Synthesis of Photochromic Dyes Based on Annulated Coumarin Systems

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Novel 2*H*-chromenes derived from hydroxycoumarins were synthesized, and their photochromic behaviour was studied under flash-photolysis conditions, showing a wide absorption range in the visible region. All the compounds exhibit low fluorescence, which apparently has no negative effect on their photochromic properties.

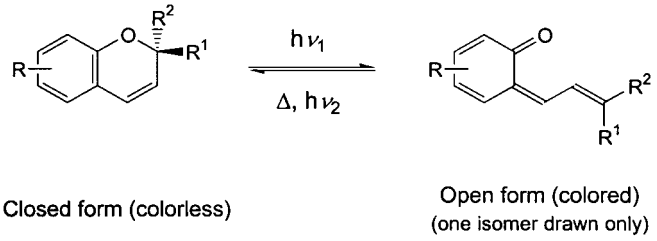
1. Introduction. – Photochromic systems have the ability to undergo a reversible transformation between two states giving rise to different absorption spectra, induced, at least in one direction, by electromagnetic radiation [1]. If one of the states absorbs in the visible region under appropriate conditions, a noticeable, reversible change of color occurs as a consequence of the transformation. Such phototransformations open a wide field of potential applications based upon the reversible color change or upon reversible changes in physical or chemical properties as a consequence of the structural modification accompanying such transformations [2].

In the last two decades, the commercial success of plastic ophthalmic lenses that darken in sunlight, increased the interest in the search for new matrix-compatible organic molecules that allow the development of photochromic systems with enhanced properties. In the field of these variable-transmission optical materials, the main characteristics strived for, are *i*) the ability to be activated by sunlight (heliochromism) and bleached through a thermal process, *ii*) extended absorption in the visible region to provide a neutral colour upon irradiation, *iii*) a suitable fading rate (which is related to the stability of the coloured state), *iv*) high efficiency of coloration upon irradiation ('colorability'), and *v*) a high resistance to photodegradation ('fatigue resistance') [3].

Together with spiro-pyrans and spiro-oxazines, the 2*H*-chromenes (2*H*-[1]benzopyrans) have been extensively studied. These colorless molecules undergo, upon near-UV irradiation, a photo-induced reversible cleavage of the C(2)–O bond, followed by isomerization, leading to a (quasi-planar) colored open form that returns to the starting material by heating or by irradiation with visible light (*Scheme 1*).

In the activated state, these molecules display a yellow-orange color (400–500 nm) making them very attractive to be incorporated into lenses together with spiro-oxazines. The latter are excellent photochromic compounds, but they exhibit relatively narrow absorption bands, usually in the 560–630 nm range, making it difficult to obtain

Scheme 1

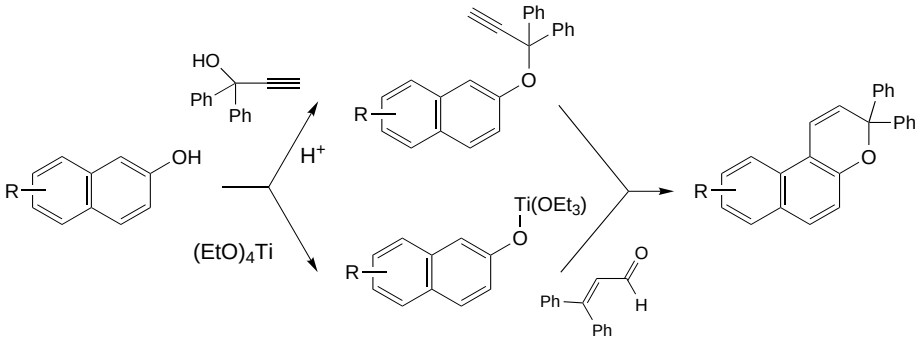


a neutral colour in systems with a single photochromic pigment. The use of mixtures of compounds with complementary absorption spectra seems to be an obvious way to overcome this difficulty; however, the problem of matching the kinetics of the photochromic responses of different families of compounds remains [4].

During our research of new photochromic molecules [5–7], we decided to study new 2*H*-chromenes (including a coumarin nucleus) and to investigate their photochromic and spectrokinetic behaviour as reported in this paper.

