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DABCO effect on the photodegradation of photochromic compounds in spiro[indoline-pyran] and spiro[indoline-oxazine] series

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Abstract

Photochromic compounds are involved in secondary oxidative reactions of photodegradation leading to the loss of their properties. The analytical studies of this process in toluene solution of both photochromic molecules, i.e. the 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,2'-[3H]naphth[2,1-b]pyran] and the 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]-naphth[2,1-b][1,4]oxazine], have allowed us, by identification of the main photoproducts, to propose some mechanisms for the oxidative degradation processes which occured by radical structures or singlet oxygen. In order to prove the implication of this last species in the degradation process, we have tested the effect of a singlet oxygen quencher with experimental spectrophotometric apparatus: the 1,4-diazabicyclo[2,2,2]octan (DABCO) which exhibits an important increase of the fatigue resistance of photochromic compounds. This quantitative aspect of the DABCO effect has been completed by a qualitative degradation approach concerning a comparative analytical study by gas chromatography between degradation of photochromic compounds with and without DABCO. In those conditions we have observed a significant change in the chromatographic profiles.

Keywords: DABCO; Photodegradation; Photochromism; Spiro[indoline-pyran]; Spiro[indoline-oxazine]

1. Introduction

Photochromic compounds are thermally reversible dyes under UV light irradiation [1]. The colored open photomerocyanine takes place after the heterolytic and/or the homolytic cleavage (Scheme 1) of the C–O bond of the colorless form with formation of a biradical in the second case [2]. These species reacting with the molecular oxygen have been considered for a long time as the major factor responsible [3] for the degradation of the photochromic compounds. This process represents a severe restriction for some industrial uses of these dyes.

After Gautron who had initiated degradation studies [4] on spiropyrans in the 1960s concluding that oxygen was involved in photodegradation, few general studies of the degradation processes have been undertaken according to a qualitative approach by the identification of the different photoproducts generated after the continuous irradiation of some photochromic molecules in toluene solution [5,6] or in the solid state [7]. Subsequently some mechanisms about the photodegradation processes [8] have been proposed and particularly the intervention of the singlet oxygen in those oxidative reactions. In order to support these last mechanisms concerning the singlet oxygen involvement in the photodegradation processes, we have proposed a quantitative approach completed by a qualitative one. This study was carried out by using a singlet oxygen quencher, 1,4-diazabicyclo[2,2,2]octan, also called DABCO. This structure was advised by the literature [9] for its well-known deactivation singlet oxygen properties dispensed without interaction with the photochromic characteristics of the compounds studied (UV transparency, chemically unreactive).

An experimental spectrophotometric prototype [10] available in our laboratory is designed to measure the fatigue resistance of the photochromic compounds. So, in terms of quantitative aspects of the photodegradation, the DABCO has been tested by using this apparatus called Degraphot on both photochromic molecules, the 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-

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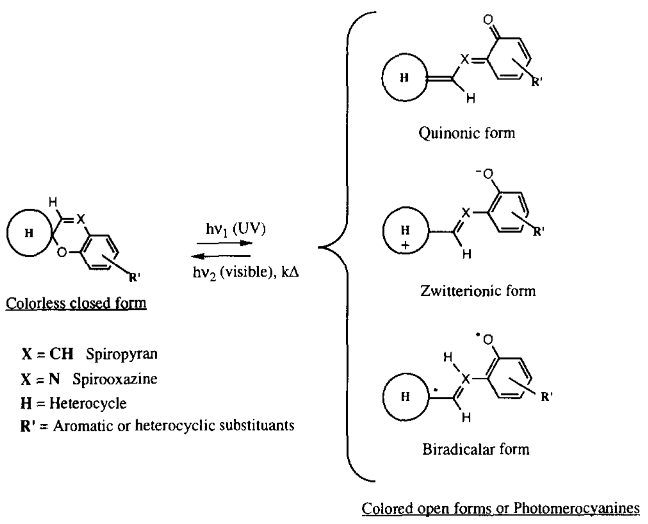
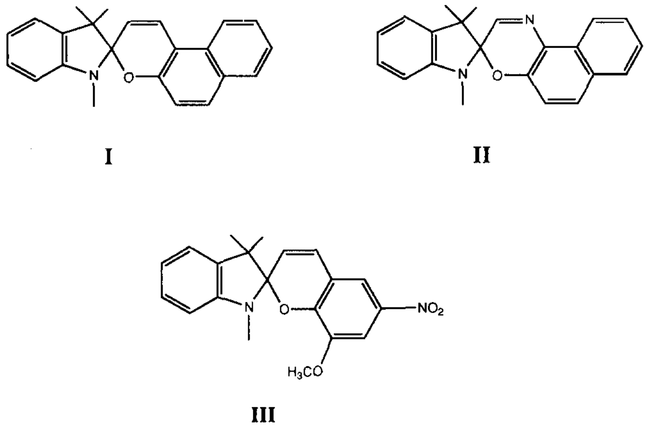


