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Unexpected formation of new photochromic compounds derived from 3,3-diphenyl-*3H*-naphtho[2,1-*b*]pyran-1-one

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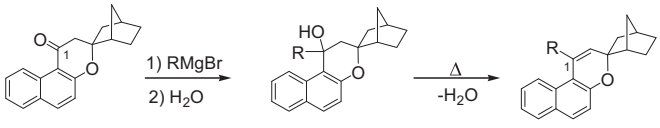
ABSTRACT

Two new unexpected photochromic compounds were obtained from naphtho[2,1-*b*]pyran-1-one **1**. The reaction of this ketone with the silyl enol ether methyl trimethylsilyl dimethylketene acetal, catalyzed by $TiCl_4$, afforded the photochromic dihydronaphtho[2,1-*b*]pyranone **2**. The Reformatsky reaction of ketone **1** with ethyl bromoacetate led to the formation of the expected alcohol that under acid treatment gave, unexpectedly, the novel photochromic benzocoumarin **6**. UV irradiation compounds **2** and **6** in solution provided thermally stable photoproducts that returned to the initial uncoloured forms under visible irradiation. The photochromic behaviour of these compounds and the structures of the photoproducts formed in these reactions were characterized by 1D and 2D NMR.

1. Introduction

Naphthopyrans are well known for their photochromic properties.[1] Under UV irradiation these uncoloured molecules undergo an electrocyclic reaction of the pyran ring leading to highly conjugated coloured species that return thermally to the closed form. The photochromic behaviour of these molecules, in particular the colour generated and the kinetics of the colouration and fading process, can be controlled by the introduction of substituents or fused rings, specially in the aromatic groups linked to the sp^3 carbon and in some positions of the naphthalene core.[2] Few reports concern the photochromic properties of naphthopyrans substituted in the pyran double bond since it is expected that such molecules should exhibit very high fading kinetics due to steric constrains and as such, the coloured species would not be unperceivable to the naked eye.[3,4,5]

The most widely used strategy to synthesise naphthopyrans applies a one pot multi-step reaction involving the Claisen rearrangement of propargylic ethers obtained in situ from the acid catalysed reaction of naphthols with 1,1-diarylprop-2-yn-1-ols.[6] Alternatively, several naphthopyrans substituted in position 1 have been prepared from naphthopyranones derived from 2-norbornanone through reaction with Grignard reagents followed by dehydration (Scheme 1).[5]



Scheme 1. Synthesis of 1-substituted 3*H*-naphtho[2,1-*b*]pyrans.

In an attempt to prepare some new 3*H*-naphtho[2,1-*b*]pyrans functionalized in position 1, we studied the reaction of naphthopyranone **1** with some nucleophiles and obtained two photochromic compounds with an unexpected structure. The photochromic behaviour of these compounds and the structures of the photoproducts formed under UV irradiation were characterized by NMR analysis of UV irradiated solutions of these new molecules.[7]

2. Results and discussion

2.1. Synthesis

The reaction of naphthopyranone **1**[8] with the silyl enol ether methyl trimethylsilyl dimethylketene acetal in the presence of an excess of $TiCl_4$ afforded the diester **2** directly (Scheme 2) that surprisingly showed photochromic properties. The *trans* configuration

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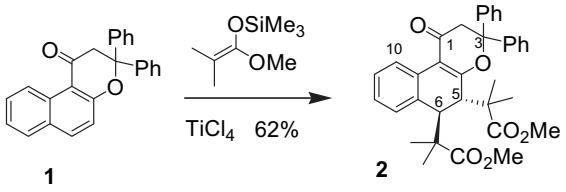
of the two ester chains in this compound was deduced from the fact that in the ^{1}H NMR spectrum, H-5 and H-6 appeared as singlets, which points to a 90° dihedral angle for these two hydrogen atom and thus to a *trans* configuration for the ester chains. Instead of the more usual mode of addition of the ketene acetal to the carbonyl group we obtained the product resulting from double addition to the naphthalene.[9] No product from the addition to the carbonyl group was detected.



Scheme 2. Synthesis of dihydronaphthopyranone **2**.

The Reformatsky reaction of **1** with ethyl bromoacetate in the presence of zinc and iodine gave the alcohol **3** along with a minor amount of the conjugated dye **4** formed by base-catalysed pyranone ring opening.[4] When the alcohol **3** was treated with HOAc under reflux two compounds were obtained: the conjugated ester **5**, formed by dehydration, and the unexpected photochromic benzocoumarin **6** (Scheme 3). The complete NMR data (1 and 2 D spectra and assignments) of compounds **1**–**6** are reported in the Supplementary data.

Since the ester **5** was stable in HOAc under reflux, the benzocoumarin **6** was probably formed from alcohol **3** by dehydration, thermal pyran ring opening, followed by enolization, rotation and acid catalyzed lactone formation (Scheme 4).

2.2. Photochromic behaviour under continuous UV irradiation of compounds 2 and 6 at 20 °C

In toluene solution (10^{-3} M) dihydronaphthopyranone **2** is nearly colourless with a very strong absorption in the near UV region (λ_{max}=314 nm). Continuous UV light irradiation of this solution at 20 °C, leads to the slow development of an intense yellow colouration with a maximal absorption at 403 nm (Fig. 1), but the photostationary state was not achieved even after 40 min of irradiation (Figs. 1 and 2).

