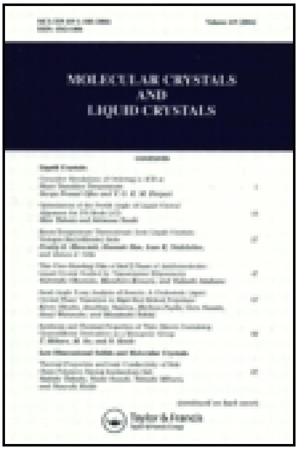

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# The Chemistry of Photomerocyanines

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# THE CHEMISTRY OF PHOTOMEROCYANINES

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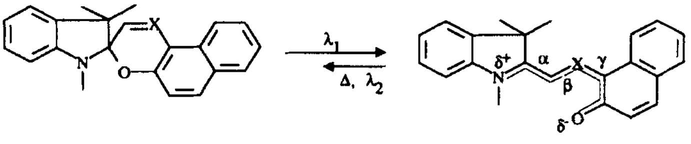
Spiropyrans(SP), spirooxazines(SO), chromenes(CH), and fulgides photo- and thermal degradation mechanisms are reviewed. For SO it is reported that thermal and photodegradation have common mechanism pathways. The reaction with free radicals results in adducts formation and loss of photochromic properties.

*Keywords:* Photochromes; spiropyrans; spirooxazines; fulgides; merocyanines

## INTRODUCTION

The most promising classes of photochromic materials so far reported are spiropyrans (SP)[1] and spirooxazines (SO)[2] in which the heterocyclic and a chromene moiety are orthogonally linked through a $C_{spiro}$ carbon atom. Upon UV excitation SP's and SO's undergo a deep color change to give the corresponding open form, a merocyanine (MC), Scheme 1



SP; X = CH
SO; X = N

MC

SCHEME 1

Practical applications such as in recording, displaying, and copying, optical fibers, sunlenses, and special gadgets have been envisaged.[3,4]

The nitroderivatives of spirobenzopyrans, $SP_{NO2}$, are endowed with high colorability but lack sufficient durability for long-term applications. On the other hand SO's are characterized by high stability with respect to photoexcitation. Resistance to photochemical fatigue is, in principle, determined by the reactivity of the excited states of the spiro and/or merocyanine form(s), and is linked to the photophysical properties of the given photochrome.

It has been reported [5,6] that in the case of $SP_{NO2}$'s, a triplet state, $^3SP_{NO2}$, plays an important role in the photocoloration process:

$$SP_{NO2} \longrightarrow {}^1SP_{NO2} \longrightarrow {}^3SP_{NO2} \longrightarrow MC$$

whereas for other spiropyrans SP's photoreaction is dominated by excited singlet states, $^1SP$

$$SP \longrightarrow {}^1SP \longrightarrow MC$$

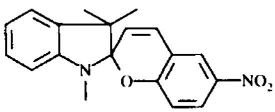
According to Malkin et al.[7] the photodegradation of nitro-substituted SP's originates from the reaction of an unstable isomer X, cis-cisoi d X isomer, with solvent or impurities

$$\text{photodegrad} \rightleftarrows X \rightleftarrows MC \rightleftarrows MC \longrightarrow \text{isomers}$$

Photooxidation is instead the result of the reaction of the closed form SP triplet state with oxygen. The fate of the X isomer has been thouroughly investigated and its role and position in elaborated photophysical schemes has been reported by many authors. [5-8]

## DEGRADATION OF SPIROPYRANS

In 1968 Gautron[9], was the first to investigate the photodegradation of 6-nitro-BIPS and several other derivatives



The isolated degradation products were 5-nitro-o-vanillin (30%), 1,3,3-trimethyloxindole (10%), and 3,3-dimethyloxindole (8.7%), with the balance being tars.

The reactivity(photodegradation) of spiropyrans substituted on the aromatic ring of the indoline moiety obeys the Hammett equation and is rationalized in terms of inductive and mesomeric effects.[8]
Gautron concluded that degradation is partially an oxidation process and autoxidation plays a role in photodegradation. Homolytic cleavage of SP's yields biradicals that react with molecular oxygen to give oxindoles and salicylaldehydes