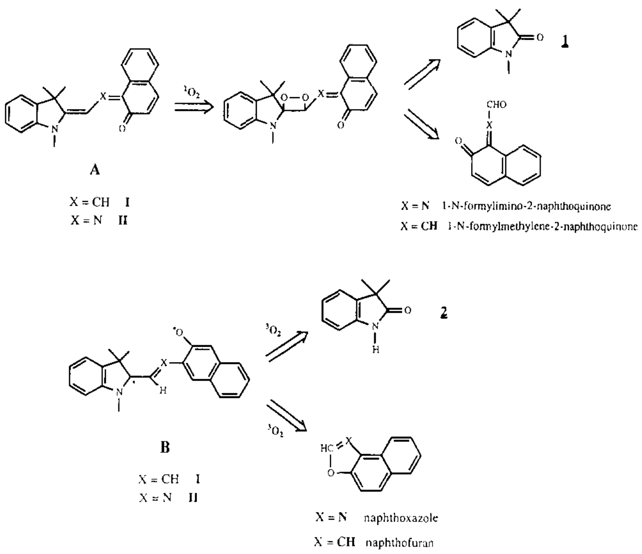
Scheme 1. Photochromic equilibrium between the closed and open forms.



Scheme 2. Structure of the studied photochromic compounds and their main identified photoproducts.

[3H]naphth[2,1-b][1,4]oxazine] **II** and the 1,3-dihydro-8'-methoxy-6'-nitro-1,3,3-trimethylspiro-[2H-indole-2,2'-[3H]benzopyran] **III** (Scheme 2). In all the cases an improve of the stability of the photochromic compounds in toluene solution has been noticed.

These preliminary results lead us to develop a qualitative study of the singlet oxygen role consisting in a comparison between the degradation in toluene solution of both photochromic compounds (Scheme 2): **I** (the 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]naphth[2,1-b]pyran]) and **II**, in presence and in absence of DABCO. This comparative study proceeds by gas chromatographic analysis of the main photoproducts generated under UV irradiation of the photochromic compound (**I** or **II**). Among these photoproducts, the 1,3,3-trimethyloxindole **1** and the 3,3-dimethyloxindole **2** resulting from the oxidation of the identical indolinic part of the studied photochromic compounds, represent the only common fragments of the two pre-cited series. Furthermore, according to the



Scheme 3. The different photoproducts generation ways.

mechanisms [8] recently proposed, **1** was a photoproduct generated via the dioxetan pathway happening after the singlet oxygen attack on the various dienic systems present in the open form (A) of these molecules. Indeed the singlet oxygen quenching by the closed and the open forms of some photochromic molecules has been previously demonstrated [11]. Secondly, the 3,3-dimethyloxindole **2** formation [12] proceeds by interaction between a biradicalar open form (B) with the triplet oxygen (Scheme 3). So in order to tackle the mechanistic aspect of the singlet oxygen involvement in the degradation processes, we have exposed in the second part of this paper, a comparative study on the formation of **1** and **2** in presence and in absence of DABCO.

