On the Photodegradation of Some 2*H*-Chromene Derivatives in Fluid Solution or in Polyurethane Matrix

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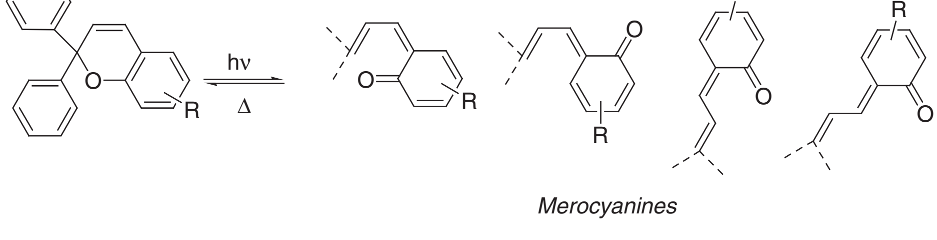
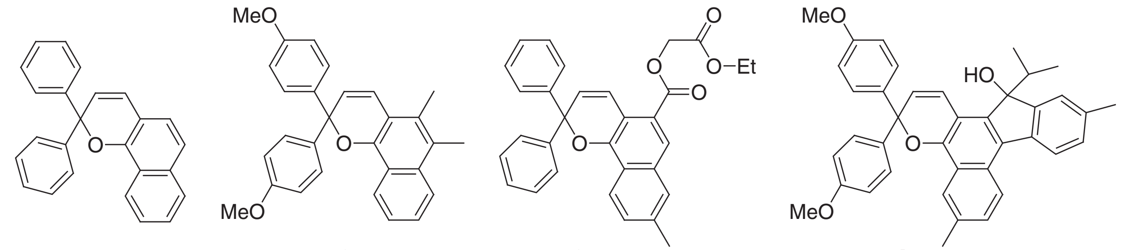
The time profile of the optical density was monitored during the photodegradation of three derivatives of 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran (**1**), namely 2,2-bis(4-methoxyphenyl)-5,6-dimethyl-2*H*-naphtho[1,2-*b*]pyran (**2**), 2,2-diphenyl-5-[(ethoxycarbonyl)methoxycarbonyl]-8-methyl-2*H*-naphtho[1,2-*b*]pyran (**3**), and 3,3-bis(4-methoxyphenyl)-6,11-dimethyl-13-hydroxy-13-isopropyl-3*H*-indeno[2,1-*f*]naphtho[1,2-*b*]pyran (**4**) either in toluene solution or in a polyurethane matrix. The photoproducts were identified using HPLC, GC/MS, and direct insertion MS techniques. High molecular weight oxygenated derivatives and new photoproducts deriving from a secondary oxidative pathway were characterized along with expected degradation derivatives. Some of the photoproducts considered responsible for the yellowing of the examined materials were identified. The effect exerted by two additives generally considered to have an inhibiting action toward radical processes was also evaluated.

The reversible phototransformation of a chemical species between two forms having different absorption spectra is normally referred to as photochromism.[1,2] Several different organic systems display this property either in solution or in a solid phase (e.g., a polymer matrix),[3] and among these an important role is played by 2*H*-chromenes and spiro[benzopyrans]. In both these species the photochromism reflects the light-induced reversible opening of the pyranic ring via cleavage of the O–C2 bond.[4] The cleavage, basically considered to have an electrocyclic nature, produces an extension of the conjugation, thus converting the virtually colorless starting compounds to deeply colored "merocyanines," normally yellow or red depending on substitution.[5,6] The latter may exist in isomeric forms characterized by different abilities to revert to the initial structures either thermally or upon ceasing the optical excitation (Scheme 1).[7,8] While the existence of a minor homolytic component to ring opening involving a biradical has also been proved,[9] it has been associated with irreversible degradation of the photochromic compounds.

The first chromene derivatives having practically acceptable photochromic behavior date back to the late '80s;[10] since then compounds have been obtained that have found applications in the production of ophthalmic lenses and sunglasses, security inks and cosmetics packaging, optical switches, mobile phone covers, skis and sportswear. As well as these compounds may perform, they are all bound to experience fatigue in their working life and to a greater or lesser extent, to undergo degradation with time. Thus their applicability is strongly linked to the time span within which their photochromic performance can be considered satisfactory. While on one side it is then clear the importance of determining the resistance to fatigue of a given photochrome prior to its practical application, the identification of the products resulting from its photodegradation, and especially those responsible of yellowing, is also a central issue. We report on a study of the photodegradation of 2,2-bis(4-methoxyphenyl)-5,6-dimethyl-2*H*-naphtho[1,2-*b*]pyran (**2**), of 2,2-diphenyl-5-[(ethoxycarbonyl)methoxycarbonyl]-8-methyl-2*H*-naphtho[1,2-*b*]pyran (**3**), and of 3,3-bis(4-methoxyphenyl)-6,11-dimethyl-13-hydroxy-13-isopropyl-3*H*-indeno[2,1-*f*]naphtho[1,2-*b*]pyran (**4**), which are shown in Figure 1 along with 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran (**1**), the archetype of the family. In a previous