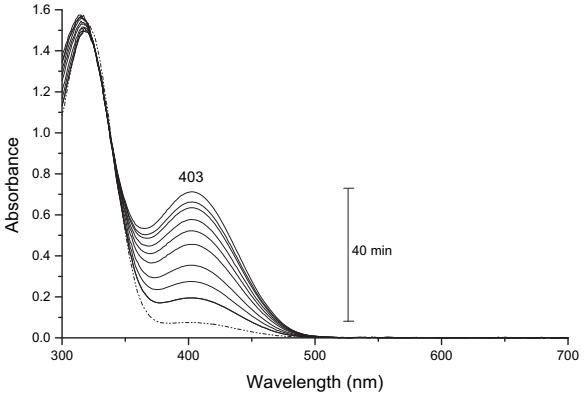
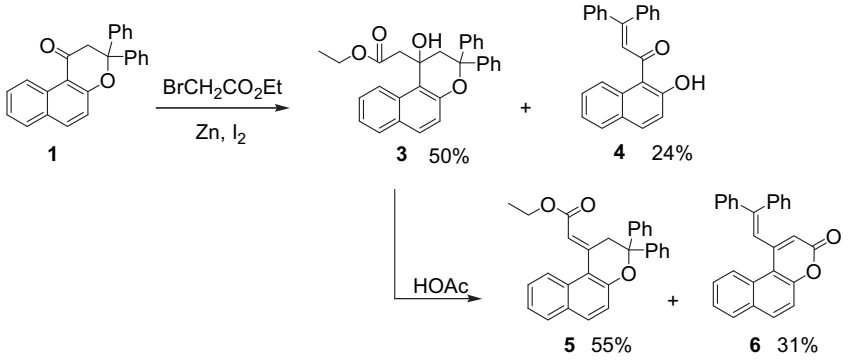
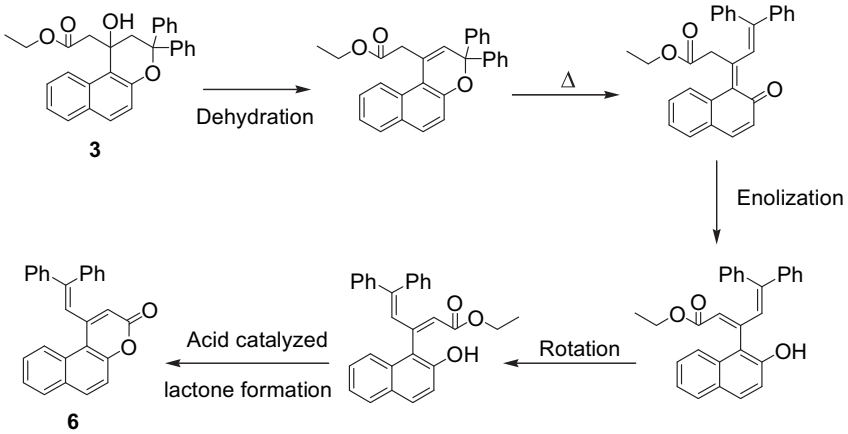


Figure 1. UV–vis absorption spectra of dihydronaphthopyranone **2** (10^{-3} M) before (––) and after (———) UV irradiation.



Scheme 3. Synthesis of 2,3-dihydro-1*H*-naphthopyran **5** and benzocoumarin **6**.



Scheme 4. Mechanism for the formation of benzocoumarin **6** from alcohol **3**.

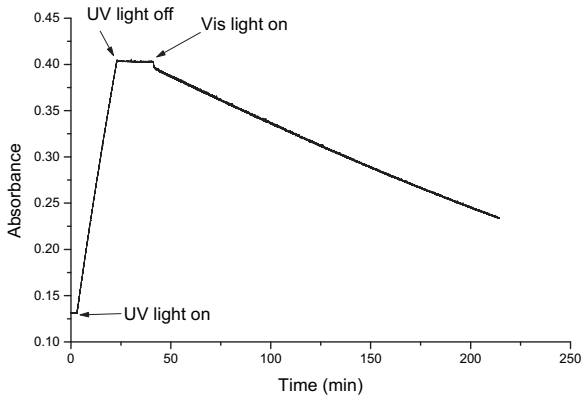


Figure 2. Colour forming and colour bleaching for dihydronaphthopyranone **2** measured at 403 nm.

When the UV light was turned off, a stable absorbance was observed underlining the formation of a long-lived coloured compound. Visible irradiation (>420 nm) induces a slow absorption decrease pointing to a photoreversible process (Fig. 2).

In toluene solution (10^{-4} M) benzocoumarin **6** was also uncoloured with a very strong absorption in the near UV region (λ_{max}=370) (Fig. 3). Continuous UV light irradiation of this solution at 20 °C, leads to the development of a yellow colouration with a maximal absorption at 432 nm (Fig. 3). As observed for compound **2**, the absorbance at the maximal absorption wavelength increases with time but the photostationary state was not achieved after 10 min of irradiation (Fig. 4). When the UV irradiation was turned off, the absorbance decreased slowly but this behaviour was not fully reproducible since the repetition of the UV irradiation (10 min)/dark cycles showed that the maximum absorbance decreases, which indicates that some degradation photoproducts are being formed.

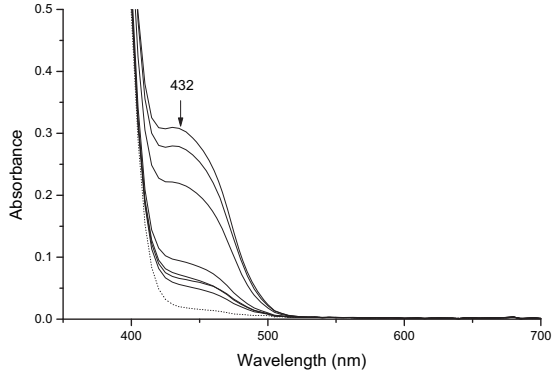


Figure 3. UV–vis absorption spectra of compound **6** (10^{-4} M) before (– – – –) and after (——) UV irradiation.

