



Synthesis and photochemical reactivity of new 4-substituted naphtho[1,2-*b*]pyran derivatives

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ABSTRACT

A new naphtho[1,2-*b*]pyran possessing an ester substituent in position 4 was prepared from 2,3-dihydro-2,2-diphenyl-4*H*-naphtho[1,2-*b*]pyran-4-one and then converted to the carboxylic acid derivative. The photochromic behaviour of these two compounds was studied by UV–vis spectroscopy and the structures of the photoproducts elucidated by NMR. Under UV irradiation the uncoloured ester derivative afforded a single coloured photoisomer having a *transoid-trans* (TT) configuration while the acid was irreversibly transformed into degradation products. In strong acid medium both compounds were converted to a spiro derivative formed through the opening of the pyran ring followed by an intramolecular lactone ring formation and electrophilic aromatic substitution.

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1. Introduction

Naphthopyrans are one of the most important classes of photochromic systems with excellent photochromic performance that met considerable success in the production of variable-transmission optical materials, namely photochromic plastic ophthalmic lenses, which darken in the sunlight [1,2].

Under near-UV light irradiation, these uncoloured or faintly coloured molecules, either in solution or incorporated in polymeric matrices, undergo an electrocyclic pyran-ring opening with formation of the *transoid-cis* isomer (TC, major product) that, upon isomerization of the double bond, leads to the *transoid-trans* isomer (TT, minor product) (Scheme 1) [3]. A photostationary state is usually reached after several minutes of irradiation. These two photoisomers, with a strong absorption in the visible part of the spectrum have different lifetimes. As a result, in the absence of light the system returns to the original colourless state by a process following a bi-exponential kinetic. While the TC isomer rapidly returns to the uncoloured closed form, the TT isomer is thermally more stable and is responsible for the persistence of a residual colour for several minutes or hours after the removal of the light source [4].

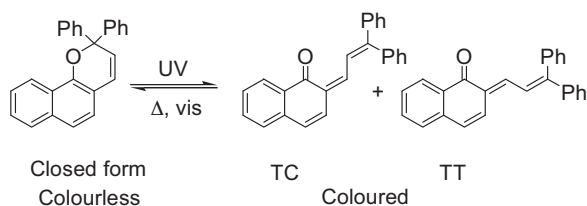
One possible way to prevent the formation of this long-lived photoisomer is to connect the pyran double bond to the naphthalene core (Scheme 2). The introduction of an alkyl bridge between carbons 4 and 5 would give rise to a new type of fused-naphthopyrans that should produce only one photoisomer and therefore exhibit mono-exponential fading kinetic, although probably very fast, thus avoiding the persistence of the residual colour [5]. In this paper we describe the photochromic properties of two new naphthopyrans substituted in position 4 by an ester or a carboxylic acid chain and an attempt to prepare such fused-naphthopyran that surprisingly afforded a spiro lactone formed through a multi-step mechanism.

2. Results and discussion

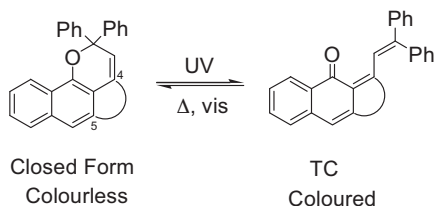
The reaction of 2,3-dihydro-2,2-diphenyl-4*H*-naphtho[1,2-*b*]pyran-4-one **1** [5,6] with the silyl enol ether 1-methyl trimethylsilyl dimethylketene acetal in the presence of an excess of TiCl₄ afforded the naphtho[1,2-*b*]pyran **2** directly. Subsequent hydrolysis in a basic medium provided the corresponding carboxylic acid **3** (Scheme 3).

In toluene solution (10^{−3} M) naphthopyrans **2** and **3** are colourless with a very strong absorption in the near UV region. Continuous UV light irradiation of a solution of naphthopyran **2** at 20 °C leads to the slow development of a pale yellow colouration with a maximal absorption at 420 nm but a photostationary state was not achieved even after 40 min of irradiation (Fig. 1).

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Scheme 1. Photochromic equilibrium for 2H-naphtho[1,2-b]pyran.



Scheme 2. Photochromic equilibrium for a fused-naphthopyran.