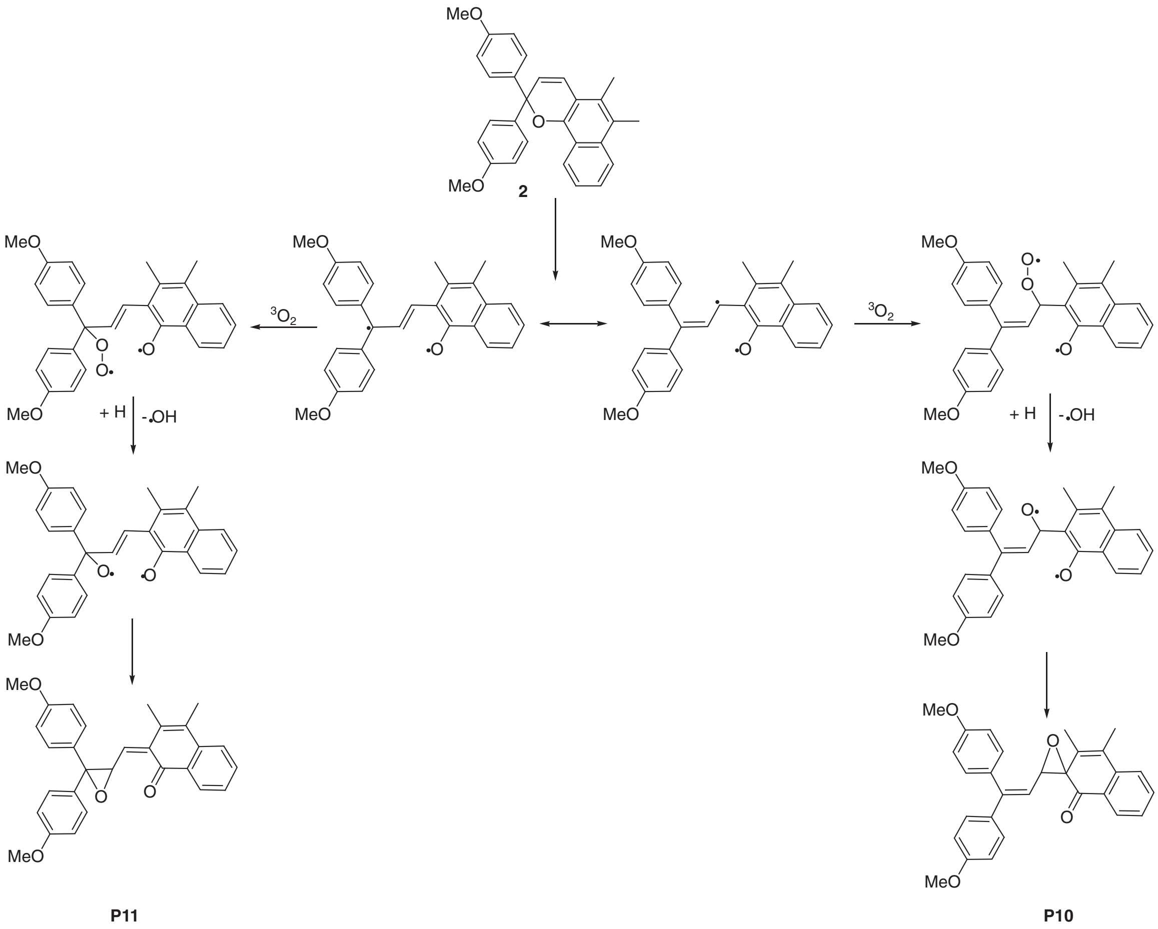


Scheme 1. Reversible photoconversion of chromenes to merocyanines.



1 **2** **3** **4**

Figure 1. Structure of the investigated chromenes.



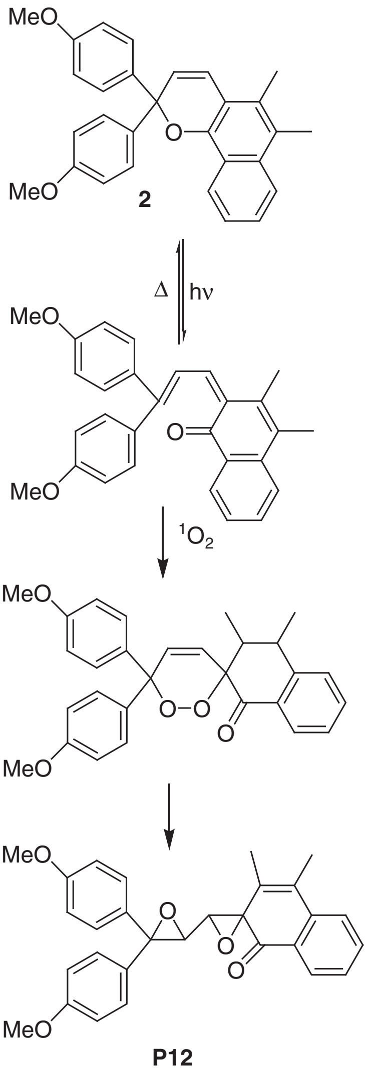
Scheme 2. Speculative mechanisms concerning the formation of epoxides **P10** and **P11**.

study on the photodegradation of **2** itself,[11] some high molecular weight photoproducts have been detected, including monoepoxide **P10** and **P11**, the formation of which is accounted for as indicated in Scheme 2. A diepoxide **P12** was also observed, and it may be hypothesized that the [4 + 2] addition of singlet oxygen to the cisoid form of the merocyanine from **2** leads to an endoperoxide which can then undergo thermal decomposition to **P12** as outlined in Scheme 3.