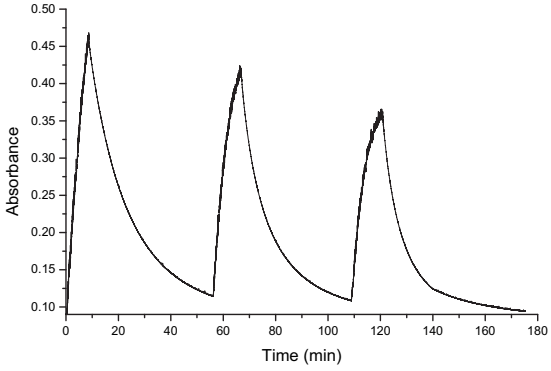


Figure 4. UV(10 min)/dark cycles for benzocoumarin **6** measured at 432 nm.

2.3. NMR analysis of UV irradiated solutions of compounds 2 and 6

*2.3.1. Photochromic behaviour of dihydronaphthopyranone **2**.* To investigate the structure of the products formed upon UV irradiation of compounds **2** and **6**, NMR studies were carried out before and after UV irradiation. Fresh samples of dihydronaphthopyranone **2** and benzocoumarin **6** in degassed toluene-d_8 were directly irradiated in the NMR tube (5 mm) at rt using a 1000 W Xe–Hg HP filtered (Schott 011FG09, 259<λ<388 nm+313 nm interferential filter) short-arc lamp (Oriel). After irradiation, the sample was rapidly transferred into the thermoregulated probe of a Bruker NMR spectrometer. The ^{1}H NMR spectra were recorded at regular time intervals to monitor the changes in peak-intensities and thus

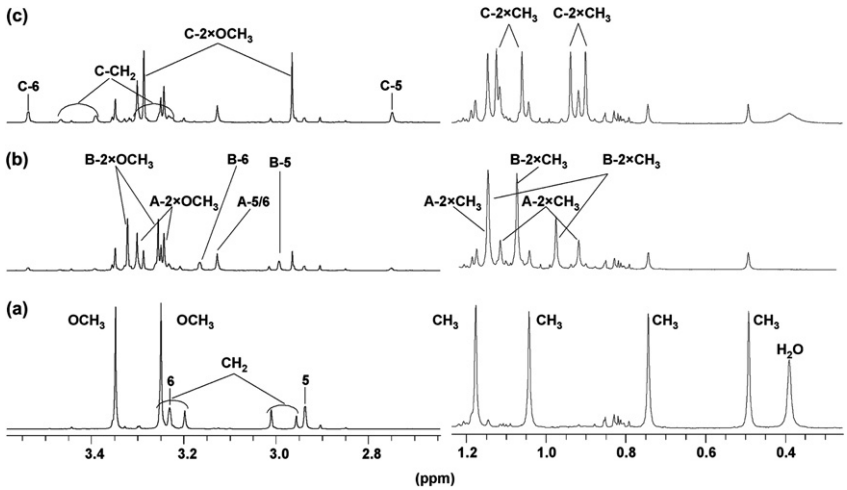


Figure 5. Aliphatic part of the ^{1}H NMR spectra of 5,6-dihydronaphthopyranone **2**: (a) before hv, (b) after 150 min of 313 nm UV light irradiation and (c) after 15 days of thermal evolution in the dark.