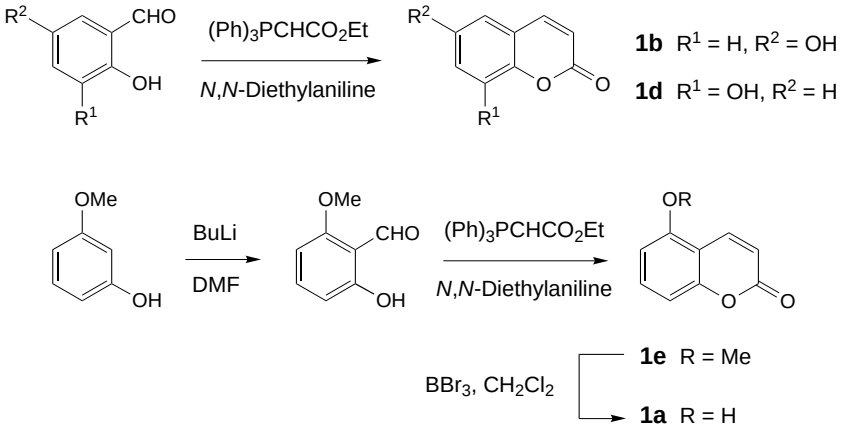
2. Results and Discussion. – 2.1. *Synthesis.* 2*H*-Chromenes can be easily prepared from phenolic precursors. The cyclization may be achieved either by thermal reaction of propynyl naphthyl ethers, first reported by *Iwai* and *Ide* [8] (see also [9]) (Method A), or by condensation of naphthols with α,β-unsaturated carbonyl compounds (Method B) [5][10] (*Scheme 2*).

Scheme 2



Our strategy required the preparation of the hydroxycoumarins **1a**–**d**. Since only 7-hydroxycoumarin (**1c**) is commercially available, the synthesis of 5-, 6- and 8-hydroxycoumarin (**1a**, **1b**, **1d**) was carried out by *Wittig* reaction [11][12] of 2-hydroxybenzaldehydes with ethyl (triphenylphosphoranylidene)acetate (*Scheme 3*). The 6- and 8-hydroxycoumarins (**1b**, **1d**) were prepared in one step from 2,5- and 2,3-dihydroxybenzaldehyde, respectively. Formylation [13] of 3-methoxyphenol followed by *Wittig* reaction led to 5-methoxycoumarin, which was demethylated with BBr_3 [14] to provide **1a** (*Scheme 3*).

Scheme 3



The condensation of **1a**–**c** with 1,1-diphenylprop-2-yn-1-ol catalyzed by *p*-tolylsulfonic acid (PTS) or pyridinium *p*-tolylsulfonate (PPTS) (Method A) provided the 2*H*-chromenes **2**–**5** in low yields. Thereby, slightly higher yields were obtained with PTS (*Table 1*). Three different solvents were used, depending on the solubility of the starting material. Compound **2** was obtained from **1a** after refluxing for 24 h with the highest yield in this series (26%). The reaction of 6-hydroxycoumarin (**1b**) with 1,1-diphenylprop-2-yn-1-ol was completely regioselective, providing the angular chromene **3**. However, the cyclization of 7-hydroxycoumarin (**1c**) led to a mixture of linear **4** and angular **5**, respectively. Under these conditions, no reaction was observed with 8-hydroxycoumarin (**1d**). When treated with $(EtO)_4Ti$ and 3,3-diphenylprop-2-enal (Method B), the chromene **6** was obtained in trace amounts.

2.2. *Fluorescence Properties of the Chromenes* **2**–**5**. The absorption and fluorescence spectra of the 2*H*-chromenes were recorded as shown in *Figs. 1* and *2*. The excitation and emission data are listed in *Table 2*. Thereby, compound **4** was the most