Our interest in these compounds stems from the fact that the presence of different substituents induces variations of the absorption spectra of both their closed and open forms with respect to that of the unsubstituted parent compound **1**.[12] As a matter of fact, the open forms of **2**–**4** have absorption λ_{max} in the range 457 to 564 nm, values that can make them suitable for interesting practical applications.

Results and Discussion

General Considerations. The UV–vis absorption spectra of the merocyanines from compounds **1**–**4** are shown in Figure 2 while their λ_{max} values are collected in Table 1. When examining these data it may be convenient to use the merocyanine from **1** as reference, having the same basic backbone common to compounds **2**–**4** but without substituents. Thus, the larger λ_{max} value exhibited by **2** with respect to **1** suggests that the presence of the methoxy groups in the *para*-position of the two phenyl rings induces a bathochromic shift of 20–25 nm, the effect of the presence of the methyl substituent being possibly less important. On the other hand, the much larger value of λ_{max} exhibited by the merocyanine from **4** can be accounted for by the extension of the conjugated



Scheme 3. Speculative mechanisms concerning the formation of **P12**.

system in this last derivative.[13] It should however be borne in mind that like **2**, **4** also features the two methoxy groups that induce a bathochromic shift. Although an exact quantification of the two contributions to the overall observed shift is impossible, it seems sensible to assume a contribution of the methoxy groups similar to that observed for compound **2**. In this light, the bathochromic shift due to the extended conjugation in **4** would then amount to ca. 65–70 nm. Although we do not have a clear-cut explanation for it, we note that the merocyanine from **3** exhibits a 14 nm hypsochromic shift with respect to that from **1**.

An additional feature emerging from the data in Table 1, is that in all cases the λ_{max} values measured in the polyurethane matrix are ca. 10 nm larger than those measured in toluene solution. Previous studies on structurally related compounds have shown that the λ_{max} values are fairly independent of solvent polarity. On the other hand, it cannot be excluded that the polyurethane matrix exerts a sort of flattening action onto the merocyanines which might result in a slightly better efficiency of conjugation and hence in a slight bathochromic shift of λ_{max} values.

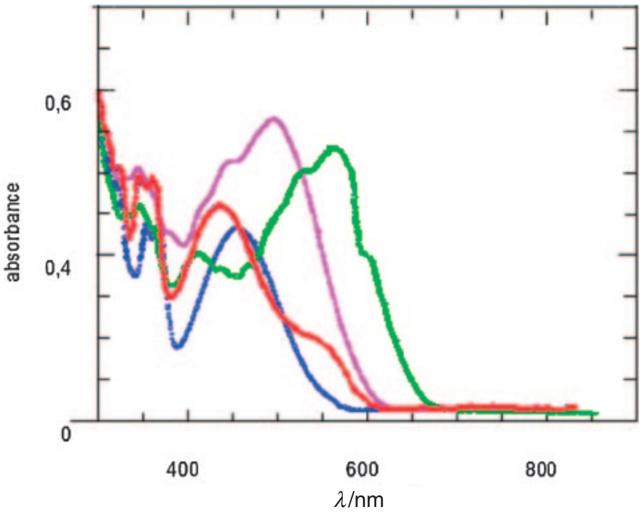


Figure 2. Absorption spectra for the merocyanines from **1** (blue), **2** (green), **3** (red), and **4** (pink) in toluene solution.

Table 1. Absorption λ_{max} for the Merocyanines from **1**–**4** in Toluene (T) Solution and in Polyurethane (PU) Matrix

Compound	λ_{max}(T)/nm	λ_{max}(PU)/nm
1	471	479
2	493	503
3	457	466
4	564	577

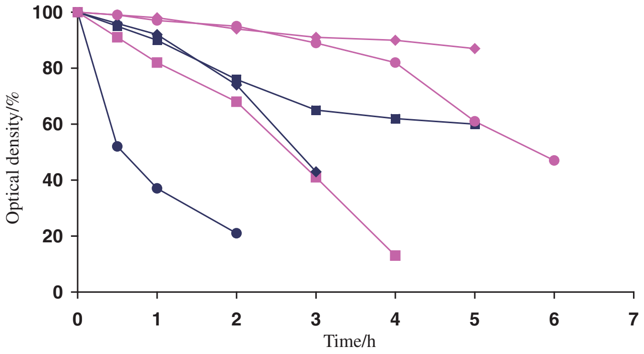
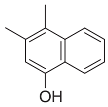
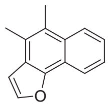
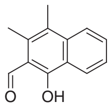
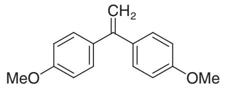
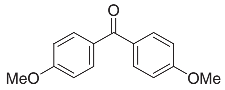
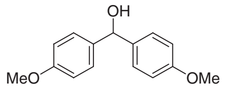
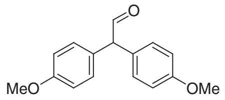
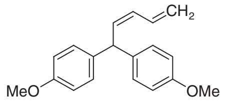
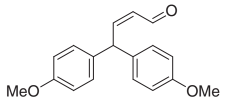
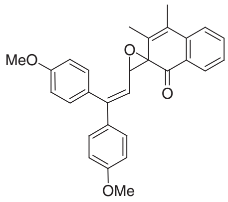
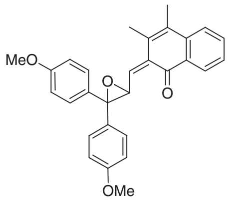
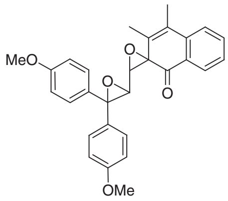


Figure 3. Time profile of the optical density exhibited by compound **2** (●), **3** (◆), and **4** (■) in toluene solution (pink) and in a polyurethane matrix (blue) under stationary irradiation with the light from a 1.5 kW Xenon lamp.