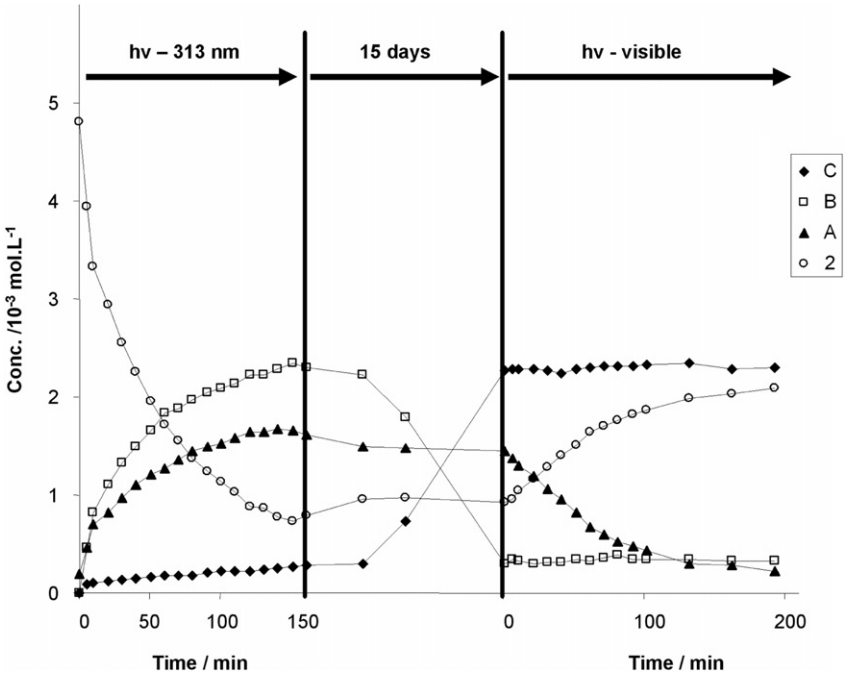


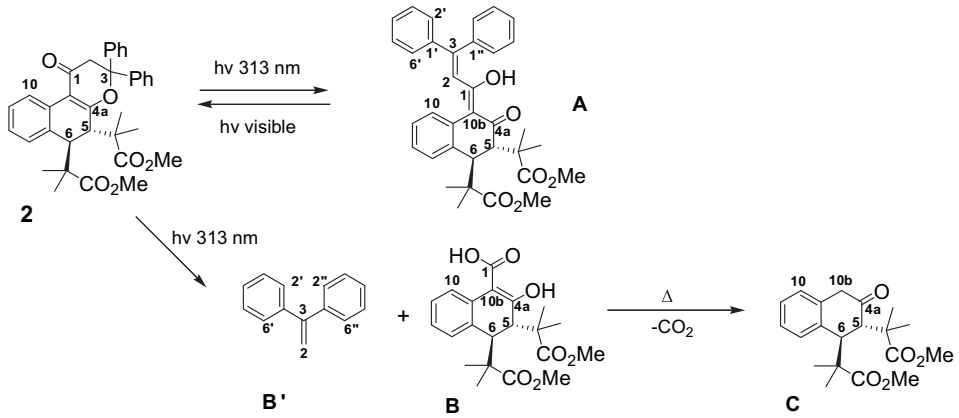
Figure 6. Time-evolution of the photoproducts of dihydronaphthopyranone **2** under UV, in the dark and under visible irradiation, at room temperature.

obtain information about the formation of photoproducts and the evolution of their concentration in time.

From the analysis of the ^{1}H NMR spectra of dihydronaphthopyranone **2** in solution before and after UV irradiation (Fig. 5) and the time-evolution of each signal, it is clear that UV irradiation of this compound results in the formation of four new photoproducts, labelled **A**, **B**, **B′** and **C** (Fig. 6). The thermal evolution of the sample for 15 days in the dark indicates that the photoproduct **B** evolves slowly towards **C**, while **A** seems to be thermally stable. Finally, irradiation of this sample with visible light converts **A** into the initial 5,6-dihydronaphthopyranone **2**, whereas, the concentrations of **B** and **C** remain constant.

Both 1D and 2D NMR experiments were carried out to identify the structures of the four photoproducts (Scheme 5) (see Supplementary data). The photoreversible compound **A** results from the opening of the pyran ring followed by a hydrogen migration from the 3-methylene group towards the oxygen atom thus generating the enol function. The opening of the initial structure was identified from ^{1}H–^{13}C long-range correlations observed in the 2D-HMBC map between the quaternary carbon C-3 at 154.5 ppm and the protons H-2 at 7.00 ppm and H-2'/6' at 7.27 ppm. The highly deshielded chemical shift of OH (δ=16.8 ppm) is in agreement with the H-bonding between OH and C=O. The OH function was located at carbon C-1 at 175.6 ppm as indicated by the cross peaks between C-1 and H-2 and OH. The ketone function was located through the correlation of the signal at 198.2 ppm (C-4a) and the signals at 3.19 ppm (H-5 and H-6).

A second and parallel irreversible process converts compound **2** to side-products **B** and **B′**, resulting from a Norrish type 1 reaction with breaking of the pyranone ring. Structure **B** presents a phenol function, characterized by a singlet signal at 13.9 ppm. The carboxylic acid proton was clearly observed as a broad signal at 12 ppm at low temperature. 1,1-Diphenylethylene **B′** was evidenced by the singlet signal at 5.38 ppm (integration=2H) assigned to the alkene protons in position 2 (Scheme 5). ^{1}H–^{13}C long-range correlations were observed in 2D-HMBC between the C-3 quaternary carbon (150.3 ppm) and the methylene protons (5.38 ppm) and the aromatic protons H-2'/6'=H-2″/6″ (7.31 ppm).



Scheme 5. Photochemical transformations of compound **2** under UV (313 nm) irradiation.

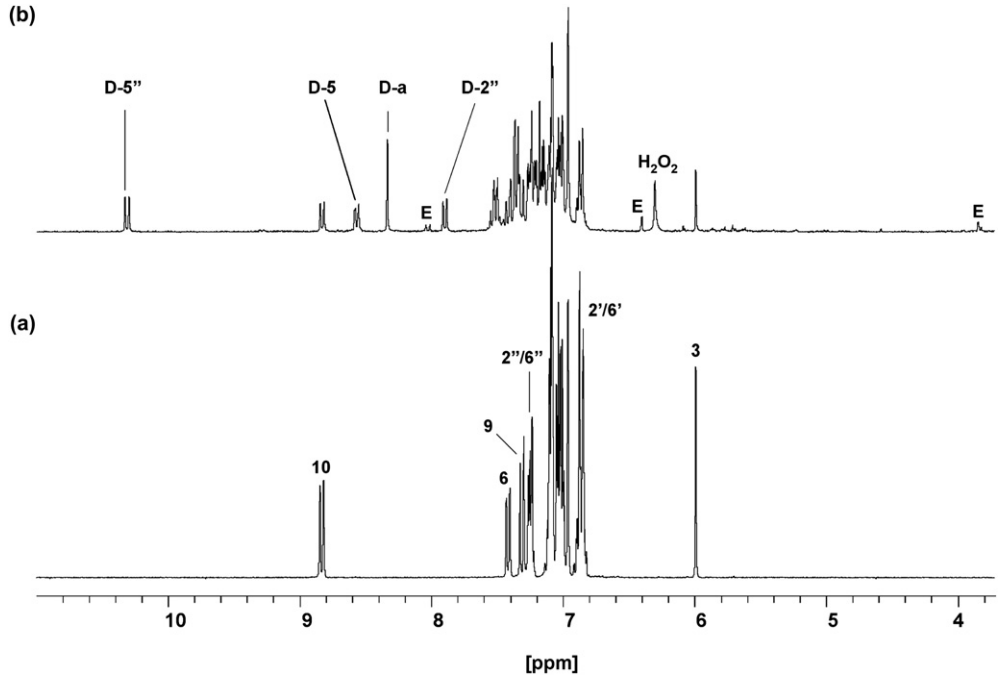


Figure 7. ^{1}H NMR spectra of benzocoumarin **6** (a) before hv and (b) after 10 min of UV irradiation at room temperature.