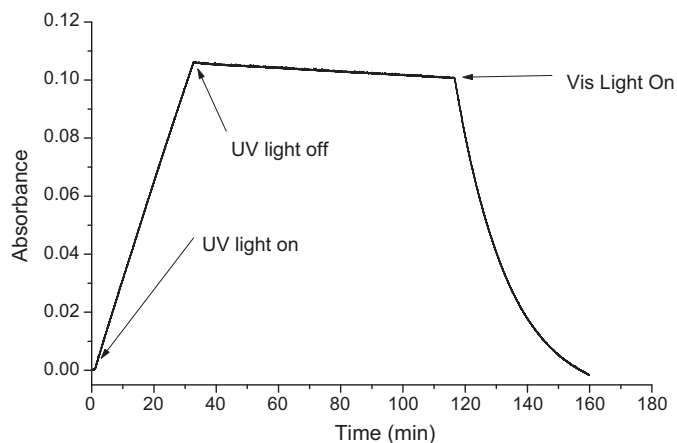


Fig. 1. Colour forming and colour bleaching for naphtho[1,2-b]pyran **2** measured at 420 nm.

When the UV light was turned off, a nearly constant absorbance was observed underlining the formation of a long-lived coloured compound ($t_{1/2} = 18$ h). The visible light irradiation ($\lambda_{\text{max}} > 420$ nm) of this solution induces a slow absorption decrease following a first

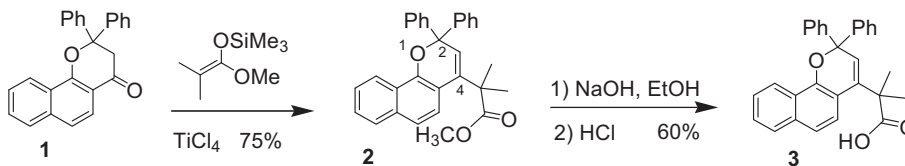
order kinetics pointing to a photoreversible process involving only one photoisomer (Fig. 1).

To investigate the structure of the products formed upon UV irradiation of naphthopyran **2**, NMR studies were carried out in toluene- d_8 (10^{-2} M) after UV irradiation with a 1000 W UV lamp, directly in the NMR tube at room temperature. The ^1H NMR spectra were recorded at regular time intervals to monitor the changes in peak-intensities and thus to obtain information about the number of photoproducts and the evolution of their concentration in time [7].

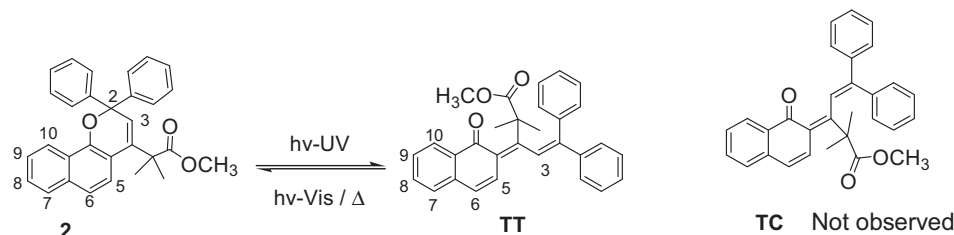
As displayed in Figs. 2 and 3, UV irradiation results in the formation of only one photoproduct (20% at the photostationary state). In the ^1H NMR spectrum, one can observe two distinct resonances at 1.61 and 1.41 ppm for the two methyl groups, which are not equivalent probably due to sterical hindrance, preventing a rapid rotation. The singlet signal at 6.59 ppm was assigned to proton H-3 which was more deshielded than in the closed form, due to the extension of the conjugation. A 1D selective NOESY experiment indicated a dipolar correlation between H-3 and a doublet signal at 7.06 ppm, attributed to H-5. Both 2D ^1H - ^1H COSY and 1D selective-TOCSY experiments have been recorded to identify the scalar coupling between H-10 at 8.20 ppm and three signals at 6.89, 7.01 and 6.76 ppm assigned to H-9, H-8 and H-7, respectively, and between H-6 at 6.17 ppm and H-5 at 7.06 ppm. From this set of data, the photoproduct was identified as the open form of compound **2** with a *transoid-trans* configuration (TT) (Scheme 4).

The relatively high thermal stability of this photoproduct and the fact that visible light irradiation is very effective to regenerate the initial naphthopyran are also in agreement with the TT configuration. The same experiment was repeated at low temperature to examine whether the second possible photoisomer (*transoid-cis*) is formed or not, as this open form is usually less thermally stable than the TT isomer. However, at 228 K, UV irradiation generated only the TT isomer. Therefore the presence of the ester chain in C-4 increases the difference in the stability of the two possible photoisomers and probably the more unstable TC isomer is rapidly converted through C=C double bond isomerization to the more stable TT form [8].