2. Quantitative study

The Degraphot apparatus allows measurements in order to establish a structure–property relationship between different series or within a series, between different photochromic compounds. These investigations are described in terms of fatigue resistance by the determination of a parameter $t_{Ao/2}$ (time in minutes necessary to reduce the initial colorability Ao to Ao/2). The irradiation is realized in a continuous mode by use of a 250 W xenon arc lamp (XBO Osram with a filter, WG Schott France, cutting off at 295 nm) presenting a spectrum closed to the solar one.

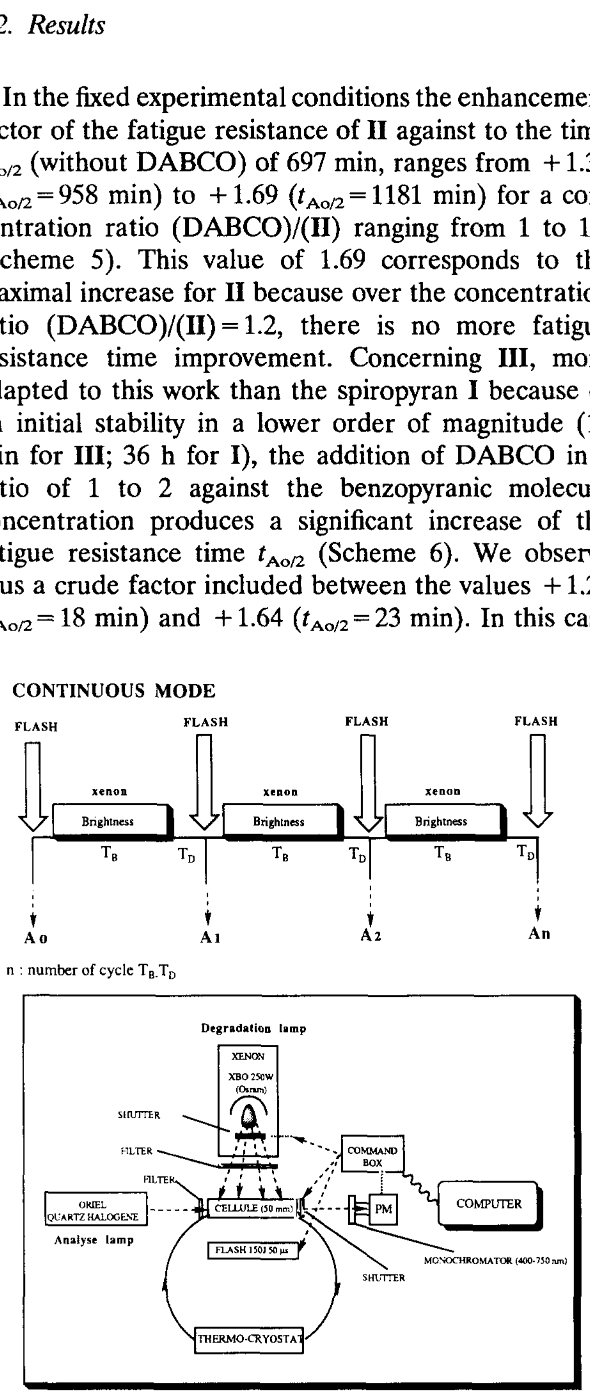
2.1. Apparatus description

For the measurement of the fatigue resistance, a specific apparatus simulating irradiation conditions closed to the daylight exposure, has been developed.

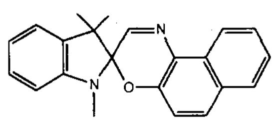
This computer-controlled apparatus is designed to monitor and analyse the photodegradation process by continuous xenon lamp irradiation. The continuous degradation mode (Scheme 4) is characterized by a sequence of successive brightness (T_B) and darkness (T_D) periods. At the end of every sequence (T_B–T_D), a brightness shutter is closed, a measurement flash is triggered and a kinetic scan is started. Simultaneously, an $I=f(t)$ graph is registrated. At the end of the experiment the fatigue resistance time $t_{Ao/2}$ (time when Ao/2 absorbance is reached) is calculated by an interpolation method.

