PHOTOCHEMICAL REACTIVITY OF 3H-NAPHTHO[2,1-b]PYRANS :
AN EXAMPLE OF PHOTOINDUCED ISOMERISATION

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Abstract

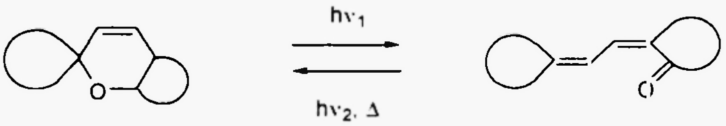
UV irradiation of 3.3-diphenyl-3H-naphtho[2.1-b]pyrans usually induces the pyranic ring cleavage and a thermodynamic equilibrium between the pyranic and open forms: we observe for the parent compound and two 8-substituted derivatives that recyclisation leads either to the starting pyranic or to a furanic compound. For the 8-ethynyl 3.3-diphenyl-3H-naphtho[2.1-b]pyran. the influence of a solid or liquid matrix is discussed.

Introduction

Photochromic compounds. whose structure and optical properties are controlled by light energy. present a large field of interest [1-8]. These organic systems have possible applications as photo-controlled optical switches in logic devices and light-modulators.

Chromenic compounds including the 3H-naphtho[2.1-b]pyranic system are studied in our laboratory since several years. as their properties appeared interesting. mainly for photosensitive optical glasses [9].

Under a suitable UV irradiation. the photochromic reaction of chromenes involves the C(sp^3)-O bond cleavage of the pyranic ring and an extended π conjugation. leading to an open-closed forms equilibrium (Scheme 1).



Scheme 1

Otherwise. the photochemical resistance of these organic compounds is limited. ultra violet irradiation affording degradation products [5. 6. 10] and the colorability decrease.

Resistance to the fatigue depends on the chromene structure and on the medium: with the aim to study some parameters involved in the photo-degradation of chromenes. we considered as a model the 3H-naphtho[2.1-b]pyranic system developed in our laboratory [11. 12].

Materials and methods

The 3.3-diphenyl-3H-naphtho[2.1-b]pyran **P1.** 8-ethynyl 3.3-diphenyl-3H-naphtho[2.1-b]pyran **P2.** 8-bromo 3.3-diphenyl-3H-naphtho[2.1-b]pyran **P3** and the 2-benzhydryl-naphtho[2.1-b]furan **F1** were synthetized in our laboratory [15. 16].

The photochrome-matrix system was irradiated with an intensity of 40 W.m^{-2} at the constant temperature of 293K. using a Sun Test CPS ATLAS device.

Ultra-Violet absorption spectra were recorded on a CARY 50 Varian spectrophotometer (2.0 nm spectral band pass) from 10^{-5} M (ethyl alcohol or cyclohexane. spectroscopic grade) solutions.

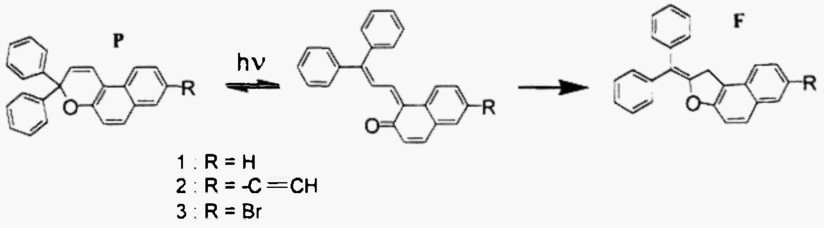
The **F/P** ratios were quantified using GC-MS analysis on a HP 6890 GC / HP 5973 MS device. Separations were performed on a capillary column HP 19091 J-431 HP-5 5% Phenyl Methyl Siloxane. 30m.250µm.0.25µm.

Results and discussion

According to the literature, isomerization of naphthopyrans into naphthofurans is difficult and needs high temperatures [13, 14].

Regarding photochromic compounds like chromenes, it appeared to us interesting to verify if this ring contraction should occur by the mean of UV energy instead of thermic energy.

We thus considered the possibility of a light induced mechanism, *i.e.* involving the open form of the chromene (Scheme 2).



Scheme 2

This photochemical process is studied with some chromenes, and we wish to report here the first results concerning the characteristic behaviour of the pyranic compounds **P1**, **P2** and **P3**.

***3,3-diphenyl-3H-naphtho[2,1-b]pyran* P1**

As a matter of fact, a previous study in our laboratory [15] showed that 3,3-diphenyl-3H-naphtho[2,1-b]pyran **P1** isomerizes into the non-photochromic 2-benzhydryl-naphtho[2,1-b]furan **F1** with a 66% yield, when heated in DMF during 12 hours.

First experiments allowed to observe that irradiation during 30 minutes of a cyclohexanic solution of 3,3-diphenyl-3H-naphtho[2,1-b]pyran **P1** does not afford 2-benzhydryl-naphtho[2,1-b]furan **F1**, but that only a small amount of the furan **F1** is obtained when irradiation occurs in ethyl alcohol.