The photochemical behaviour of naphthopyran **3** was also examined by UV-vis spectroscopy and then by NMR. In contrast to naphthopyran **2**, no colouration and consequently no absorption in the visible range of the spectrum was observed when a toluene solution of naphthopyran **3** was irradiated with a 150 W UV lamp, suggesting that this compound would not be sensitive to UV light. However, NMR investigations on irradiated solutions of naphthopyran **3** with a 1000 W UV lamp evidenced the formation



Scheme 3. Synthesis of naphthopyrans **2** and **3**.



Scheme 4. Photochromic reaction for naphtho[1,2-b]pyran **2**.

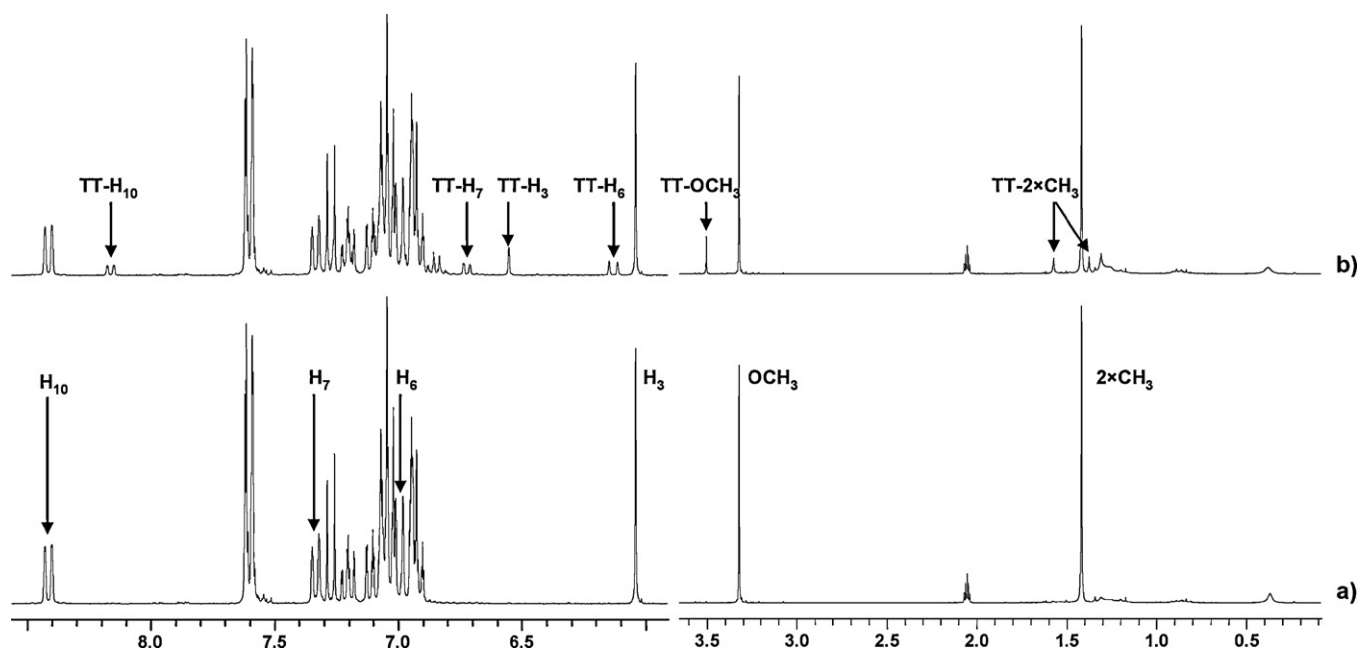


Fig. 2. Parts of ^1H NMR spectra of naphtho[1,2-*b*]pyran 2 (a) before and (b) after UV irradiation at room temperature.