Figure 3 shows the time profile of the decrease of optical density observed for compounds **2**–**4** under photostationary conditions of irradiation at 25 °C. As it can be seen, the degradation is fairly slow in toluene for compounds **2** and **3** and definitely faster in the polymer matrix, while the reverse is true for compound **4** which degrades faster in the former medium.

It is also important to ascertain that the decrease in optical density does indeed parallel the degradation of the photochromes, as the formation of colored by-products might alter the O.D. time profile. HPLC studies, carried out in order to correlate the O.D. decrease with the actual degradation of the photochrome under examination, have shown that some photo-

Table 2. Photoproducts Detected in the Photodegradation of Compound **2** after Two Hours of Irradiation

Structure	Code	MS /g mol^{-1}	Retention time/min	In toluene	In PU	In PU 10% Tinuvin 144	In PU 10% TPMPDTF
	**P1**	172	8.51	++	++	+++	+++
	**P2**	196	9.61	+++	+++	++	+++
	**P3**	200	10.14	++	++	++	++
	**P4**	240	11.96	+	+	++	+
	**P5**	242	13.63	++++	++++	++++	++++
	**P6**	244	12.53	T$^{a)}$	T$^{a)}$	T$^{a)}$	++
	**P7**	256	12.79	+	+	+	+
	**P8**	266	14.90	n.d.$^{b)}$	n.d.$^{b)}$	++	n.d.$^{b)}$
	**P9**	268	14.90	+++	+++	+++	++++
	**P10**	438	47.16	++	++	+++	+++
	**P11**	438	47.37	++	++	+++	+++
	**P12**	454	47.51	+	+	++	+++

a) T: trace amount. b) n.d.: not detected.

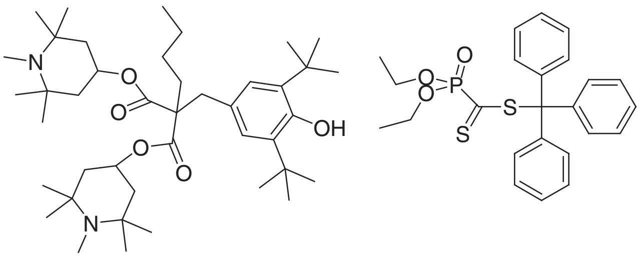

Tinuvin 144 TPMPDTF

Figure 4. Structures of additives.

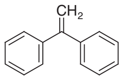
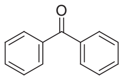
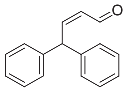
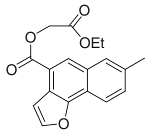
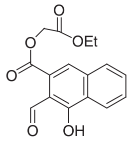
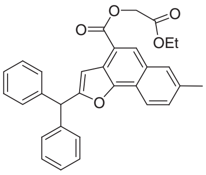
products do absorb in the region of activation of the photochromes, thus affecting their "colorability." Although in solution the O.D. correlates well with the residual amount of the photochromes, in the polymer matrix the accumulation of colored photoproducts may originate a screen-effect that, as time goes by, renders impossible the correlation of the O.D. decrease with the photochrome degradation. This effect is especially evident during the irradiation of compound **4**, the degradation of which in polyurethane is initially similar to that in toluene but slows down significantly after the first three hours of treatment.

It also seemed to us sensible that radical processes of some sort might contribute to the fast degradation of **4** in toluene. Thus additional experiments were carried out in the presence of substances amenable to inhibiting radical processes. As a matter of fact, the photodegradation of **4** in toluene solution containing a substantial (10%) amount of either Tinuvin 144, a light stabilizer of the HALS family,[14] or of triphenylmethyl diethoxyphosphoryldithioformate (TPMPDTF), an efficient trapping agent for carbon- or oxygen-centered radicals,[15] represented in Figure 4, was found to proceed exactly as found for toluene solution not containing any additive.

The addition of the same amount of either of the two additives to a polyurethane matrix containing **4** had instead a noticeable stabilizing effect during the first half hour of irradiation, and although the stabilizing effect seemed to decrease with time, after 4 h the residual O.D. was still 10% greater than observed in the absence of additives.

