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# Sensitized Photochromism: Effect on Degradation Product Distribution

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# SENSITIZED PHOTOCHROMISM: EFFECT ON DEGRADATION PRODUCT DISTRIBUTION.

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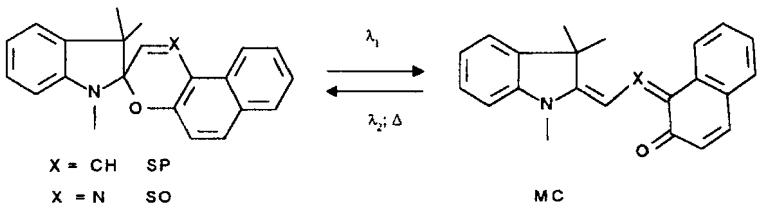
Abstract In the presence of a triplet sensitizer such as camphorquinone the photodegradation of spiro-indolinonaphthoxazines in oxygen-saturated acetonitrile solutions can be achieved with visible light. From the resulting degradation product distribution it becomes evident that the formation of 3,3-dimethyloxindole and its derivatives is enhanced when compared to UV-induced photolysis, thus suggesting that these compounds originate from the spiro-indolinonaphthoxazine promoted to the first excited triplet state by energy transfer from the sensitizer.

## INTRODUCTION

Photochromism of spiro-indolinonaphthoxazines and -pyrans results from their ability to undergo a reversible ring-opening[1] from the colorless closed spiro form to the open colored merocyanine form when submitted to UV-irradiation (SCHEME 1).




SCHEME 1

This characteristic could be exploited in a number of industrial applications if compounds resistant to photochemical fatigue i.e. able to sustain a large number of cycles without degradation were available. Unfortunately, after a prolonged exposure of the

photochromes to UV-irradiation secondary reactions set in, both in the presence[2-5] and in the absence[6] of oxygen, leading eventually to a complete loss of the photochromic properties.

The present study was carried out in the context of the research into the mechanisms governing the photodecomposition of spiro-oxazines and consisted in the examination of the product distribution obtained from exhaustive photolysis of a spirooxazine such as 1,3,3,4,5-pentamethylspiro-indoline-2,3'[3H]naphth[2,1-b][1,4]oxazine (PHD) under different conditions.



## RESULTS AND DISCUSSION

Prolonged exposure of a solution of PHD in acetonitrile (ACN) to UV-irradiation results in a change of the blue color of the merocyanine to greenish, turning more and more yellow as the photolysis proceeds. After some 30-40h, a number of degradation products are present, some of which show as strongly fluorescent spots on the silica surface of a thin-layer chromatography plate. The oxidation products resulting from the splitting of the initial molecule into two halves, i.e. 1,3,3- trimethyloxindole (I) and naphth[1,2-d]oxazole (II) (FIGURE 1) are always present in consistent amounts and are identified by comparison with known standards using HPLC chromatography. GC-mass spectrometry in this case could be unreliable as the presence of these products may result from the decomposition of some thermolabile photodecomposition product.

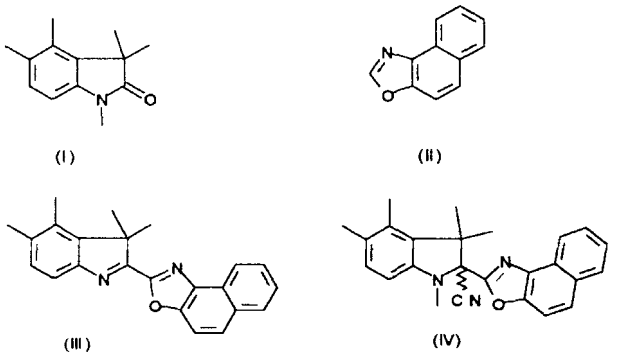
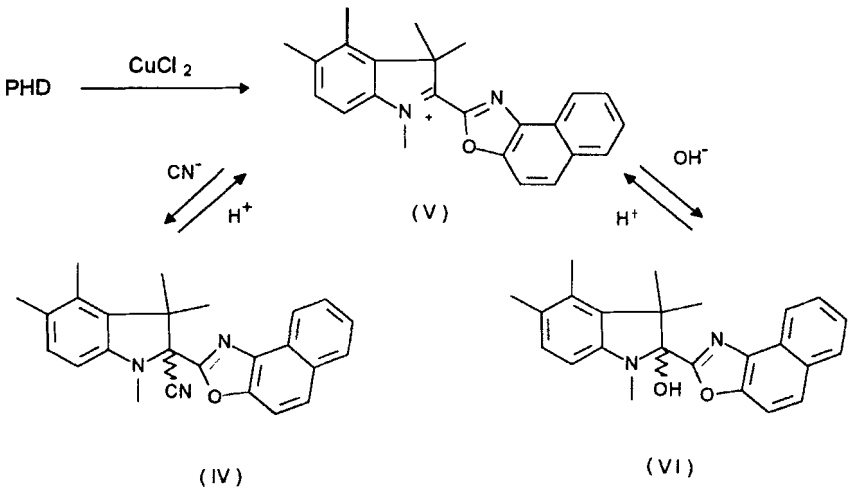