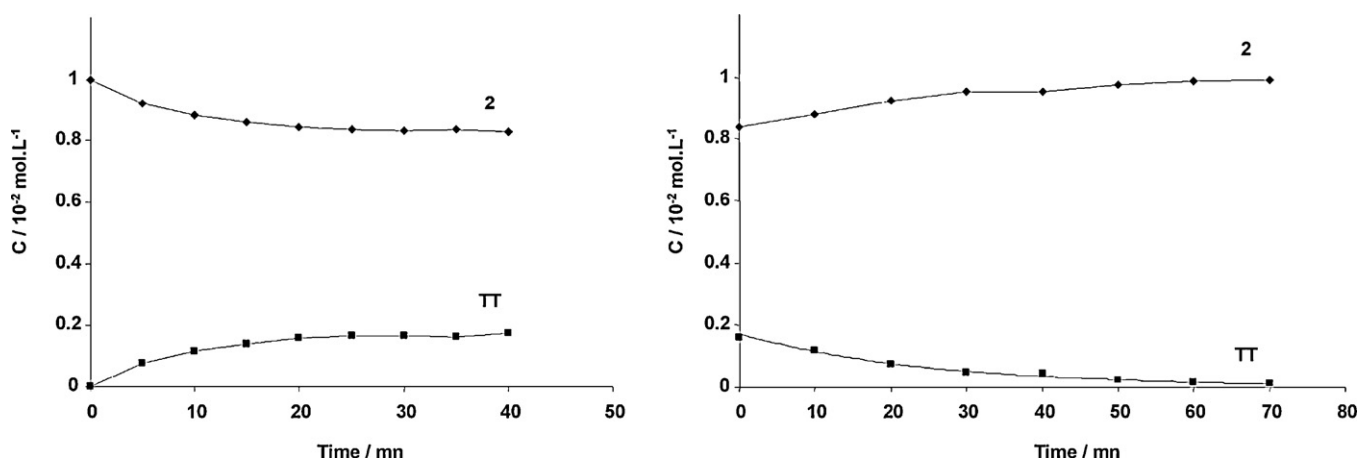
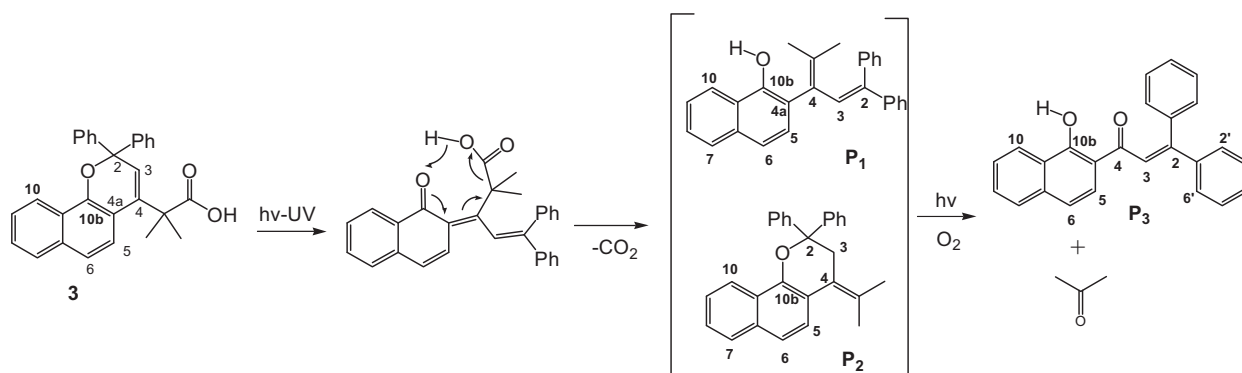


Fig. 3. Kinetics of colouration under UV irradiation (left) and photobleaching with visible light (right) of naphtho[1,2-*b*]pyran 2.

of three photoproducts labeled **P**₁, **P**₂ and **P**₃ which are thermally and photochemically (with visible light) stable (Fig. 4). **P**₁, **P**₂ and **P**₃ were therefore assigned to degradation photoproducts and their structures deduced from 1 and 2D NMR experiments (Scheme 5).

P₁ is a conjugated phenol formed by pyran ring opening followed by decarboxylation of the acid function. The phenol function is characterized by a broad signal at 5.18 ppm while the two methyl groups give two distinct signals at 1.48 ppm and 1.70 ppm and



Scheme 5. Photochemical behaviour of naphtho[1,2-*b*]pyran 3.