2.2. Results

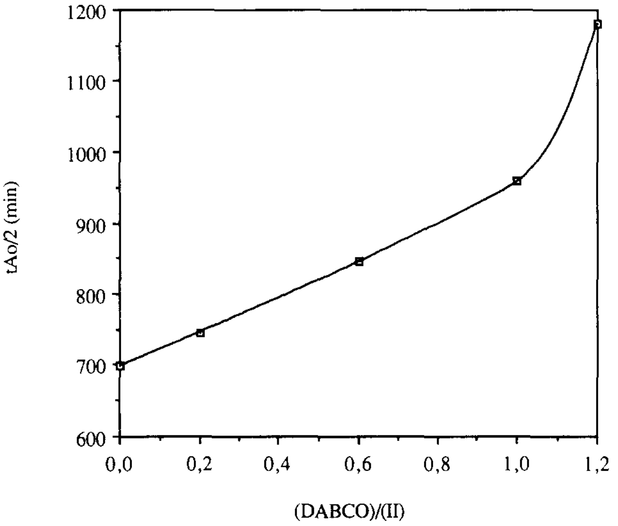
In the fixed experimental conditions the enhancement factor of the fatigue resistance of **II** against to the time $t_{Ao/2}$ (without DABCO) of 697 min, ranges from +1.37 ($t_{Ao/2}=958$ min) to +1.69 ($t_{Ao/2}=1181$ min) for a concentration ratio (DABCO)/(**II**) ranging from 1 to 1.2 (Scheme 5). This value of 1.69 corresponds to the maximal increase for **II** because over the concentration ratio (DABCO)/(**II**) = 1.2, there is no more fatigue resistance time improvement. Concerning **III**, more adapted to this work than the spiropyran **I** because of an initial stability in a lower order of magnitude (14 min for **III**; 36 h for **I**), the addition of DABCO in a ratio of 1 to 2 against the benzopyranic molecule concentration produces a significant increase of the fatigue resistance time $t_{Ao/2}$ (Scheme 6). We observe thus a crude factor included between the values +1.28 ($t_{Ao/2}=18$ min) and +1.64 ($t_{Ao/2}=23$ min). In this case the highest increment (3.86) of $t_{Ao/2}$ (54 min) occurs with an important ratio (DABCO)/(**III**) = 100.



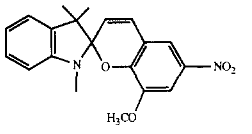
Scheme 4. Description of the degradation mode of Degraphot apparatus.



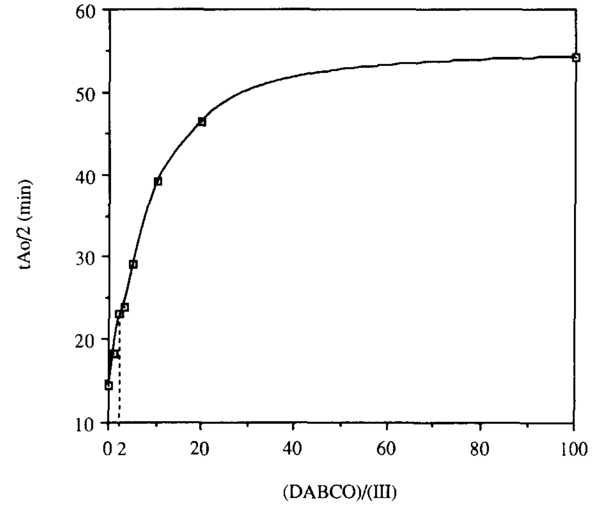
II



Scheme 5. Improvement of the fatigue resistance of II consecutive to the DABCO addition.



III



Scheme 6. Improvement of the fatigue resistance of III consecutive to the DABCO addition.