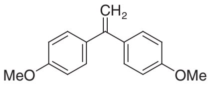
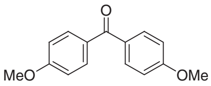
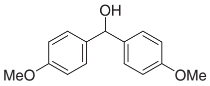
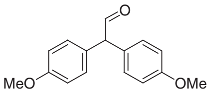
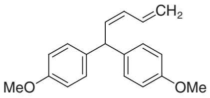
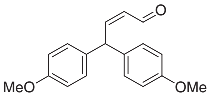
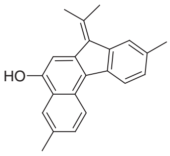
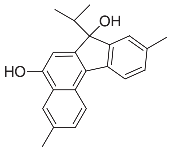
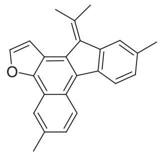
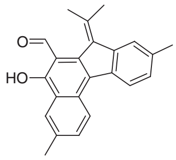
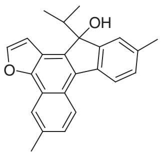
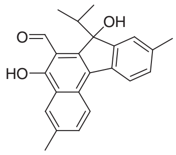
Photoproducts. Early studies on the photodegradation of naphthopyrans carried out in the late '90s[16] have led to the identification of some of the photoproducts. It was then evidenced the major role played by oxygen in the process. In order to get a better understanding of the photodegradation process we have endeavored in a GC/MS study aimed at the characterization of the products originating in the photodegradation of compounds **2**–**4**. To this purpose, toluene solutions of compounds **2**–**4** or polyurethane films containing these compounds were subjected to irradiation in a Sun Test set for two hours. After this time, the toluene was removed under a flow of nitrogen and the photoinduced fragments were dissolved in acetonitrile and then directly injected in a GC/MS apparatus. When dealing with the polyurethane films, the photoproducts were extracted by refluxing the films for 45 min in acetonitrile at 60 °C. The extracts were then evaporated and redissolved in very small amounts of acetonitrile for analyses. Similar experiments were also carried out in the presence of the additives Tinuvin 144 and TPMPDTF, to try and improve the resistance to light of compounds **2**–**4** and also to check if and how their presence affected the photoproduct composition. We chose Tinuvin 144 because it exerts a dual radical-based action, due to the simultaneous presence in its molecule of hindered pyrimidines and of a hindered phenol. As for the dithioformate TPMPDTF, it has been shown to be a versatile spin trapping agent toward both nucleophilic (e.g., carbon centered) and electrophilic (e.g., oxygen centered) radicals and has been found to be a very efficient process stabilizer in the extrusion of polypropylene. However, preliminary trials having indicated that both additives had little or no effect in toluene solutions whereas they did in cases affect the relative amounts of the photoproducts in the PU matrices, experiments with additives were only carried out in the latter medium. A summary of the detected products and their retention times can be found in Tables 2–4. The retention time of the products in Tables 2–4 were compared with those of commercially available samples **P4**–**P9** and **P13**–**P15** or of samples provided by an industrial partner of ours **P19**–**P24**, while authentic **P1**–**P3**[17–19] were synthesized for this purpose.

Table 3. Photoproducts Detected in the Photodegradation of Compound **3** after Two Hours of Irradiation

Structure	Code	MS /g mol^{-1}	Retention time/min	In toluene	In PU
	**P13**	180	8.28	+	+
	**P14**	182	9.08	++++	++++
	**P15**	208	10.93	+++	+++
	**P16**	312	15.19	++	++
	**P17**	316	15.27	+	+
	**P18**	478	21.69	++	++

The well-expected formation of "classic" primary and secondary photoproducts, i.e., **P2**, **P5**, **P9**, **P14**, and **P15** as main products, along with minor amounts of **P1**, **P3**, **P4**, **P7**, **P16**, and **P17**, is in line with the results of similar studies carried out by some of us on a number of spiro[fluorene–naphthopyrans],[20] and, as outlined in Scheme 4 for compound **2**, is thought to reflect an initial homolytic cleavage of the C–O bond to form a biradical intermediate followed by its reaction with either triplet or singlet oxygen.

Table 4. Photoproducts Detected in the Photodegradation of Compound **4** after Two Hours of Irradiation

Structure	Code	MS /g mol^{-1}	Retention time/min	In toluene	In PU	In PU 10% Tinuvin 144
	**P4**	240	11.96	++	++	+++
	**P5**	242	13.63	++++	++++	++++
	**P6**	244	12.53	+	+	n.d.[a]
	**P7**	256	14.90	+	+	+
	**P8**	266	14.90	n.d.[a]	n.d.[a]	T[b]
	**P9**	268	14.90	+++	+++	+++
	**P19**	300	19.26	+	+	n.d.[a]
	**P20**	318	17.70	++	++	+++
	**P21**	324	19.49	++	++	+++
	**P22**	328	19.22	+	+	n.d.[a]
	**P23**	342	17.76	+++	+++	++
	**P24**	346	18.00	++	++	+++