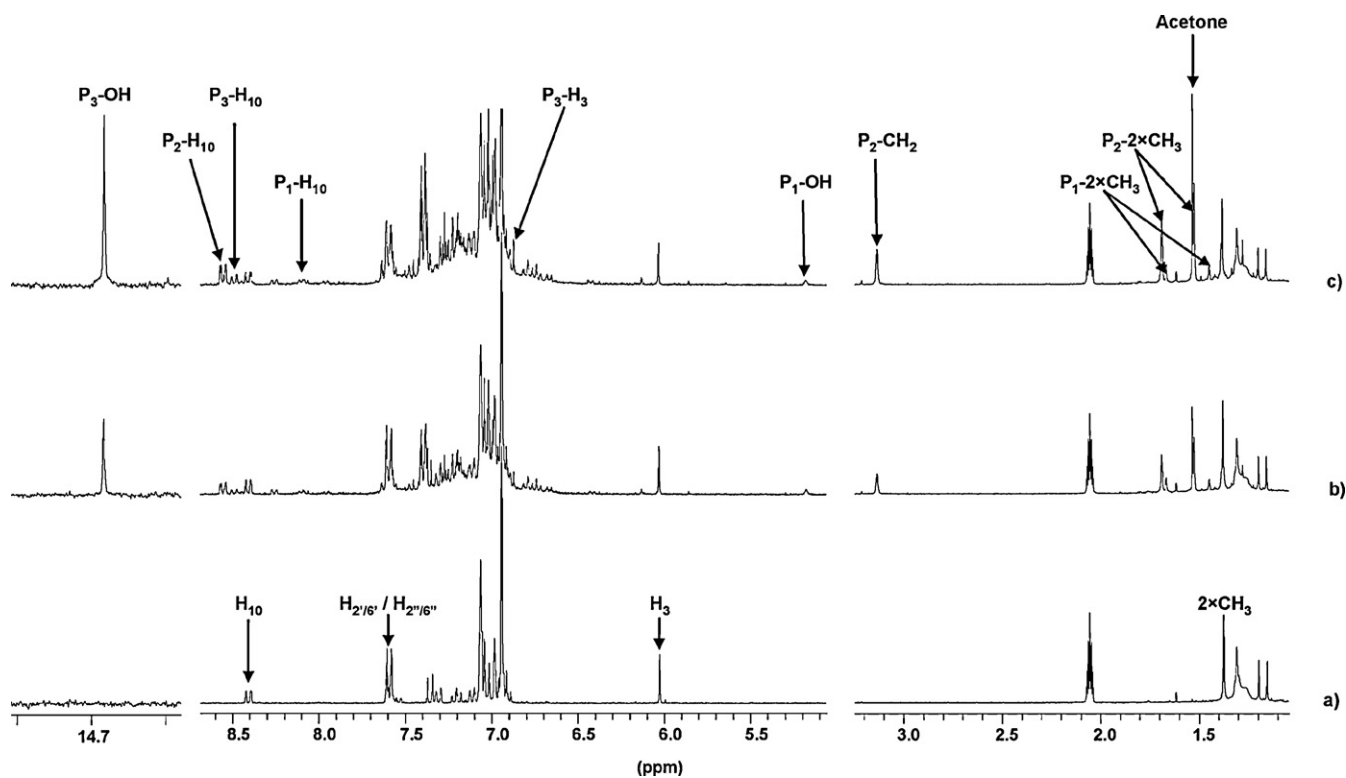
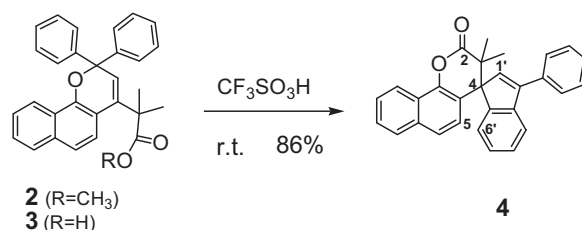


Fig. 4. Parts of ^1H NMR spectra of naphtho[1,2-*b*]pyran **3** (a) before, (b) after 30 min of UV irradiation and (c) after 60 min of UV irradiation.

are thus diastereotopic. **P**₁ evolves thermally through cyclisation towards **P**₂. Such bond-reforming between C-2 and oxygen requires the hydrogen-migration from the phenol to C-3.