2.3. Discussion

In all the cases, we have verified that this stabilization takes place without any modification of the other spectrophotometric parameters (initial colorability Ao measured in OD:$Ao_{II}=0.4$, $Ao_{III}=0.72$; thermal bleaching kinetic constant k_D: $k_{DII}=0.38$ s^{-1}, $k_{DIII}=0.03$ s^{-1}) measured with identical conditions by the Degraphot apparatus. Therefore for the ratios 1 to 2 we can outline a similar stabilization rate by the DABCO for the both series ranging from +1.28 to +1.69. However the limit value for the DABCO effect depends on the series and we observe that this limit is lower ((DABCO)/(**II**) = 1.2) in the case of a more resistant molecule like the compound **II** than for a rapidly degradable dye as the benzopyran **III** ((DABCO)/(**III**) = 100). This indicates that the molecule structure influences the singlet oxygen contribution in the degradation processes. Indeed, the activation of oxygen (singlet oxygen formation) occurs by reaction of excited triplet sensitizers as the xanthene dyes (rose bengal or erythrosin) with oxygen [13,14]. It is possible that every photochromic compound, in terms of dye through the photomerocyanine formation, shows different efficiencies for photosensitizing the triplet oxygen $O_2(^3\Sigma_g^-)$ to the lowest excited singlet state $O_2(^1\Delta_g)$. This presumption is supported by two photophysic considerations: firstly, a nitro substitution, as for **III**, induces for the photomerocyanine formation a major triplet pathway, while for unsubstituted indolinospiropyrans (type **I**) or indolinospirooxazines (type **II**), photocoloration proceeds mainly via the singlet channel [15–17]. Secondly, according to the calculations of the formation heat of the lowest triplet state of the photomerocyanines realized by the AM1 method [18,19], the energy–transfer reaction necessary for the singlet oxygen formation [14] could occur more efficiently with the triplet excited state of the photomerocyanine of **III** than with the triplet excited state of the photomerocyanine of **II**. We have to precise that those calculated energies are surestimed. So, the correlated results of the limit value for the DABCO effect with the AM1 calculations are in agreement with the assumption that the photomerocyanine could be involved with a more or less high efficiency as a triplet sensitizer in the singlet oxygen generation.

On the other hand, these experiments of DABCO addition show the weakly fatigue resistance of **III** when compared with the naphthoxazine **II** which could be attributed to the triplet pathway for two reasons: the triplet channel is known to be more efficient in the photocoloration process than the singlet one [15,16]; when photocoloration proceeds preferentially via the singlet channel, as observed for unsubstituted **I** or **II**, low quantum yields of photomerocyanine formation have been reported [17]. Thus, lower fatigue resistance of **III** could be due firstly to a higher concentration of open forms subjected to oxidative photodegradations and secondly to a high ratio of diradicalar species [2] (directly issued from the triplet state) induced during the spiro ring opening processes, which react easily with molecular oxygen. These observations confirm that the oxidative degradation of photochromic compounds proceeds in part via the interaction of the singlet oxygen species with preferentially the dienic open forms [11].

Indeed using the parameter $t_{Ao/2}$ determination, we have evaluated the DABCO effect. Nevertheless, we have developed a complementary qualitative approach by carrying out photoproduct analysis in order to know whether the oxidative way takes place partly due to attack by singlet oxygen on the various diene systems [13,14] present essentially in the quinonic open (A) form (Scheme 3).