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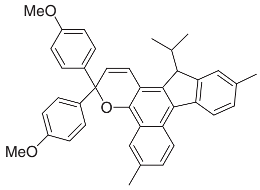
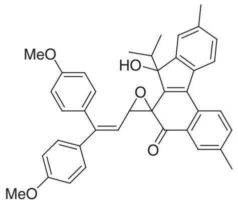
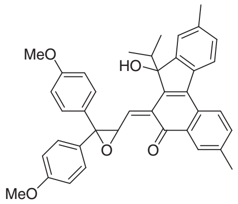
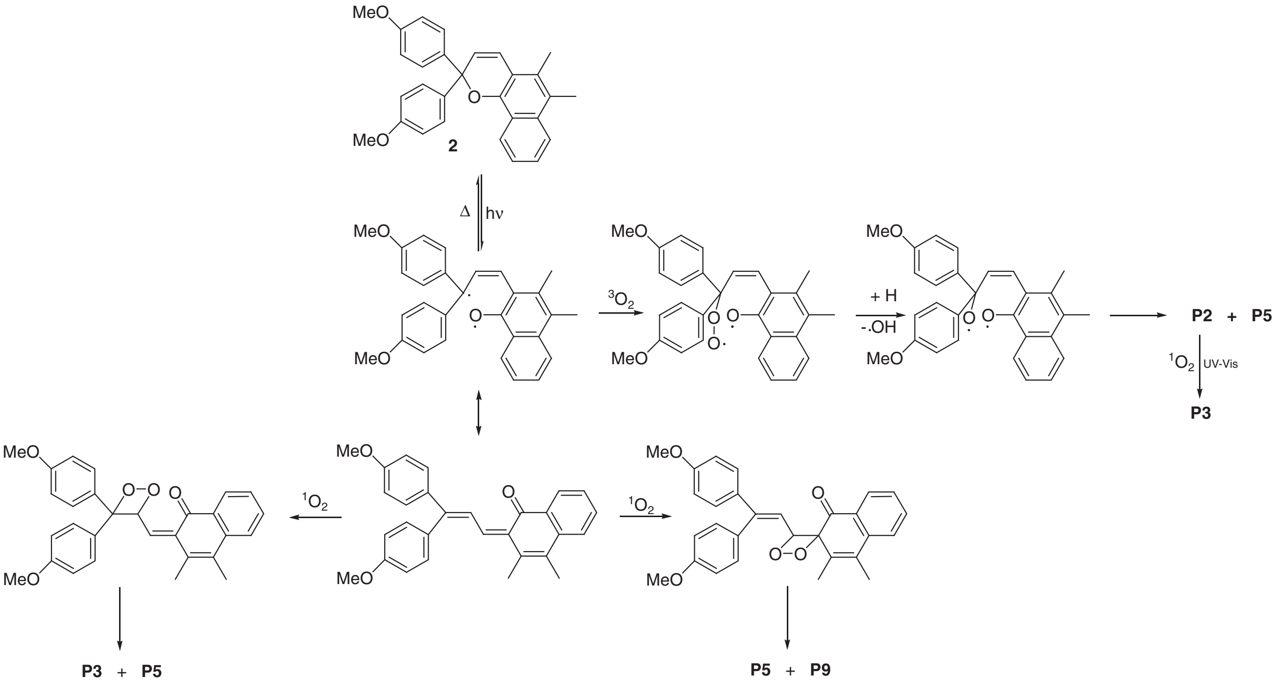
Structure	Code	MS /g mol^{-1}	Retention time/min	In toluene	In PU	In PU 10% Tinuvin 144
	**P25**	552	Direct insertion	n.d.[a]	n.d.[a]	++
	**P26**	584	Direct insertion	T[b]	T[b]	n.d.[a]
	**P27**	584	Direct insertion	T[b]	T[b]	n.d.[a]

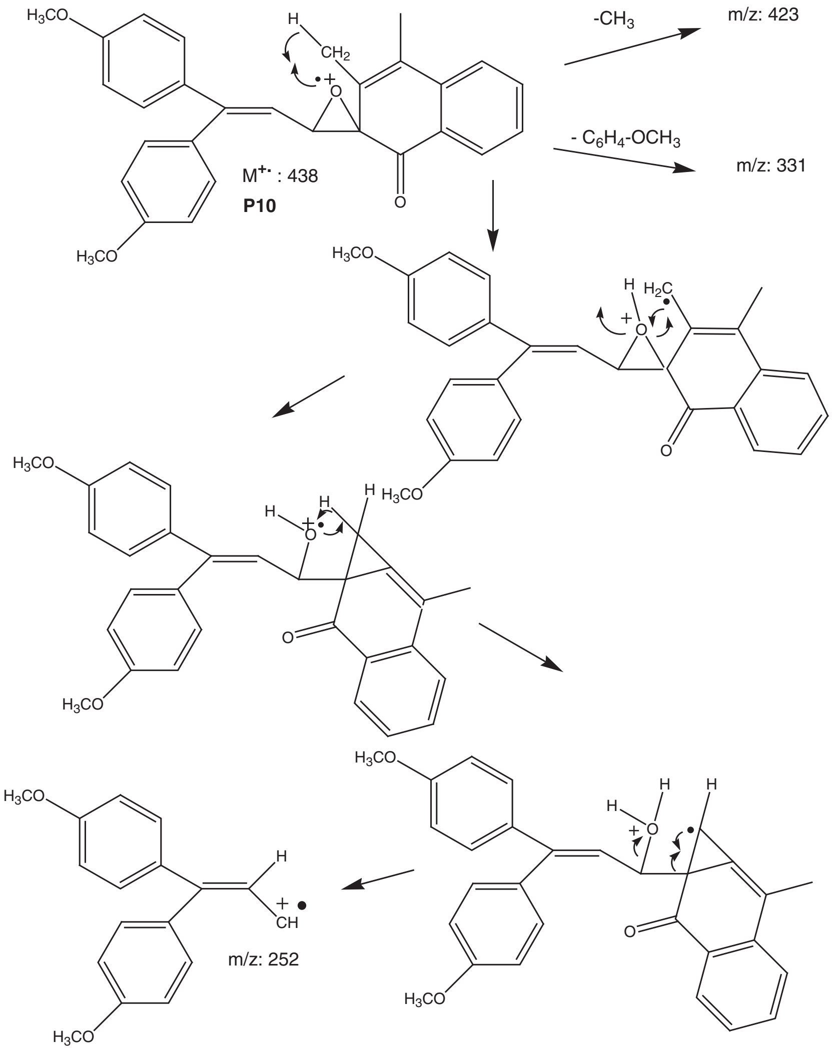
a) n.d.: not detected. b) T: trace amount.