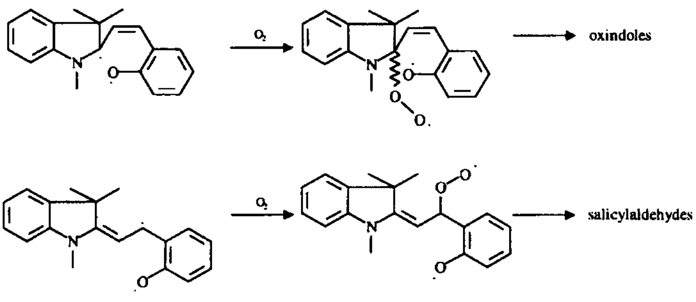


FIGURE 1

In 1990 Malkin et al.[7] critically reviewed the structure-photostability correlation proposed by Gautron. They have shown that the degradative quantum yield $\Phi_d$ is mostly determined by the structure of the chromene moiety and independent of the heterocyclic part of the SP structure. Photodegradation and photooxidation are two parallel and concurrent processes the first one being determined by the reaction of the cis-cisoid X isomer with solvent and impurities. Photooxidation results instead from the reaction of the triplet state of MC with $O_2$. The solvent affects photodegradation that is about 100 times slower on going from hexane to acetonitrile.[9]

The presence in the system of excited-state quenchers or sensitizers may slow down or accelerate the fatigue.[8]

## PHOTODEGRADATION OF SPIROOXAZINES

SO's are in general more stable than SP's. Photodegradation is a function of the irradiation wavelength and light intensity.[10] Most effective in promoting photodegradation is the absorption at 294 and 320 nm. Polarity of the solvents does not appreciably affect photodegradation of spirooxazines.

The major photodegradation products are 1,3,3-trimethyloxindole, 3,3-dimethyloxindole and 1,2,3,4-tetrahydro-2,3-dioxo-4,4-dimethyl quinoline and naphth[1,2-d] oxazole.[11]

The photooxidation of SO's may result from the interaction of the biradicaloid form of MC with $O_2$ or from the reaction of singlet oxygen $^1O_2$, derived from the sensitizing action of an unspecified sensitizer, with MC.[11]

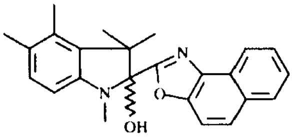
A study of Malatesta et al.[12] has shown that SP and their MC forms are not able to sensitize $^1O_2$ formation and, on the contrary, are good physical quenchers of $^1O2$ if generated in solution.

A solvent dependence of the photooxidative degradation process was noted[12] with degradation being much faster in more polar solvents. This behavior seems to support the formation of a charge-transfer (CT) complex of the type $MC^+ \ldots\ldots O_2^-$ on the reaction coordinate

$$\mathbf{SO(SP)} \rightarrow \mathbf{MC} \rightarrow {}^1\mathbf{MC} \rightarrow {}^3\mathbf{MC} \rightarrow [\mathbf{MC^+ \ \ O_2^-}]$$

$$\rightarrow \quad \text{oxidation products}$$

Under controlled irradiation conditions a rearranged oxidized product was isolated and its structure confirmed by X-ray[12]



Firth at al.[13] have reached the same conclusions of Malatesta et al.[12]

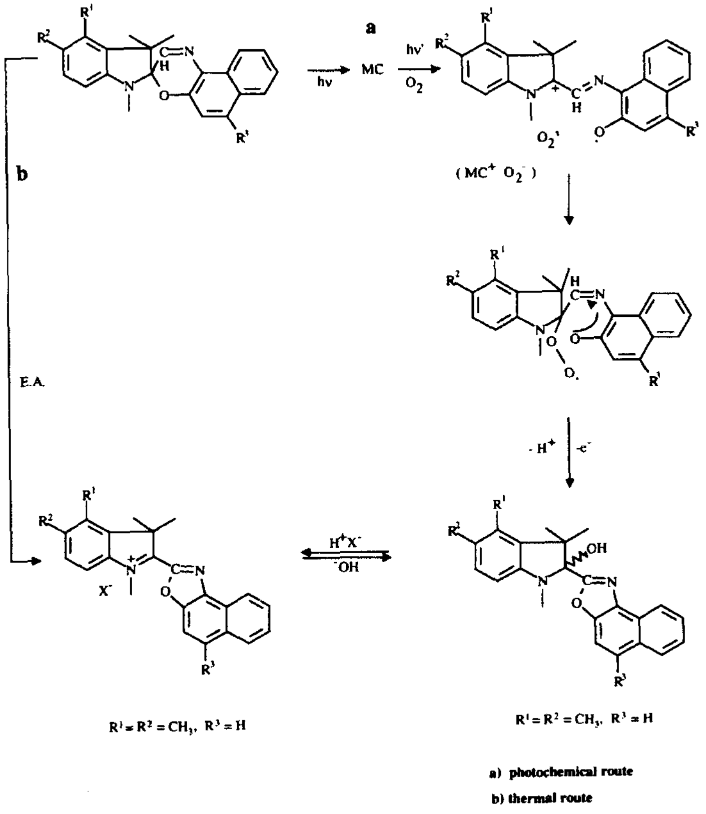
Guglielmetti and coworkers[14] invoke formation of ‘$O_2$ to explain the different product distribution observed where toluene solution of SO's and SP's are photolyzed in the presence or absence of a typical singlet-oxygen quencher such as 1,4 diazabicyclo[2.2.2.] octane, DABCO

$^3O_2$ and $^1O_2$ by reacting with MC's give different products.