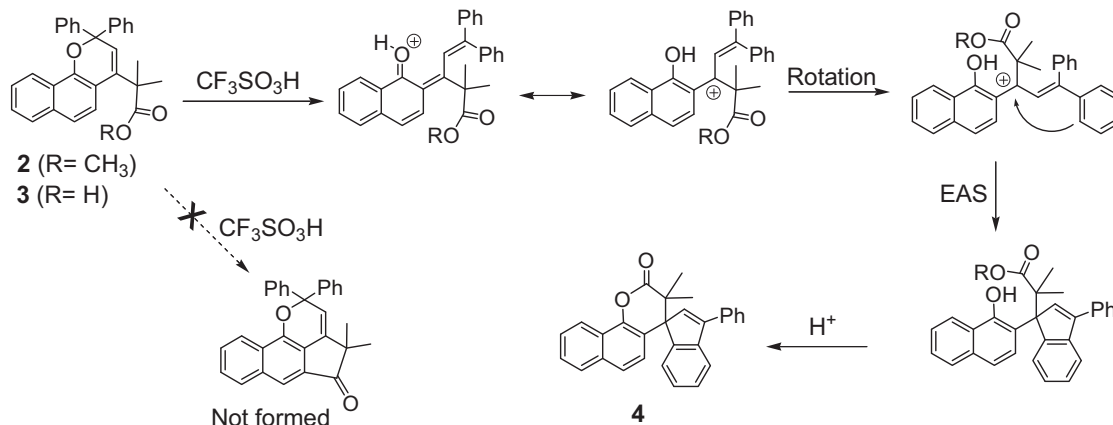
The pyran ring in **P**₂ was characterized by a 2D ^1H - ^{13}C HMBC experiment which displayed long-range correlations between the quaternary carbon C-2 at 83.9 ppm, the methylene protons in C-3 at 3.17 ppm and the aromatic protons H-2'/2''/6'/6'' at 7.81 ppm. The presence of an ethylenic function was apparent from ^1H - ^{13}C long range correlations between the quaternary carbon assigned to C-4 at 122.9 ppm and the diastereotopic methyl protons at 1.56 ppm and 1.73 ppm, and between the quaternary carbon bearing the two methyls at 127.7 ppm and the methylene protons (H-3) at 3.17 ppm.

P₃ was identified as a conjugated phenol containing a carbonyl function resulting from the opening of the pyran ring and oxidation of the double bond at C-4. The formation of acetone in the sample was also observed ($\delta^1\text{H}$ =1.6 ppm) [9]. The phenolic proton exhibited a highly deshielded chemical shift,



Scheme 6. Synthesis of lactone **4**.

14.78 ppm, due to hydrogen-bonding with the C=O function at C-4. In the 2D ^1H - ^{13}C HMBC spectrum long-range correlations were observed between the quaternary carbon at 154 ppm (C-2) and the aromatic protons at 6.94 ppm (H-3) and 7.25 ppm (H-2' = H-6'), and between the quaternary carbon C-10b at 163.8 ppm and



Scheme 7. Mechanism for the formation of lactone **4**.

the phenolic proton at 14.78 ppm, H-10 at 8.57 ppm and H-5 at 7.51 ppm. Finally, the carbonyl function (C=O at 196.9 ppm) is correlated with the aromatic protons H-3 at 6.94 ppm and H-5 at 7.51 ppm.

The presence of the acid chain at C-4 allows the pyran ring opening but leads to an open form that rapidly loses CO₂, affording compounds **P**₁ and **P**₂ that cannot reform the pyran ring and upon *in situ* oxidation give compound **P**₃. Therefore naphthopyran **3** does not show a reversible photochemical behaviour and is irreversibly converted to **P**₃.

The intramolecular cyclisation of naphthopyran **3** was attempted by converting this acid to the acyl chloride using SOCl₂ followed by Lewis acid treatment and by the direct action of strong acids (H₂SO₄, H₃PO₄, PPA) at room or low temperature, but under these conditions only degradation products were observed. We were unable to obtain the desired fused-naphthopyran using this approach. However, the treatment of naphthopyran **3** with triflic acid (CF₃SO₃H) [10] at room temperature gave a clean reaction and afforded a new lactone **4** in 86% yield (Scheme 6). The same compound was obtained under identical conditions from naphthopyran **2** even when the reaction was performed in the dark. In the ¹H NMR spectrum of lactone **4**, the two signals at 1.14 ppm and 1.46 ppm were assigned to the two methyl groups and the singlet at 6.61 ppm was attributed to H-1'. Long range scalar correlations in the HMBC spectrum between the quaternary carbon C-4 at 60.5 ppm and the methyl protons at 1.14 and 1.46 ppm, the aromatic protons H-1' at 6.61 ppm, proton H-5 at 7.08 ppm and proton H-6' at 7.34 ppm were observed. The lactone function was identified from correlation between the carbonyl C-2 at 173.4 ppm and the methyl protons at 1.14 ppm and 1.46 ppm.