3. Comparative analytical qualitative study

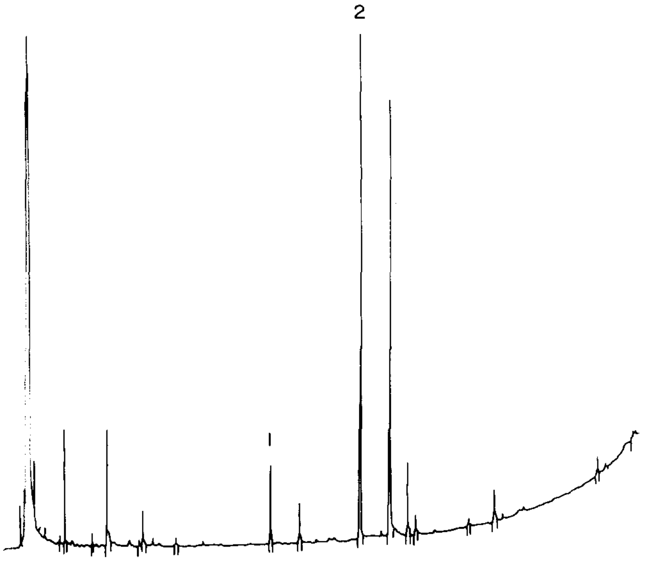
3.1. Results

The compounds **I** and **II** were degradated under UV light irradiation using a 500 W mercury lamp in toluene solution. After the analysis of the main photoproducts by gas chromatography, their own structure [6] was determined by comparison with synthesised standards. Further different mechanisms of degradation were suggested in order to explain the photoproducts generation due to attack of singlet oxygen on probably the dienic open forms [8] or molecular oxygen on biradicalar species [12]. In the first case (singlet oxygen intervention) we should obtain the compound **1**. The second one (triplet oxygen–biradicalar open forms interaction) leads to the compound **2** (Scheme 3). Therefore a singlet oxygen quencher should prevent the singlet oxygen-dependent photoproduct formation like for the compound **1** against the compound **2** becoming from oxidation by the triplet oxygen. That is what we observed in the present work.

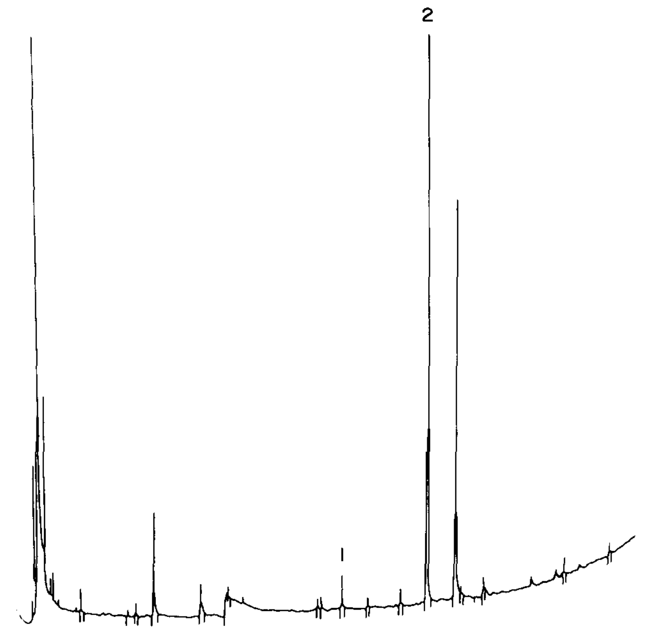
The separated photoproducts chromatographic plots in presence of DABCO or not are represented for the spiropyran **I** in Schemes 7 and 8 and concerning the spirooxazine **II** in Schemes 9 and 10. The most striking feature emerging from the comparison of both chromatograms of each series is the enhanced production of 3,3-dimethyloxindole **2** against its trimethylated homologous the 1,3,3-trimethyloxindole **1** in presence of DABCO (Table 1).

Table 1
Increased production of the 3,3-dimethyloxindole **2** against the 1,3,3-trimethyloxindole **1** relative to the DABCO addition, during the photodegradation of the naphthopyran **I** and the naphthoxazine **II**

	I	II
2/1 ratio without DABCO	6.5	0.5
2/1 ratio with DABCO	20	4.6



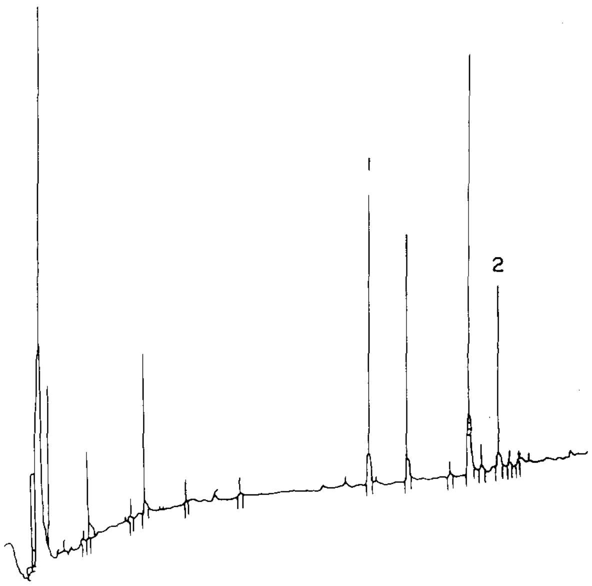
Scheme 7. GC-FID chromatogram of the degradated photochromic compound **I** without DABCO and under a 500 W/2 high pressure mercury lamp (HBO Osram).