In order to take into account the properties of the medium, we considered the spectroscopic UV absorption data (λmax values in nanometers, Table 1).of three pyranic compounds **P1**, **P2, P3** solved in ethyl alcohol (**Pi/E**) or cyclohexane (**Pi/C**)

Chromene	Bands - 1	- 2	- 3 (shoulder)	- 4	- 5	- 6	- 7	- 8
P1 / E	214	-	262	290	302	315	346	358
P1 / C	228	-	263	290	303	316	347	360
P2 / E	215	235 (K)	264	287	-	313	351	368
P2 / C	222	235 (K)	259	288	-	314	353	369
P3 / E	227	-	261	288	303	316	350	367
P3 / C	230	-	260	287	304	316	353	369

Table 1 - Spectroscopic UV data of **P1**, **P2, P3** naphto[2,1-b]pyrans

No significant solvent effects are observed for the absorption bands 3-8, except for **P2** (band 3: 5 nm hypsochromic shift from ethyl alcohol to cyclohexane). The band 2, related to the aromatic ethynic group in **P2**, is not either shifted. On the other hand, the aromatic band 1 undergoes significant solvent effects for the three chromenes.

If we now consider the bands shifts as a function of the 8-substituent, we observe a bathochromic effect from **P1** to **P2**, **P3**) for bands 7 and 8.

Insofar as the electronic effect of the 8-substituent involves the pyranic moiety of the molecule, it may have an influence on the reactivity of the chromene: the same conclusion concerns a solvent effect.

***8-ethynyl-3,3-diphenyl-3H-naphtho[2,1-b]pyran* P2**

The pyranic compound **P2** was irradiated in liquid (cyclohexane or ethyl alcohol) and solid matrixes: we describe hereunder the particular behaviour observed in a poly(butyl methacrylate) matrix.

When **P2** is dispersed (solid solution) in a poly(butyl methacrylate) film (Aldrich, ref. 18.152-8), isomerization is not observed after 20 hours of irradiation with the Sun Test lamp, despite the fact that ring opening still occurs in the solid matrix, as displayed by the intense photochromism of the chromene-polymer system.

GC-MS analysis shows that the 8-ethynyl-3,3-diphenyl-3H-naphtho[2,1-b]pyran **P2** is weakly degraded after 20 hours of irradiation, affording benzophenone and several other degradation compounds. When **P2** is dissolved in cyclohexane, the isomerization into 2-benzhydryl-7-ethynyl-naphtho[2,1-b]furan **F2** is not observed after one hour of irradiation, and a small amount of benzophenone is formed. After 15 hours of irradiation, GC-MS analysis shows that the 8-ethynyl-3,3-diphenyl-3H-naphtho[2,1-b]pyran **P2** has nearly disappeared, but that **F2** is not formed.

When **P2** is dissolved in ethyl alcohol, the isomerization reaction occurs, affording 2-benzhydryl-7-ethynyl-naphtho[2,1-b]furan **F2** in 55 % yield after 30 minutes of irradiation and in 95 % yield after one hour of irradiation.

With the aim to reveal an eventual direct solvent effect, the **F2-P2** mixture resulting from a 15 minutes irradiation was allowed to stand in the dark at the constant temperature of 293K, in order to maintain constant every thermodynamic equilibrium coefficients. The system was then periodically analysed by GC-MS chromatography.

The time evolution of the calculated **F2/P2** ratio (Figure 1) suggests either that the 2-benzhydryl-7-ethynyl-naphtho[2,1-b]furan **F2** is degraded faster than the 8-ethynyl-3,3-diphenyl-3H-naphtho [2,1-b]pyran **P2**, either that **F2** is converted into **P2**. We discarded this second possibility as **P2** formation is not observed from an ethyl alcohol solution of pure **F2** (chromatographic sample).

In this polar and protic medium, we thus mainly correlate the formation of benzophenone with the degradation of the furanic compound **F2** (Figure 2), as benzophenone is not detected from an ethanolic solution of the pure **P2**.

This assumption is likewise supported by the fact that UV irradiation during four hours of the pure furanic compound **F1** in ethyl alcohol affords benzophenone with a 0.32 **benzophenone/F1** ratio.

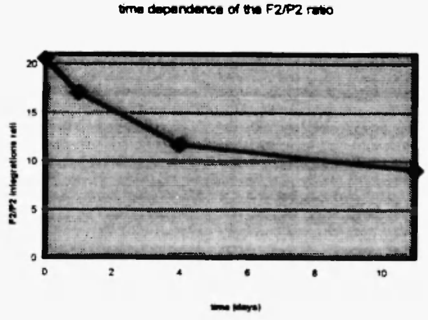


Figure 1

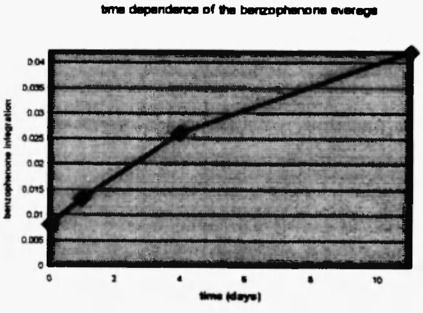


Figure 2

The 8-ethynyl group significantly facilitates the isomerization reaction. As this behaviour may be the result of a π electronic assistance, we considered the electronic effect of a non conjugated substituent at the same 8 position, *i.e.* a bromine atom.