The formation of this compound from naphthopyrans **2** and **3** can be explained by considering an initial acid-promoted opening of the pyran ring followed by C–C bond rotation, intramolecular aromatic substitution and acid catalyzed lactone formation (Scheme 7). Instead of an electrophilic aromatic substitution (EAS) promoted by the triflic acid that could lead to the desired fused-naphthopyran, these molecules behave differently and in strong acid medium a series of reactions occurred affording a non-photochromic spiro compound with a completely different structure to the expected one.

3. Conclusion

UV irradiation of naphtho[1,2-*b*]pyran **2** substituted on the pyran double bond by an ester chain leads to the slow formation of only one photoisomer possessing a *transoid-trans* (TT) configuration that shows a high thermal stability and is converted back to the original naphthopyran under visible irradiation. The corresponding acid derivative **3** exhibits a different behaviour under UV irradiation and is irreversibly converted to several degradation products involving decarboxylation and oxidation of one double bond. Upon treatment with CF₃SO₃H, both naphthopyrans were converted to a non-photochromic spiro lactone **4** formed by opening of the pyran ring followed by intramolecular cyclisation.

4. Experimental part

4.1. Spectrokinetic studies under continuous irradiation

UV-vis irradiation experiments were made using a CARY 50 Varian spectrometer coupled to a 150 W Ozone free Xenon lamp (6255 Oriol Instruments), equipped with a filter Schott 011FG09 (259 < λ < 388 nm with λ_{max} = 330 nm and T = 79%). The light from the UV lamp was filtered using a water filter (61945 Oriol Instruments) and then carried to the spectrometer holder at the right

angle to the monitoring beam using an optical fiber system (77654 Oriol Instruments). 40 W m⁻² light flux was used (Goldilux Photometer with UV-A probe). Visible irradiation experiments were performed using a long-pass filter, Schott GG 420 (Oriol 59480). A thermostated (20 °C) 10 mm quartz cell (3.5 mL sample solution) equipped with magnetic stirring was used. In a preliminary experiment, the UV-vis absorption spectra of the closed and open forms and the λ_{max} of the open form were determined. In a second experiment the absorbance at the photostationary equilibrium, A_{eq}, was measured at λ_{max} and then the decrease in the absorbance vs. time was monitored.

4.2. NMR studies

For NMR investigations, samples in toluene-d₈ were irradiated directly in the NMR tube (5 mm), thermo-regulated, using a 1000 W Xe-Hg HP filtered short-arc lamp (Oriol) equipped with a filter for UV irradiation (Schott 011FG09, 259 < λ < 388 nm + 313 nm interference filter). After irradiation had been stopped, the samples were transferred to the thermoregulated probe of the NMR spectrometer (¹H, 300 MHz).

The complete NMR data (1 and 2 D spectra and assignments) of compounds **2–4** and the NMR characterization of the photo-products of compounds **2** and **3** are reported in the supplementary data.

4.3. Synthesis

*Methyl 2-methyl-2-(2,2-diphenyl-2H-naphtho[1,2-*b*]pyran-4-yl)propanoate 2.* TiCl₄ (0.70 mL, 6.7 mmol) was added to a solution of naphtho[1,2-*b*]pyranone **1** (200 mg, 0.677 mmol) and 1-methyl trimethylsilyl dimethylketene acetal (0.700 mL, 3.4 mmol) in CH₂Cl₂ (0.5 mL) at r.t. After 30 min the solution was quenched with HCl (5%, 25 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic phases were dried (Na₂SO₄) and the solvent evaporated under reduced pressure leaving a brown oil that was purified by column chromatography (2% EtOAc/ether petroleum, silica gel) to give **2** as slightly yellow crystals (187 mg, 75% yield). Mp 118–121 °C. IR (KBr, cm⁻¹): 3054, 2944, 2866, 1728, 1642, 1587, 1493, 1446, 1383, 1265, 1187, 1132, 983. ¹H NMR (toluene-d₈): 8.45 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 8.4 Hz, 4H), 7.35 (d, J = 8.6 Hz, 1H), 7.31 (d, J = 8.7 Hz, 1H), 7.24 (dd, J = 8.4, 6.8 Hz, 1H), 7.14 (dd, J = 8.6, 6.8 Hz, 1H), 7.08 (dd, J = 8.4, 7.9 Hz, 4H), 7.03 (d, J = 8.7 Hz, 1H), 6.96 (dd, J = 7.9, 2H), 3.36 (s, 3H), 1.45 (s, 6H). ¹³C NMR (toluene-d₈): 177.0, 148.4, 145.2, 137.8, 134.1, 127.9, 127.8, 127.4, 127.2, 126.4, 125.6, 125.5, 124.2, 122.5, 121.4, 120.5, 116.2, 82.3, 51.6, 44.4, 25.5. MS: m/z (%): 434 (45), 357 (100), 334 (96), 333 (99), 283 (38), 165 (45). EI-HRMS: calculated for C₃₀H₂₆O₃: 434.1882; found: 434.1884.