Finally, the thermal evolution of **B** to **C** was observed. This reaction results from the loss of CO_2 as proved by the disappearance of the carboxyl proton resonance and the appearance of two doublet signals at 3.48 and 3.33 ppm (^{2}J=22 Hz), characterizing a diastereotopic methylene group at C-10b. Besides, $^{1}H-^{13}C$ correlations were observed between protons H-10b (3.48 and 3.33 ppm), H-5 (2.91 ppm), H-6 (3.61 ppm) and the carbonyl function C-4a (208 ppm).

*2.3.2. Photochromic behaviour of benzocoumarin **6**.* At room temperature, UV irradiation of benzocoumarin **6** (10^{-2} M, toluene) leads to the development of a yellow colouration. ^{1}H NMR spectra analysis before and after UV irradiation (Fig. 7) and the time-evolution of each signal indicate that the UV irradiation of benzocoumarin **6** results in the formation of one major and thermally stable photoproduct, labelled **D**, as well as hydrogen peroxide (singlet signal at 6.30 ppm). Signals of an additional form, labelled **E**, are also observed, but they were not identified due to the very low concentration of this product.

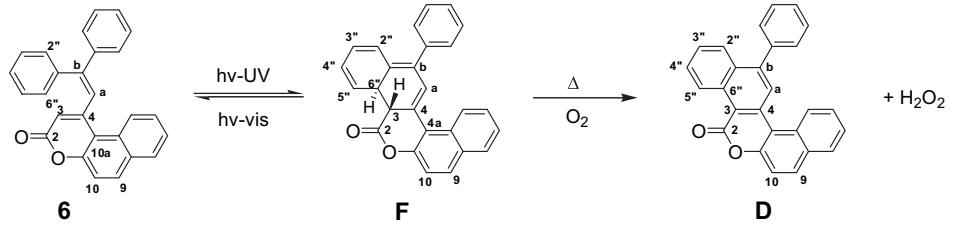
To elucidate the structure of **D** (Scheme 6), 1 and 2D NMR experiments were carried out. More particularly, $^{1}H-^{1}H$ long-range scalar correlations were measured in TOCSY-1D experiment, from H-5″ at 10.38 ppm up to H-2″ at 7.97 ppm, via H-4″ at 7.58 ppm and H-3″ at 7.31 ppm. The two quaternary carbons C-3 and C-6″ resulting from a cyclization product were evidenced at 115.8 ppm and 132.8 ppm, respectively, from a 2D HMBC experiment. Carbon C-3 was long-range correlated with H-5″ at 10.38 ppm and H-a at 8.39 ppm, while carbon C-6″ was correlated with H-2″ at 7.97 ppm and H-4″ at 7.58 ppm. Compound **D** was therefore identified as a lactone derivative formed by a stilbene-type electrocyclization followed by an oxidation reaction (Scheme 6). The absorbance decrease observed in Figure 4 after the UV light was turned off is therefore due to degradation of the original compound and not to the return to the uncoloured initial form.

To prevent the oxidation reaction and therefore the formation of **D**, the experiment was repeated with a degassed solution of **6**. Under these conditions a new compound **F** was detected, which reverts photochemically to benzocoumarin **6** (Scheme 6, Figs. 8 and 9).

As expected, **F** corresponds to the electrocyclised structure of the benzocoumarin **6** that upon oxidation is transformed to **D**. The formation of the cyclisation product **F** was evidenced by two doublet signals in ^{1}H NMR spectrum at 3.23 and 3.84 ppm (^{3}J=22 Hz), assigned to H-3 and H-6″, respectively. A $^{1}H-^{1}H$ COSY experiment established the connectivity between H-3/H-6″ at 3.84 ppm, H-6″/H-5″ at 6.61 ppm, H-5″/H-4″ at 5.90 ppm, H-4″/H-3″ at 6.02 ppm and H-3″/H-2″ at 6.30 ppm.

3. Conclusion

Two new unexpected photochromic compounds were obtained from naphtho[2,1-*b*]pyran-1-one and their behaviour studied by NMR techniques. UV irradiation of dihydronaphthopyranone **2** lead to the opening of the pyranone cycle with formation of the very stable yellow enol **A** that returned to the initial closed form under visible irradiation. Both transformations are slow and the



Scheme 6. Photochemical transformations of benzocoumarin **6** under UV (313 nm) irradiation.

