regarding the mechanism of photoaddition of oxygen. However, the hypothesis made by Forbes and Griffiths [20,21] that singlet oxygen involved in the reaction is produced in an energy transfer process with the triplet substrate, in our case seems supported by the fact that irradiating **1** under the same conditions, but in a methanol instead than in an acetonitrile solution, the formation of **5** and **6** is ten times slower. These differences, also observed by other authors [22,23], could reflect the different life times of singlet oxygen in methanol and acetonitrile. In fact, it has been found that the $-OH$ group has a quenching effect on $^1O_2$.

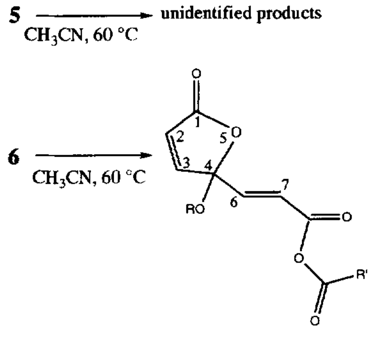
Surprisingly, the irradiation under O_2 atmosphere (see Section 2.3.3) resulted in a slower photoaddition with respect to that performed under air atmosphere (see Section 2.3). This can be rationalised considering the bimolecular nature of the photooxygenation processes. In a simplified reaction scheme [11], the quantum yield for endoperoxide production, Q, depends on the concentration of the organic substrate [Trp] as follows:

$$Q \alpha q \frac{[\mathrm{Trp}]^2}{[\mathrm{Trp}]+\beta}$$

where q is the quantum yield for $^1O_2$ formation, that is proportional to $[O_2]$, and β is a reactivity parameter of $^1O_2$ strongly solvent-dependent. In the irradiation under O_2, [Trp] was ca 1/3 of that under air, while $[O_2]$ was about fivefold. To this lower [Trp] probably corresponds a lowering to 1/9 of the ratio in the above formula, if $\beta \gg [\mathrm{Trp}]$. This lowering is, here, not sufficiently counteracted by the rising of q, ending up into a lower Q.

3.2. Photo- and thermo-reactivity of photoproducts

In order to investigate if the photoproducts can be converted back to their precursor, solutions of **5** and **6** in acetonitrile have been irradiated with UV light. While **5** gives only decomposition products, **6** photoisomerizes to **5**. No photoreversion to the precursor **1** was observed; this behaviour appears to be different from that shown by endoperoxides of some polycyclic aromatic compounds (ARPOS) for which an irradiation wavelength-dependent photochemistry was observed [27,28]. For example the 1,4-endoperoxides prepared from 1,4-dimethylanthracenes showed partial cycloreversion on irradiating at $\lambda = 320$ nm, while they rearranged to diepoxides on irradiating at $\lambda = 395$ nm [29]. This was due to a $\pi \rightarrow \pi^*$ excitation of the aromatic moiety in the first case, and to a $\pi^*_{\text{o-o}}\sigma^*_{\text{o-o}}$ excitation of the endoperoxide chromophore in the second one. With our substrates the situation is quite different as the peroxidation changes drastically the electronic nature of the original tropone nucleus.



11

R=C_6H_{13}, R'= $C_6H_4OC_{12}H_{25}$

Scheme 4.

A thermal treatment of solutions of **5** in acetonitrile gives many unidentified products, whereas an analogous treatment of **6** brings to a single product, **11** (see Scheme 4). The intensity of the chromatographic peak relative to **6** was measured as a function of time. It has been found that the thermal decomposition of **6** is a first order reaction with a rate constant of 2.9×10^{-3} min^{-1}.

These investigations show that the photoproducts obtained from **1**, in solution, are not reversible to the precursor, neither via photochemical nor via thermal processes. Moreover, oxygenated photoproducts derived from **2** and from **3** cannot be satisfactorily converted back to their respective precursors in solution phase. The stability tests, described in Section 2, show some differences between the six endoperoxides, which, however, are all very stable to the usual work-up, in opposition to what usually found for this kind of compounds. Finally, polarizing optical microscopy studies indicate that they do not show any mesophase.

4. Conclusions

The idea that the phototransformation of the 2-acyloxy-5-alkoxytropone core, responsible for the mesomorphism of two of the three compounds here studied, could be performed and, consequently, that photoregulation of this property was possible, revealed to be correct. The photogenerated endoperoxides do not show any liquid crystalline phase, so that the phototransformation of mesogenic 2-acyloxy-5-alkoxytropones at a target point destroys the mesomorphic molecular local order. This is a writing process. Using Vis light to read, the fading of information, which is a shortcoming of pure photochromic substrates, could be avoided. Unfortunately, the lack of both thermal and photochemical reversibility to the precursors, at least in solution, might detract some interest in these substrates. On the other side, the neat production of stable endoperoxides is interesting from a synthetic point of view. In fact this reaction proved to be particularly efficient for the regio- and diastereoselective oxyfunctionalization of cyclic dienes [12,13,29].