FIGURE 1

By column chromatography a strongly fluorescent blue fraction was separated that after evaporation of the solvent yielded pale yellow crystals, identified by $^{1}H$ -NMR, $^{13}C$ - NMR and mass spectromery as (III) (FIGURE 1).This is the first oxidation product containing both the naphthoxazine and the oxindole moieties identified in a photolysis mixture. This compound starts to form straight away when oxygenated solutions of PHD are irradiated with UV-light. It is itself stable towards photolysis and in the analytical conditions of gaschromatography.

A second main photodegradation product (IV) was isolated that has a cyano group attached to the former $C_{spiro}$ and, in analogy with the precedently described decomposition product, has undergone an irreversible ring-closure to a 5-membered oxazine ring (FIGURE 1). The identification of this photodecomposition product was accomplished by $^{1}H$-NMR and $^{13}C$-NMR spectrometry and confirmed by comparison with a reference sample prepared according to SCHEME 2.

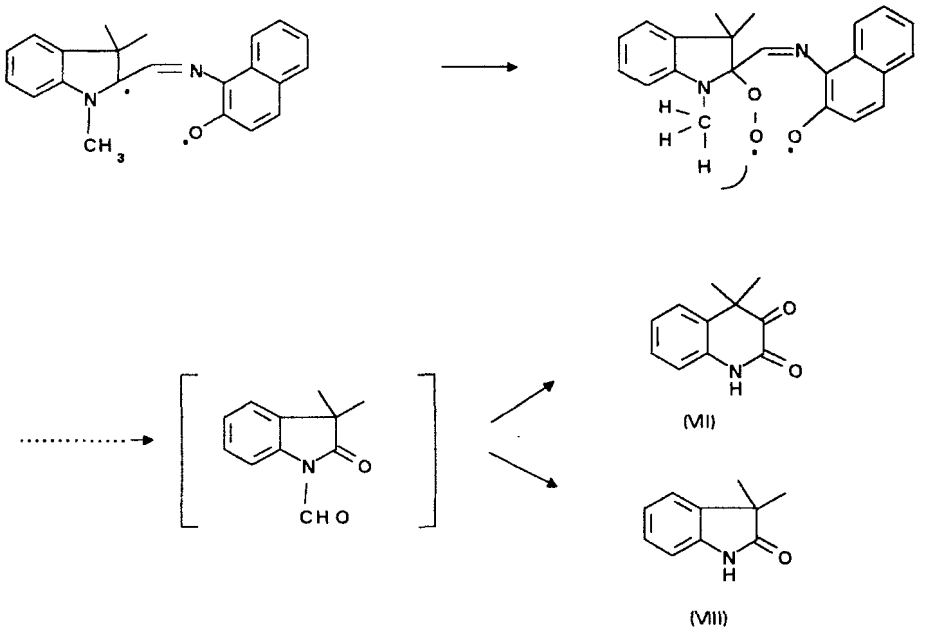



SCHEME 2

Compound (VI) has been described previously[7] in a study on the mechanisms of photo-oxidation. This compound was found to degrade to (I) and (II) when submitted to

UV-light. This may be the reason why this compound is detected only in limited amounts in irradiated solutions.

Oxidation of the N-$CH_3$ group of the indoline moiety leads to more degradation products. A mechanism is proposed[3] consisting in an initial homolytic cleavage of the $C_{spiro}$ -O bond of SO to the biradical that reacts then with molecular oxygen. A N- formyl intermediate is proposed that can rearrange to (VII) or react further to give 3,3-dimethyloxindole (VIII). (SCHEME 3)




SCHEME 3

When irradiation of PHD is carried out with visible light in the presence of camphorquinone (CQ) the amount of 1,3,3-trimethyloxindole is lower than was found in UV-induced photolysis, whilst the formation of 3,3-dimethyloxindole and its derivatives, particularly (VII), is significantly enhanced.

Since CQ acts as a triplet sensitizer[8] and triplet states of SO's are reported to follow preferentially the biradical pathway,[9,10] our results indicate that (VIII) and related compounds form when SO ring opening takes place from the first excited triplet state

CQ-sensitized photodegradation in toluene did not proceed to any significant extent, indicating that the lifetimes of the reactive intermediates are strongly affected by the solvent polarity. Attempts are being made to measure the triplet lifetimes in different media.