*2-Methyl-2-(2,2-diphenyl-2H-naphtho[1,2-*b*]pyran-4-yl)propanoic acid 3.* A mixture of naphthopyran **2** (320 mg, 0.739 mmol) and NaOH (1.5 g, 37.5 mmol) in EtOH (30 mL) was heated under reflux for 24 h. After return to r.t., the solvent was removed under reduced pressure and water (50 mL) and ethyl acetate (20 mL) were added. The organic phase was discarded and the aqueous phase acidified with HCl (25 mL, 5%) and then extracted with ethyl acetate (3 × 50 mL). The combined organic phases were dried (Na₂SO₄) and the solvent evaporated under reduced pressure leaving an off-white solid that was washed with Et₂O (5 mL) to give **3** as white solid (187 mg, 60% yield). Mp 224–226 °C. IR (KBr, cm⁻¹): 3062, 2989, 2885, 2657, 2530, 1691, 1639, 1446, 1378, 1262, 1147, 1100, 970. ¹H NMR (toluene-d₈): 8.44 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 4H), 7.39 (d, J = 8.8 Hz, 1H), 7.35 (d, J = 8.2 Hz, 1H), 7.24 (dd, J = 8.4, 6.9 Hz, 1H), 7.15 (dd, J = 8.2, 6.9 Hz, 1H), 7.13–6.91 (m, 7H), 6.06 (s, 1H), 1.41 (s, 6H). ¹³C NMR (toluene-d₈): 179.9, 148.6, 145.3, 137.7, 134.5, 128.2,

127.7 (two signals), 127.5, 126.7, 125.8, 122.7, 120.9, 120.7, 122.0, 124.8, 116.4, 82.7, 44.5, 25.7. MS: m/z (%): 420 (3), 402 (2), 376 (21, M-CO₂), 334 (24), 333 (100), 299 (89), 209 (23), 165 (21). EI-HRMS: calculated for C₂₉H₂₄O₃: 420.1725; found: 420.1720.

Spiro[3-phenyl-1*H*-indene-1,4'-3',3'-dimethylnaphtho[1,2-*b*]pyran-2'-one] **4**. Trifluoromethanesulfonic acid (0.4 mL, 4.5 mmol) was added to naphthopyran **2** (100 mg, 0.23 mmol) and the mixture stirred for 3 h at r.t. Water (10 mL) was added and the solid formed filtered and dissolved in Et₂O (10 mL). The organic solution was dried (Na₂SO₄) and the solvent evaporated under reduced pressure leaving compound **4** as a white solid (89 mg, 86%). Mp. 89–92 °C. IR (KBr, cm⁻¹): 3061, 2962, 2920, 2852, 1770, 1463, 1375, 1244, 1098. ¹H NMR: 8.42 (d, *J* = 8.4, 1H), 7.82 (d, *J* = 8.0, 1H), 7.73 (d, *J* = 8.3, 2H), 7.63 (dd, *J* = 8.4, 7.0, 1H), 7.60–7.45 (m, 6H), 7.34 (d, *J* = 8.0, 1H), 7.32 (dd, *J* = 7.2, 6.9, 1H), 7.20 (dd, *J* = 8.0, 6.9, 1H), 7.08 (d, *J* = 8.6, 1H), 6.61 (s, 1H), 1.46 (s, 3H), 1.14 (s, 3H). ¹³C NMR: 173.4, 148.3, 148.1, 146.7, 142.0, 134.9, 133.9, 133.0, 128.9, 128.6, 127.9, 127.7, 127.6, 126.8, 126.7, 126.6, 124.3, 123.6, 123.2, 123.0, 121.4, 121.3, 119.8, 60.6, 43.2, 23.0, 18.7. MS: m/z (%): 402 (46), 374 (7), 359 (44), 332 (100), 302 (24), 300 (19), 255 (47). EI-HRMS: calculated for C₂₉H₂₂O₂: 402.1620; found: 402.1619.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2010.09.009.

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