In polar solvents the spiro-form cleaves heterolytically to MC and $^1O_2$ degradation pathway is thought to be dominating.[14]

## THERMAL DEGRADATION OF SPIROOXAZINES

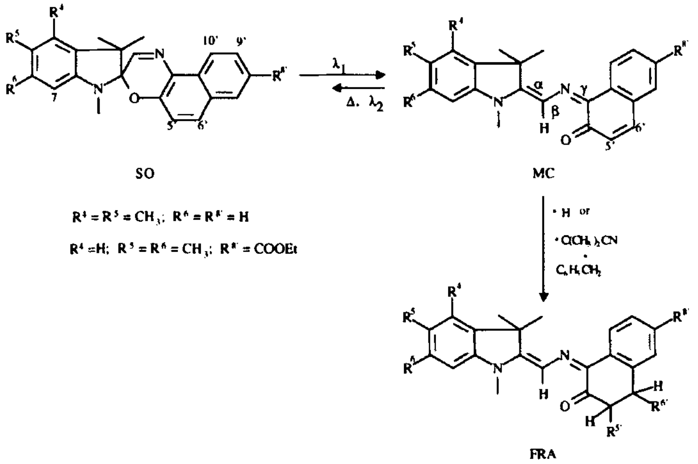
Malatesta et al.[15] have shown that thermal dark reactions yield the same intermediate oxidation products as those formed during photodegradation as a result of electron-transfer process from SO or its MC form to a suitable electron-acceptor EA.



SCHEME 2

## REACTION OF SO's WITH FREE RADICALS

It has been clearly shown that the 5',6' double bond of the merocyanine form of SO's is easily attacked by free radicals to give free radicals adducts (FRA), thermally stable highly coloured degradation products Malatesta et al. [16] have isolated such products and found that free radicals are detrimental for the stability of SO's.



SCHEME 3

We have recently reported [17] that in the case of 6,8-dinitroBIPS a proton of the methine bridge is easily exchanged with deuterium and may concur to degradation of MC through a mechanism not thoroughly investigated.

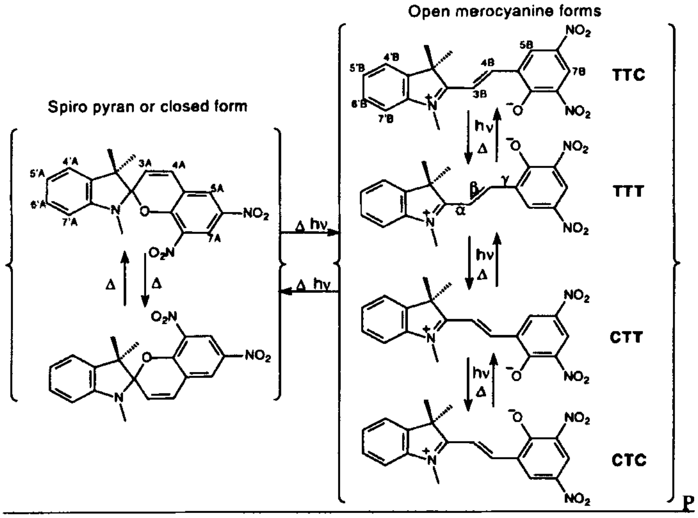
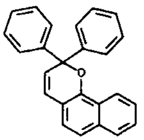


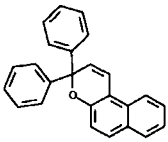
FIGURE 2

## PHOTODEGRADATION OF CHROMENES

CH's undergo degradation to give among other products benzophenone(s) and β-phenylcynnamaldehyde(s). The two series A and B give a different ratio of these two products, 3.9 and 0.98 respectively and this seems to suggest a different degradation pattern.



**Series A**



**Series B**

## PHOTOSTABILITY OF FULGIDES

The photocoloration of fulgides is based on the photocyclization reaction to a 1,8 α-dihydronaphthalene.

Many fulgides undergo a range of remarkable reactions, including [1.5]hydrogen shift, photochemical [1.3]-hydrogen shifts and oxidation

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