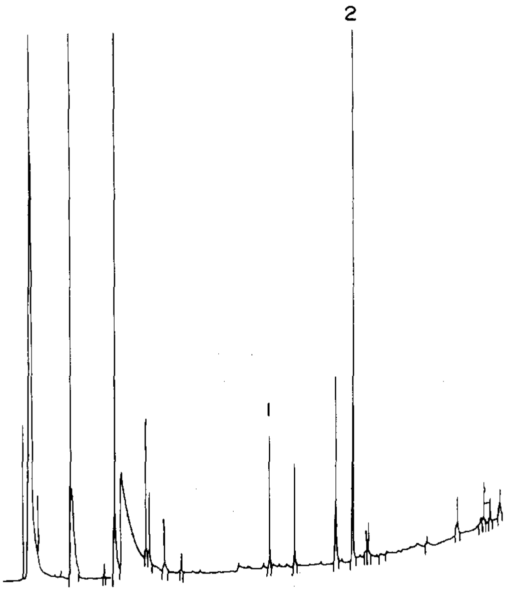
Scheme 8. GC-FID chromatogram of the degradated photochromic compound **I** in DABCO presence and under a 500 W/2 high pressure mercury lamp (HBO Osram).

3.2. Discussion

This phenomenon was reported in the both series even with an inversion of the quantitative ratio (**1**)/(**2**) for the spiro molecule **II**. Further studies reveal the DABCO effect on the other fragments production. Presently we can affirm a general quantitative and qualitative modification of the naphthopyran and naphthoxazine behaviour by the DABCO addition.



Scheme 9. GC-FID chromatogram of the degradated photochromic compound **II** without DABCO and under a 500 W/2 high pressure mercury lamp (HBO Osram).



Scheme 10. GC-FID chromatogram of the degradated photochromic compound **II** in DABCO presence and under a 500 W/2 high pressure mercury lamp (HBO Osram).

4. Experimental part

The studied photochromic compounds, **I**, **II** and **III**, are prepared in the Group “Photochromes organiques-Matériaux” URA CNRS 1320, Faculté de Luminy, Marseille, France.

4.1. Degraphot experiments

The spectrophotometric apparatus is described in a recent publication [10]. The studied photochromic compounds, **I** and **II** ($C = 0.5 \times 10^{-5}$ M) and the DABCO, commercially available (Aldrich), are dissolved in anhydrous toluene (SDS France).

4.2. Photodegradation experiments

The molecules **I**, **II** ($C=10^{-3}$ M) and the DABCO ($C=0.5\times10^{-3}$ M) were also dissolved in anhydrous toluene (SDS France). The aerated solutions were irradiated in a quartz flask with magnetic stirring with a 500 W/2 high pressure mercury lamp (HBO Osram) housed in a light box (Arquantiel, Ile St Denis, France). The different irradiated solutions are analyzed regularly by gas chromatography till the complete bleaching of the solutions.

4.3. Photoproducts analyses

The gas chromatography system (GC) consists of a Girdel equipped with a Ross injector, a FID detector and a column SGE 0.32mm*12 m capillary column (SGE Corp.) coated with BP5 (film 0.5 μm, pHe = 0.9 bar).

5. Conclusion

The involvement of the singlet oxygen in the photodegradation processes is supported by the DABCO effect on the measurements of the times $t_{Ao/2}$ and on the evolution of the chromatographic profiles. Indeed, this stabilizer is able to considerably increase the fatigue resistance time of the studied photochromic compounds. This tendancy is directly related to the photochromic structure and probably to the nature of the pathway (singlet or triplet) implicated in the photomerocyanine excited states formation. Qualitatively, according to the mechanisms refering a singlet oxygen dependent generation for the fragment **1**, the production of **2** (issued exclusively from a biradicalar process) is largely favoured against its trimethylated homologous, the 3,3-trimethyloxindole **1**.

These preliminary results could be confirmed and extended with the developement of this quantitative and qualitative study to further compounds.

Acknowledgements

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