***8-bromo-3,3-diphenyl-3H-naphtho[2,1-b]pyran* P3**

When **P3** is irradiated in ethyl alcohol, the isomerization occurs, but we equally observe the loss of the bromine atom. Thus, UV irradiation of **P3** affords 2-benzhydryl-7-bromo-naphtho[2,1-b]furan **F3** and directly 2-

benzhydryl-naphtho[2.1-b]furan **F1**. The amounts for **F3** and **F1** are respectively of 4.7% and 17% after 1.5 hours of irradiation and of 7% and 24% after 3.5 hours of irradiation. Moreover, the formation of a $(-OCH_2CH_3)$ substituted compound $C_{27}H_{21}O_2Br$. (m/z = 456. 458) is observed (respective amounts 1.5% and 2.7% for 1.5 and 3.5 hours of irradiation). The fact that we don't observe on the chromatograms the **P1** peak even with a very low intensity, suggests that the loss of a bromine atom occurs from F3, leading directly to the furanic compound **F1**. This possibility corresponds to the A process: Obviously, a competition with the direct process B cannot be excluded, involving simultaneous steps A1 and A2 (Figure 3).

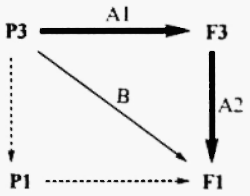


Figure 3

Conclusion

Ring isomerization of 3.3-diphenyl-3H-naphtho[2.1-b]pyrans contributes to the photochrome ageing, as the resulting non photochromic furanic compound cannot be photo-chemically or thermically converted in the photochromic pyranic form. This reaction appears to depend on substituent effects and on the media properties. According to our experimental conditions, a solid poly(butyl methacrylate) matrix allows the photochromism behaviour and avoids the ring photoisomerization of the 8-ethynyl-3.3-diphenyl-3H-naphtho[2.1-b]pyran **P2**.
The chromene **P2** in ethyl alcohol undergoes an irreversible ring isomerization when irradiated in the UV range, and the corresponding furan **F2** is obtained in high yield.
Furthermore, the formation of benzophenone and the evolution of a **P2**-**F2** mixture show that the furanic form is faster degraded than the pyranic form. Otherwise, the 8-bromo derivative **P3** behaviour suggests that debromination probably occurs from the furanic form **F3** rather than from the starting compound.
Other aspects of this reaction will be described in a further study.

References

[1] I. Willner. S. Rubin. *Angew. Chem. Int. Ed. Engl.*, *35* (1996). 367.
[2] C.B. Mc Ardle, in C.B. Mc Ardle (ed.), *Applied Photochromic Systems*. Blackie, London, 1992. 1.
[3] D.M. Junge. D. Mc Grath. *J. Chem. Soc. Chem. Commun.*, 1997. 857.
[4] G. Tsivgoulis, J.M. Lehn. *Chem. Eur. J.*, *2* (1996). 1399.
[5] R. Guglielmetti. Chaps. 8. 23 in H. Dürr. H. Bouas-Laurent (eds.) *Photochromism: Molecules and Systems*. Elsevier. Amsterdam. 1990.
[6] B.V. Gemert. M. Bergomi. D. Knowles. *Mol. Cryst. Liq. Cryst.*, *246* (1994). 67.
[7] D. Knowles. B.V. Gemert. *US Pat 546567*. 1995.
[8] M. Uchida. M. Kume. M. Irie. *Bull. Chem. Soc. Jpn.*, *69* (1996). 1023.
[9] Photochromism : Molecules and Systems. Dürr. H. and H. Bouas-Laurent. Eds., Amsterdam : Elsevier. 1990.
[10] A. Padwa. A. Au. G.A. Lee. W. Owens. *J. Org. Chem.*, *40* (1975). 1142.
[11] J.L. Pozzo. V. Lokshin. R. Guglielmetti. *J. Chem. Soc. Perkin. Trans 1*. 1994. 2591.
[12] K. Chamontin. V. Lokshin. V. Rossolin. A. Samat. R. Guglielmetti. *Tetrahedron* 55 (1999). 5821.
[13] P.E. Brown. R. Lewis. *J. Chem. Soc. Perkin Trans. 1*. 1992. 573.
[14] N.D. Dmitrieva. R. M. Liberzon. Y. Rayabokobylko. *J. Org. Chem. USSR (EN)*. 1985. 1219.
[15] D. Levi. Ph. Thesis. 2000. Marseille Luminy (France).
[16] M. Frigoli. C. Moustrou. A. Samat. R. Guglielmetti. *Helv. Chim. Acta (2000)*. 83. 3043.

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