Scheme 4. Possible degradation pathway from compound **2**.

Although the formation of epoxides **P10** and **P11** and diepoxide **P12** as minor products in the photodegradation of **2** in solution has been reported,[11] the identification of these compounds upon irradiation of **2** in the PU matrix is unprecedented. Indeed in the present investigation we found that the amount of **P10**, **P11**, and **P12** is actually greater in the polymer matrix than in toluene solution. Furthermore, we also found that the presence of Tinuvin 144 in the system significantly enhances the formation of these derivatives.

While analogous epoxidic compounds were not detected in the photodegradation of compound **3**, monoepoxides **P26** and **P27** were detected for the first time, albeit in trace amount, after irradiation of **4** in toluene solution. On the other hand, we failed to detect these compounds among the photoproducts of



Scheme 5. Proposed fragmentation of **P10** following electron impact.

the irradiation of **4** in PU matrix, even when Tinuvin 144 had been added to the system. We wish however to stress that this failure might be associated with a low efficiency of the acetonitrile extraction of the matrix, taken into account that these derivatives are probably formed in very small amount.

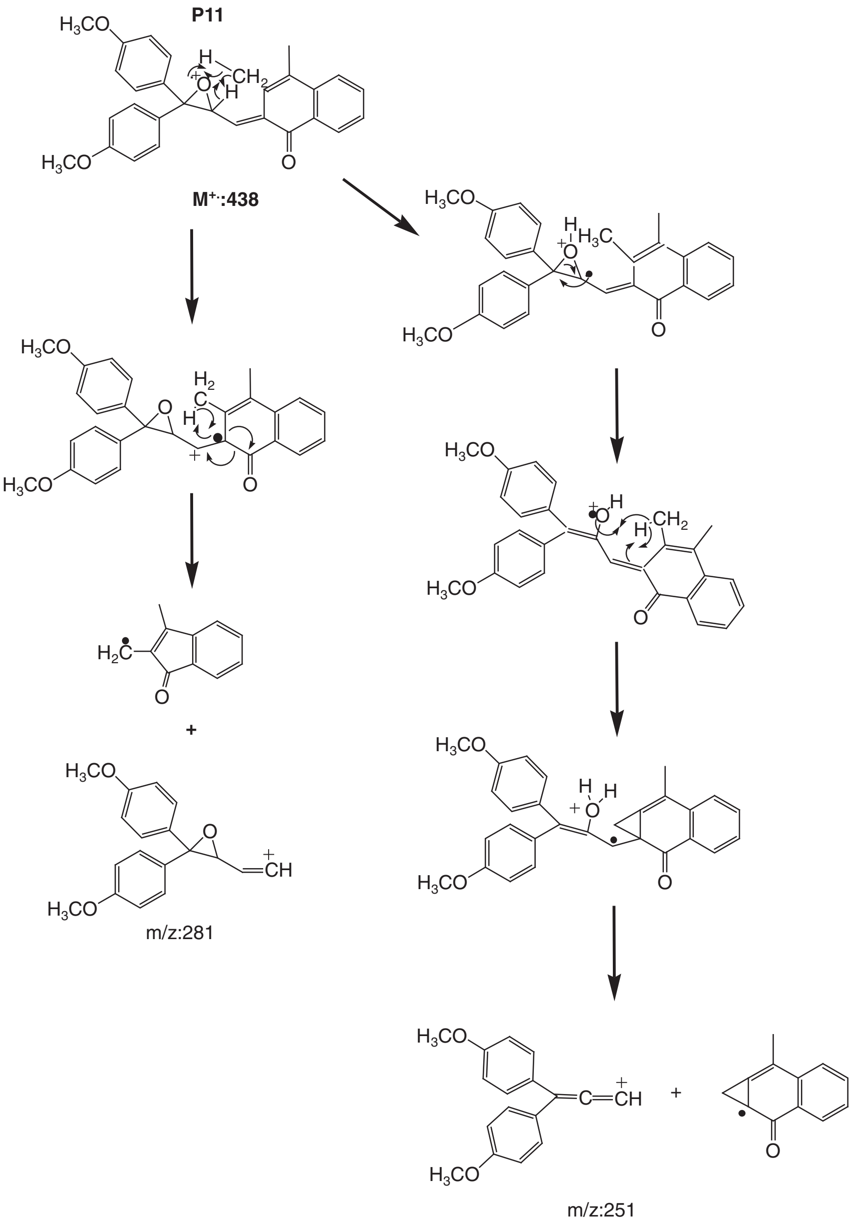
The two isomeric epoxides had similar but distinguishable GC retention times (e.g., 47.16 min for **P10** and 47.37 min for **P11**) and the very different fragmentation pattern found in their MS spectra allowed the discrimination between the two isomers.