Acknowledgements

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References

[1] A. Mori, M. Uchida, H. Takeshita, J. Am. Chem. Soc. 112 (1990) 8635.
[2] K. Kida, A. Mori, H. Takeshita, Mol. Cryst. Liq. Cryst. 199 (1991) 387.
[3] A. Mori, H. Takeshita, R. Nimura, M. Isabe, Liq. Crystals 14 (1993) 821.
[4] S. Masamune, A.W. Kemp-Jones, J. Green, D.L. Rabenstein, M. Yasunami, K. Takase, T. Nozoe, J. Chem. Soc. Chem. Commun. (1973) 283.
[5] O.L. Chapman, D.J. Pasto, J. Am. Chem. Soc. 82 (1960) 3645.
[6] D.J. Pasto, Organic Photochemistry 1 (1967) 155.
[7] O.L. Chapman, in: W.A. Noyes, G.S. Hammond, J.N. Pitts (Eds.), Advances in Photochemistry, Vol. 1, Interscience, New York, 1963.
[8] H. Dürr, in: H. Dürr, H. Bouas-Laurent (Eds.), Photochromism Molecules and Systems, Chap. 6, Elsevier, Amsterdam, 1990.
[9] L. Calucci, D. Catalano, M. Cavazza, C.A. Veracini, Mol. Cryst. Liq. Cryst. 266 (1995) 197.
[10] D. Catalano, M. Cavazza, E. Ciampi, C.A. Veracini, Mol. Cryst. Liq. Cryst. 275 (1996) 163.
[11] H.D. Brauer, R. Schmidt, in: H. Dürr, H. Bouas-Laurent (Eds.), Photochromism Molecules and Systems, Chap. 15, Elsevier, Amsterdam, 1990.
[12] M. Balci, Chem. Rev. 81 (1981) 91.
[13] Yu.A. Arbuzov, Russian Chem. Rev. 34 (1965) 558.
[14] I. Saito, S. Sarma, in: S. Patai (Ed.), The Chemistry of Functional Groups, Peroxides, Wiley, 1983.
[15] T. Nozoe, T. Hirai, T. Kobayashi, H. Hayashi, Tetrahedron Letters 40 (1970) 3501.
[16] T. Kobayashi, T. Hirai, J. Tsunetsugu, H. Hayashi, T. Nozoe, Tetrahedron 31 (1975) 1483.
[17] M. Cavazza, R. Cimiraglia, M. Persico, M. Zandomeneghi, F. Pietra, J. Photochem. Photobiol. A: Chem. 61 (1991) 329.
[18] M. Cavazza, M. Zandomeneghi, F. Pietra, J. Chem. Soc. Chem. Commun. (1990) 1336.
[19] M. Oda, Y. Kitahara, Tetrahedron Letters 38 (1969) 3295.
[20] E.J. Forbes, J. Griffiths, J. Chem. Soc. (C), (1968) 572.
[21] E.J. Forbes, J. Griffiths, J. Chem. Soc. (C), (1968) 575.
[22] A. Mori, H. Suizu, H. Takeshita, Bull. Chem. Soc. Jpn. 60 (1987) 3817.
[23] A. Mori, H. Takeshita, Bull. Chem. Soc. Jpn. 60 (1987) 3037.
[24] E.J. Forbes, J. Griffiths, J. Chem. Soc. (C), (1966) 2072.
[25] E.J. Forbes, J. Griffiths, J. Chem. Soc. (C), (1967) 600.
[26] J. Rigaudy, M.C. Perlot, D. Simon, N.K. Cuong, Bull. Soc. Chim. Fr. (1976) 493
[27] J. Rigaudy, A. Defoin, J. Baranne-Lafont, Angew. Chem. Ed. Int. Engl. 91 (1979) 443.
[28] J. Rigaudy, A. Caspar, M. Lachgar, D. Maurette, C. Chassagnard, Bull. Soc. Chim. Fr. 129 (1992) 16.
[29] A.G. Griesbeck, T. Deufel, K. Peters, E.-M. Peters, H.G. von Schnering, J. Org. Chem. 60 (1995) 1952.