## EXPERIMENTAL

Acetonitrile, toluene,hexane and ethyl acetate were from Aldrich and used as received. PHD was synthetised according to literature methods.[1] Camphorquinone was purchased from Aldrich. UV-induced photolysis of oxygen-saturated solutions of PHD ($3x10^{-3}$ M) was carried out in 36 hrs in a photochemical reactor (Applied Photophysics, U.K.) equipped with 6 fluorescent lamps (12W) peaking at 320 nm. For sensitized photolysis, CQ was added to PHD in a 5 to 50-fold excess before irradiating the solution for 18 hrs with two 150W tungsten lamps under a continuous flow of oxygen. Column chromatography was carried out using a 70-230 mesh silica gel purchased from Merck. For HPLC analysis a HP 1090 Series II liquid chromatograph equipped with a Hypersil 5μ 10x2.1 mm column was used, with hexane/ethylacetate 95:5 as the eluent. GC-mass spectra were obtained with a HP 5970 mass spectrometer connected to a HP 5890 Series II gas chromatograph equipped with a 15m HP-1 methylsilicone capillary column. $^1$H-NMR of (III) (300MHz; $CDCl_3$/TMS): δ = 1.90 (2-$CH_3$ at C3); 2.37 (C4-$CH_3$); 2.47 (C5-$CH_3$); 7.24 (C6-H); 7.63 (C7-H); 7.80 (C5'-H); 7.98 (C7'-H); 7.58 (C8'-H); 7.71 (C9'-H); 8.65 (C10'-H) ppm. $^{13}$C-NMR of (III) (300 MHz; $CDCl_3$/TMS): δ = 21.62 (2$CH_3$ at C3); 19.68 (C4-$CH_3$); 14.86 (C5-$CH_3$); 55.20 (C3); 128.70 (C6); 111.10 (C7); 120.00 (C5'); 129.70 (C6'); 128.10 (C7'); 125.71 (C8'); 127.32 (C9'); 122.33 (C10') ppm. $^1$H-NMR of (IV) (300 MHz; $CDCl_3$/TMS): δ = 1.06 (C3-$CH_3$); 1.98 (C3-$CH_3$); 2.26 (C4-$CH_3$); 2.23 (C5-$CH_3$); 2.98 (N-$CH_3$); 7.03 (C6-H); 6.51 (C7-H); 7.73 (C5'-H); 7.87 (C6'-H); 7.98 (C7'-H); 7.58 (C8'-H); 7.70 (C9'-H); 8.62 (C10'-H) ppm. $^{13}$C-NMR of (IV) (300 MHz; $CDCl_3$/TMS): δ = 23.36 (C3-$CH_3$); 24.87 (C3-$CH_3$); 14.50 (C4-$CH_3$); 20.07 (C5-$CH_3$); 33.70 (N-$CH_3$); 52.55 (C3); 130.11 (C6); 107.36 (C7); 111.26 (5'); 127.47 (C6'); 128.90 (C7'); 126.22 (C8'); 127.78 (C9'); 122.83 (C10'); 115.85 (CN) ppm. MS *m/e*(relative intensity): 340 (100, $M^+$); 325 (80, M-$CH_3$).

## REFERENCES


1. N. Y. C. Chu In Photochromism: Molecules and Systems, edited by H. Durr and G. Bouas-Laurent, Elsevier (Amsterdam), pp. 493-509 and 879-882 (1990).
2. G. Baillet and G. Giusti, J. Photochem. Photobiol. A: Chem., 70, 157 (1993).
3. G. Baillet, M. Campredon, R. Guglielmetti, G. Giusti and C.Aubert, J. Photochem. Photobiol. A: Chem. , 246, 147 (1994).
4. G. Baillet, V. Lokshine, R. Guglielmetti and G. Giusti, C. R. Acad. Sc. Paris, Série II, 319, 41 (1994).
5. G. Baillet, G. Giusti and R. Guglielmetti, Bull. Chem. Soc. Jpn., 68, 1220 (1995).
6. V. Malatesta, M. Milosa, F. Renzi, L. Montanari, M. L. Wis and D. Scotti, J.Org.Chem., 60, 5446 (1995).
7. V. Malatesta, M. Milosa, R. Millini, L. Lanzini, P. Bortolus and S. Monti, Mol.Cryst. Liq. Cryst., 246 ,303 (1994).
8. G. Favaro, V. Malatesta, C. Miliani and A. Romani, J. Photochem. Photobiol. A: Chem., in press (1996).
9. a) R. Gautron, Bull. Soc. Chim. Fr. , 3200 (1968). b) A. Kellmann, F. Tfibel, R. Dubest, P. Levoir, J. Aubard, E. Potier and R. Guglielmetti, J. Photochem. Photobiol. A: Chem., 49, 63 (1989).
10. D. Elloy and P. Jardon, J. Chim. Phys. ,91, 489 (1994).
11. J. Ericsen and C. S. Foote, J. Am. Chem. Soc. , 102, 6083 (1980).