As is outlined in Scheme 2 for compound **2**, to account for the formation of epoxides **P10**, **P11**, **P26**, and **P27** we suggest that the fraction of biradical formed upon irradiation of the photochromes combine with triplet oxygen. After fragmentation (loss of a hydroxy radical) biradicals are again formed, the rearrangement of which to give the epoxides can be easily envisaged.

Actually, in the case of **2** the MS spectral fragmentation patterns were **P10**: $M^+ = 438$ (100), 423 (40), 331 (47), 252 (50), 145 (32), 121 (41) and **P11**: $M^+ = 438$ (13), 422 (71), 315 (48), 281 (21), 251 (46), 207 (100), 77 (24). The main fragmentations occurred by cleavage of the charged open form structure rather than the closed form. Scheme 5 outlines possible fragmentations routes leading to fragment 252 that can only result from the fragmentation of **P10**. The fragment ion observed at m/z 438 corresponds to the base peak and the loss of ($-CH_3$) and ($-C_6H_4-OCH_3$) lead to stable ions m/z: 423 and m/z: 331, respectively. Other fragmentation pathways for **P11** leading to fragment m/z: 251 are presented in Scheme 6.

We are aware that epoxidic photoproducts have only been observed from compounds **2** and **4** which share the presence of the methoxy groups as common feature. On the other hand, the monoepoxide derivatives **26** and **27** were only detected in toluene solution and not in the PU matrix, and the diepoxide from **4** could not be identified in both media. On this basis, and in view of the fact that compounds **P10**, **P11**, **P12**, **P26**, and **P27** are minor photoproducts we do not feel to presently have in our hands enough results neither to state that the presence of the methoxy groups is critical to the formation of these epoxidic derivatives, nor to suggest the possible role played by these substituents.

Finally, parallel to the GC/MS studies, the extracts obtained from the irradiated samples of compounds **2**–**4** either in toluene solutions or in PU films, were chromatographed through a



Scheme 6. Proposed fragmentation of **P11** following electron impact.

HPLC equipped with a UV–vis diode-array detector in order to identify the photoproducts responsible for the appearance of a yellow color as the irradiation proceeds. It was then ascertained that the photoproducts responsible for the observed yellowing were essentially **P3**, **P18**, **P19**, **P21**, **P22**, and **P23** which exhibit absorptions in the visible region.

Experimental

Samples. Compound **1** was synthetised according to the literature.[5,10] Chromenes **2–4** (PPG Industries, Inc.) were recrystallized from ethanol.

The copolymer polyester–polyurethane available from Aldrich poly(4,4′-methylenebis(phenylisocyanate)-*alt*-1,4-butanediolpoly(butylene adipate)) was used to prepare polymer samples. The T_g value of the polymer matrix, measured using differential scanning calorimetry, is −18 °C.

The photochromic polymer films were prepared mixing dye and PU in THF that had been previously distilled in order to eliminate the BHT stabilizer. The mixture was deposited on glass plates (ORMA CR39 support) after soaking.

The polymer samples were 14 mm thick and contained $2 \times 10^{-5}\,\mathrm{mol\,g^{-1}}$ (dye/polymer). Some polymer films were formulated without dye in order to obtain blank extractions.

UV–vis Experiments. The UV–vis spectra were recorded on a Beckman DU 7500 diode array spectrophotometer using a quartz cell with path length of 1.0 cm, enclosed in a thermoregulated copper block (20 °C). The photochromic compounds were dissolved in anhydrous toluene (10^{-4} M) (Aldrich, spectroscopic grade). The loss of optical density O.D. detected at the absorption $\lambda_{\max}$ of the merocyanine, was followed with the UV–vis spectrophotometer at the photostationary state, reached after 10 min of irradiation with a 150-W Xenon lamp at 20 °C.

Degradation Experiments. All the degradation experiments were performed in a Sun Test (Atlas) equipped with a 1500 W Xenon lamp and a 290 nm filter at 25 °C. Light intensity was 80 W m^{-2} measured between 300 and 400 nm. The mass spectra were obtained under electronic impact (EI 70 eV). The GC/MS (6890 HP GC system and 5973 MS detector) apparatus was equipped with a short column (0.2 µm, 12 m × 0.2 mm). The injector was heated to 255 °C. The GC system was also run using direct insertion probe interface. For analysis, direct probe temperature was programmed from 50 to 200 °C at 30 °C min^{-1} and the ion source was held at 200 °C.

The HPLC analyses were run on a Beckman Gold system coupled with a UV–vis diode array detector. Separations were carried out using a 4.6 mm × 25 cm, C18-5 µm reversed-phase column with a linear gradient of acetonitrile in water from 30% to 100% during a 45 min set at 1 mL min^{-1}.

Conclusion

The presence of epoxides among the photodegradation products of chromenic photochromes in PU matrix is unprecedented, and parallels a previous finding in toluene solution. The present results seem however to suggest that the presence of the methoxy sustituents in the phenyl rings is crucial. Some of the photoproducts responsible for the yellowing of the starting material have been identified.

Finally, it would appear that the HALS Tinuvin 144 exerts a more efficient protective action than the spin trap TPMPDTF, which led us to envisage the utility of carrying out further degradation studies in an inert environment.

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