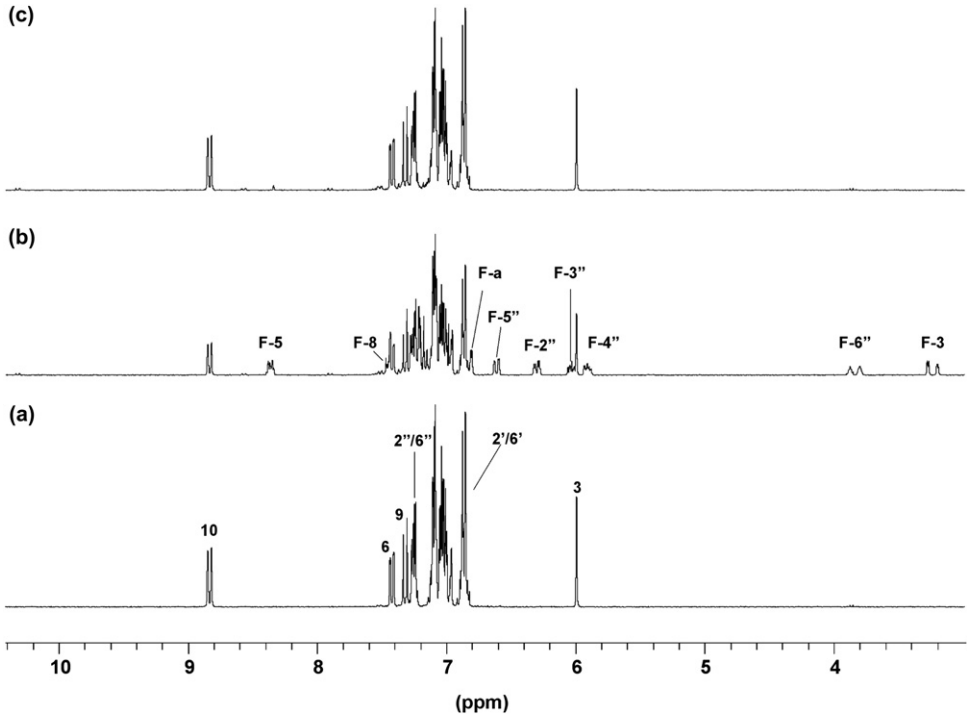


Figure 8. ^{1}H NMR spectra of benzocoumarin **6** in degassed toluene solution at room temperature: (a) before hv, (b) after UV irradiation and (c) after visible irradiation.

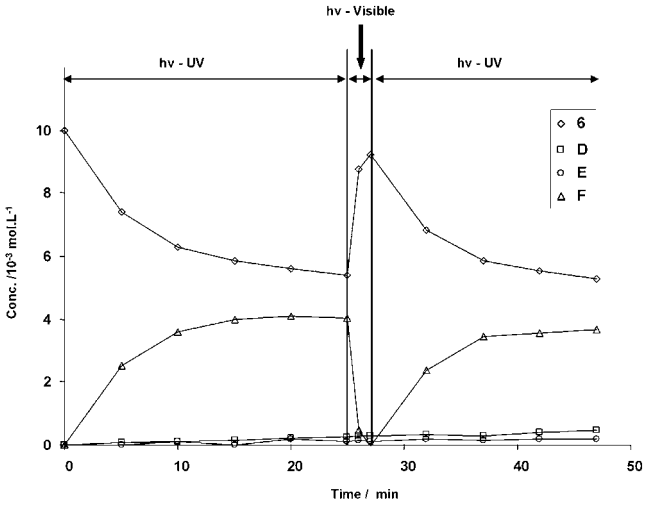


Figure 9. Time-evolution of the photoproducts of benzocoumarin **6** in degassed toluene solution under UV and visible irradiation, at room temperature.

irreversible transformation of **2** into three degradation products, **B**, **B′** and **C**, was also observed. UV irradiation of a degassed solution of benzocoumarin **6**, formed by a multi-step reaction in the acidic treatment of alcohol **3**, lead to the formation of a yellow and stable photoproduct **F**, formed by an electrocyclic stilbene-type electrocyclisation reaction that under visible irradiation reverts to the original form **6**. In the presence of oxygen, the photoproduct **F** was irreversibly converted to the uncoloured lactone **D**.

4. Experimental

4.1. General methods

The reactions were monitored by thin-layer chromatography on aluminium plates precoated with Merck silica gel 60 F_{254} (0.25 mm). Column chromatography (CC) was performed on silica gel 60 (70–230 mesh). The new compounds were determined to be >95% pure by ^{1}H NMR spectroscopy. The ^{1}H and ^{13}C NMR spectra in $CDCl_3$ were recorded at 298 K in $CDCl_3$ using a Bruker ARX400 spectrometer (at 400.13 and 100.62 MHz). Chemical shifts (δ) are reported in parts per million UV–vis spectra were recorded on a CARY 50 Varian spectrophotometer. IR spectra were obtained on a Perkin–Elmer FTIR 1600 spectrometer using KBr disks (wavenumbers in cm^{-1}).

4.2. 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 Oriel Instruments), equipped with a filter Schott 011FG09 ($259<\lambda<388$ nm with $\lambda_{max}=330$ nm and $T=79\%$). The light from the UV lamp was filtered using a water filter (61,945 Oriel Instruments) and then carried to the spectrophotometer holder at a right angle to the monitoring beam using an optical fibre system (77,654 Oriel 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 (Oriel 59,480). 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 photostationary equilibrium, A_{eq}, was measured at λ_{max} and then the decrease in the absorbance vs time was monitored.

4.3. NMR studies

For NMR investigations, samples in toluene-d_8 were irradiated directly in the NMR tube (5 mm), thermo-regulated, using a 1000 W Xe–Hg HP filtered short-arc lamp (Oriel) equipped with a filter for UV irradiation (Schott 011FG09, $259<\lambda<388$ nm+313 nm interferential filter) and a filter for visible irradiation (Schott SCFIKG1503: $295<\lambda<800$ nm+oriel 3–74, $\lambda>400$ nm). After irradiation had been stopped, the samples were transferred to the thermoregulated probe, QNP (^{1}H–^{13}C–^{19}F–^{31}P) or TXI (^{1}H–^{13}C–^{15}N), of a Bruker Avance-500

spectrometer (ν_0 (^{1}H)=500 MHz, ν_0 (^{13}C)=125 MHz, ν_0 (^{19}F)= 470 MHz).

4.3.1. 1,2-Dihydro-3,3-diphenyl-3H-naphtho[2,1-b]pyran-1-one ***1***. A suspension of 2-hydroxy-1-acetonaphthone (1.05 g, 5.6 mmol), benzophenone (4.0 g, 22 mmol), sodium (1.0 g, 43 mmol) and *tert*-butanol (5.0 mL, 52 mmol) in 30 mL of benzene was heated under reflux for 2 h. During the heating the suspension became progressively orange. After cooling to room temperature, the solution was quenched with water (100 mL), extracted with ethyl acetate (3×50 mL) and the combined organic layers dried (Na_2SO_4) and concentrated under reduced pressure. To the residue was added CH_3COOH (5 mL) and HCl concn (1 mL) and the solution was heated under reflux for 1 h. The solution was quenched with water (100 mL) and extracted with ethyl acetate (3x50 mL). The combined organic layers were dried (Na_2SO_4) and the solvent evaporated under reduced pressure leaving a brown oil residue that was purified by CC (3–4% EtOAc/petroleum ether) to give pure **1** as white crystals (656 mg, 33% yield). Mp 160–161. IR: 3081, 3050, 2998, 1664, 1616, 1592, 1565, 1509, 1432, 1371, 1230, 1216, 1205, 1120, 1000, 975, 823, 750, 698. ^{1}H NMR (toluene-d_8): 9.83 (d, J=8.7 Hz, 1H), 7.39 (d, J=9.1 Hz, 1H), 7.35 (d, J=8.4 Hz, 4H), 7.33 (t, J=6.8 Hz, 1H), 7.30 (d, J=8.2 Hz, 1H), 7.06 (t, J=6.8 Hz, 1H), 7.02–6.96 (m, 5H), 6.89 (t, J=7.2 Hz, 2H), 3.27 (s, 2H). ^{13}C NMR (toluene-d_8): 190.7, 160.9, 142.8, 136.9, 131.3, 129.3, 129.1, 128.1, 127.9, 127.4, 126.2, 126.0, 124.4, 118.9, 113.0, 85.8, 49.6. MS (TOF): *m*/*z* (%): 350 (28), 322 (24), 273 (100), 180 (80), 170 (55), 165 (49), 142 (16), 114 (19).

4.3.2. trans-5,6-Di[(1-methyl-1-methoxycarbonyl)ethyl]-3,3-diphenyl-1,2,5,6-tetrahydro-3H-naphtho[2,1-b]pyran-1-one ***2***. $TiCl_4$ (215 μl, 2.03 mmol) was added to a solution of naphtho[2,1-*b*]pyranone **1** (200 mg, 0.677 mmol) and methyl trimethylsilyl dimethylketene acetal (411 μl, 2.03 mmol) in CH_2Cl_2 (2 mL) at 0 °C. After 1 h, another equivalent of $TiCl_4$ was added (70 μl, 0.677 mmol) and the solution kept at 0 °C for 30 min more. The solution was then quenched with water (20 mL) and extracted with ethyl acetate (3×20 mL). The combined organic phases were dried (Na_2SO_4) and the solvent evaporated under reduced pressure leaving a residue that was purified by CC (10% EtOAc/petroleum ether) to give **2** as a white solid (230 mg, 62 %). Mp 67–69. IR: 3066, 2977, 2946, 2940, 1728, 1665, 1593, 1452, 1395, 1255, 1130. ^{1}H NMR: 8.34 (d, J=8.0 Hz, 1H), 7.48 (d, J=7.4 Hz, 2H), 7.40–7.20 (m, 8H), 7.23 (t, J=7.6 Hz, 1H), 7.08 (t, J=7.6 Hz, 1H), 6.97 (d, J=7.5 Hz, 1H), 3.69 (s, CH_3O), 3.45 (s, CH_3O), 3.34 (d, J=16.4 Hz, 1H) and 3.44 (d, J=16.4 Hz, 1H) AB system ($COCH_2$), 3.17 (s, 1H), 2.79 (s, 1H), 1.17 (s, CH_3), 1.06 (s, CH_3), 0.75 (s, CH_3), 0.48 (s, CH_3). ^{13}C NMR: 189.9, 177.7, 176.6, 170.5, 144.4, 142.0, 131.7, 130.8, 130.7, 128.9, 128.7, 128.0, 127.8, 126.6, 126.3, 126.1, 113.6, 87.9, 52.4, 52.1, 48.6, 48.4 (two signals), 48.0, 47.2, 25.1, 24.0, 23.8, 20.6. MS (TOF): *m*/*z* (%): 522 (10), 451 (5), 419 (22), 271 (50), 239 (81), 211 (100), 179 (23), 165 (23). HRMS: calculated for $C_{35}H_{36}O_6$: 552.2512; found: 552.2507.

4.4. Reaction of *3H*-naphtho[2,1-*b*]pyranone 1 with ethyl bromoacetate

A solution of **1** (162 mg, 0.46 mmol) and ethyl bromoacetate (0.60 mL, 5.4 mmol) in 10 mL of ethyl ether/benzene (1:4) was slowly added over 1 h to a mixture of zinc (2.0 g, 30 mmol) and iodine (six small crystals) and heated with stirring under reflux. After the addition was complete the solution was maintained under reflux with stirring for one additional hour and then poured into water. The aqueous phase was extracted with EtOAc (3×50 mL) and the combined organic layers dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by CC (8–10% EtOAc/petroleum ether) to give the alcohol **3** as a white solid (101 mg, 50%) and the dye **4** as an orange oil (38 mg, 24%).

4.4.1. 1-(Ethoxycarbonylmethyl)-1,2-dihydro-3,3-diphenyl-3H-naphtho[2,1-b]pyran-1-ol ***3***. Mp 106–108. IR: 3472, 3056, 2973, 2936, 1692, 1619, 1442, 1390, 1343, 1229, 1192, 979. ^{1}H NMR: 8.61 (d, J=8.8 Hz, 1H), 7.75 (m, 2H), 7.54 (m, 2H), 7.43 (m, 3H), 7.39–7.10 (m, 8H), 4.08 (m, 2H, OCH_2CH_3), 3.65 (s, 1H, OH), 3.45 (d, J=14.5 Hz, 1H) and 3.35 (d, J=14.5 Hz, 1H) AB system (CH_2), 3.38 (d, J=16.6 Hz, 1H) and 2.25 (d, J=16.7 Hz, 1H) AB system (CH_2), 1.15 (t, J=7.1 Hz, 3H, OCH_2CH_3). ^{13}C NMR: 172.18 (C=O), 151.53, 144.59, 143.29, 131.87, 131.06, 130.31, 128.83, 128.49, 128.38, 127.41, 127.24, 126.58, 126.21, 125.73, 125.53, 123.32, 119.43, 117.18, 80.93 (CPh_2), 69.11 (C–O), 60.48 (C–O), 46.72, 43.78, 14.02 (CH_3). MS (TOF): *m*/*z* (%): 438 (2), 420 (11), 374 (17), 350 (33), 333 (42), 273 (85), 212 (25), 180 (92), 170 (100), 165 (86). HRMS: calculated for $C_{29}H_{26}O_4$: 438.1831; found: 438.1825.

4.4.2. 1-(1-Oxo-3,3-diphenylprop-2-enyl)-2-naphthol ***4***. IR: 3488, 3053, 3026, 1727, 1617, 1556, 1501, 1315, 1237, 1182. ^{1}H NMR: 12.82 (s, OH), 8.45 (d, J=8.5 Hz, 1H), 7.87 (d, J=8.9 Hz, 1H), 7.77 (d, J=8.1 Hz, 1H), 7.52 (t, J=7.0 Hz, 1H), 7.45–7.25 (m, 11H), 7.15 (s, 1H), 7.12 (d, J=8.9 Hz, 1H). ^{13}C NMR: 196.2, 163.8, 154.1, 141.1, 139.0, 137.0, 131.7, 129.7, 129.5, 129.0, 128.9, 128.5, 128.4, 128.1, 128.0, 127.7, 124.2, 123.9, 119.4, 115.3. MS (TOF): *m*/*z* (%): 350 (24), 322 (19), 273 (100), 180 (64), 170 (50), 165 (46). HRMS: calculated for $C_{25}H_{18}O_2$: 350.1307; found: 350.1310.

4.5. Reaction of alcohol 3 with acetic acid

A solution of naphthopyran-1-ol **3** (110 mg, 0.25 mmol) in glacial HOAc (5 mL) was heated under reflux for 2 h. The solution was quenched with water (50 mL) and extracted with EtOAc (3×20 mL). The combined organic layers were dried (Na_2SO_4), concentrated under reduced pressure and the residue purified by CC (2–20% EtOAc/petroleum ether) to give the ester **5** (58 mg, 55%yield) and the more polar benzocoumarin **6** (29 mg, 31% yield).

4.5.1. 1-(Ethoxycarbonylmethylidene)-1,2-dihydro-3,3-diphenyl-3H-naphtho[2,1-b]pyran ***5***. White solid. Mp 124–126. IR: 3030, 2956, 2920, 2848, 1707, 1629, 1447, 1338, 1229, 1172, 1155. ^{1}H NMR: 8.34 (d, J=8.8 Hz, 1H), 7.81 (m, 2H), 7.59 (d, J=7.3 Hz, 4H), 7.51 (t, J=7.1 Hz, 1H), 7.42–7.22 (m, 8H), 6.38 (s, 1H), 4.37 (s, 2H, CH_2), 4.28 (q, J=7.1 Hz, 2H, OCH_2CH_3), 1.36 (t, J=7.1 Hz, 3H, OCH_2CH_3). ^{13}C NMR: 167.1, 153.3, 145.7, 143.6, 132.0, 130.2, 128.8, 128.2, 127.3 and 127.3, 125.9, 123.8 (two signals) 123.8, 123.7, 118.8, 118.6, 115.4, 84.2, 58.9, 35.3, 14.4. MS (TOF): *m*/*z* (%): 420 (56), 374 (18), 346 (17), 333 (42), 269 (47), 167 (54). HRMS: calculated for $C_{29}H_{24}O_3$: 420.1725; found: 420.1734.

4.5.2. 1-(2,2-Diphenylethenyl)-3H-naphtho[2,1-b]pyran-3-one ***6***. Pale yellow solid. Mp 181–185. IR: 3056, 3019, 1724, 1620, 1541, 1512, 1441, 1338, 1207, 997. ^{1}H NMR: 8.95 (d, J=8.0 Hz, 1H), 8.04 (d, J=8.9 Hz, 1H), 7.97 (d, J=7.3, 1H), 7.59 (m, 2H), 7.51 (d, J=8.9 Hz, 1H), 7.49–7.42 (m, 5H), 7.33–7.20 (m, 6H), 6.08 (s, 1H). ^{13}C NMR: 160.5, 154.3, 153.3, 145.7, 141.3, 138.2, 133.6, 131.1, 130.1, 130.0, 129.4, 128.6, 128.5, 128.4, 126.8, 125.8, 125.7, 125.3, 117.7, 116.6, 113.9. MS (TOF): *m*/*z* (%): 374 (100), 357 (44), 346 (47), 329 (33), 297 (24), 269 (23), 239 (41). HRMS: calculated for $C_{27}H_{18}O_2$: 374.1307; found: 374.1303.

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Supplementary data

Supplementary data for this article can be found in the online version, at doi:10.1016/j.tet.2010.07.044. These data include MOL files and InChIKeys of the most important compounds described in this article.

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