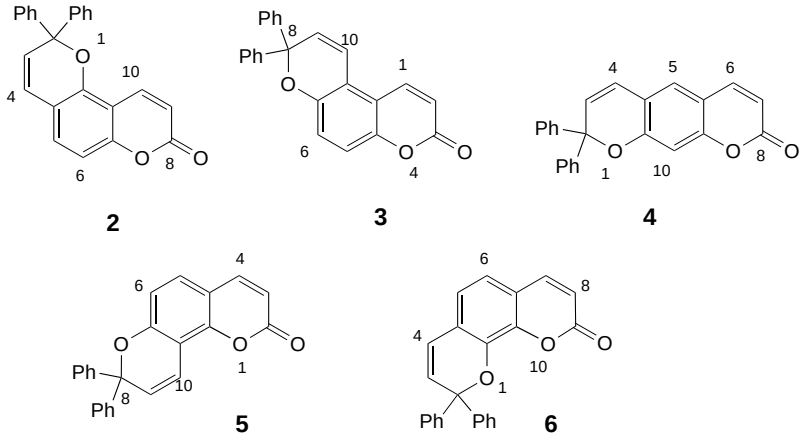


Table 1. *Synthesis of the* 2H-*Chromenes* **2**–**5** *from the OH-Substituted Coumarins* **1** *by* Method A

Coumarin		Conditions PTS-catalyzed[a])	Chromene (%)	Conditions PPTS-catalyzed[b])	Chromene (%)
1a	5-OH	PhMe, 24 h	**2** (26)	–	–
1b	6-OH	MeCN, 40 h	**3** (20)	MeCN, 30 h	**3** (16)
1c	7-OH	PhMe, 48 h	**4/5** (14 *vs.* 4)	CH_2Cl_2, 36 h	**4/5** (10 *vs.* 2)
1d	8-OH	[c])	**6** (no reaction)	[c])	**6** (no reaction)

[a]) *p*-Tolylsulfonic acid. [b]) Pyridinium *p*-tolylsulfonate. [c]) Traces obtained by Method B.

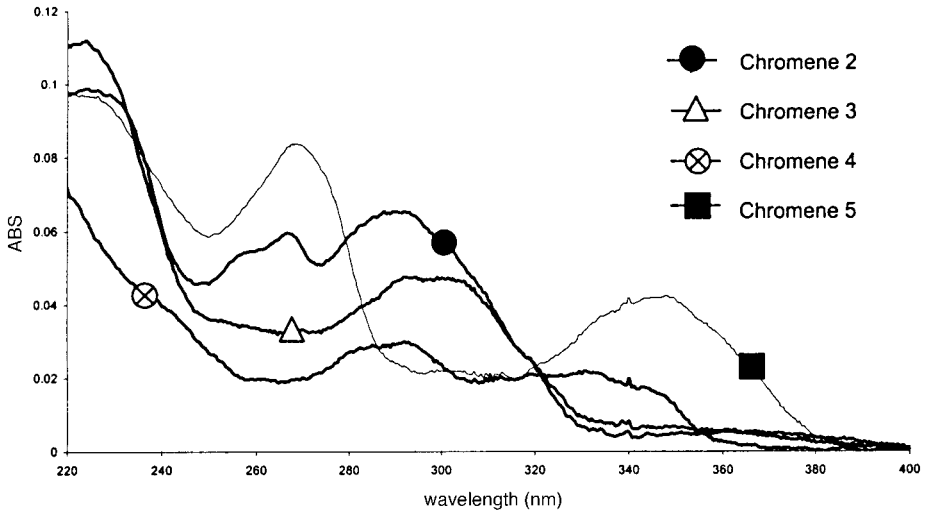


Fig. 1. *Absorption spectra of the chromenes* **2**–**5**

Table 2. *Spectroscopic Data of the Chromenes* **2**–**5** *in MeOH*

Chromene	Excitation	Emission	
	$\lambda_{excitation}$ [nm]	ϕ	$\lambda_{emission}$ [nm]
2	290	0.002	500
3	300	0.009	459
4	290	0.156	396
5	340	0.018	437

fluorescent within this series. The quantum yields ϕ were calculated using 9,10-diphenylanthracene in MeOH as the standard ($\phi = 0.95$) [15].

2.3. *Photochromic Properties.* The photochromic characteristics of the new compounds were determined using a flash-irradiation apparatus coupled to a rapid spectrometer. Details of the procedure are described in the experimental section. The results are summarised in *Table 3* including the data of two parent naphthopyrans (**Ref**$_1$ and **Ref**$_2$) for comparison [8].

Photochromic parameters which have been taken into account include absorption wavelengths λ of the open forms, rate constants (k_Δ) of thermal bleaching and

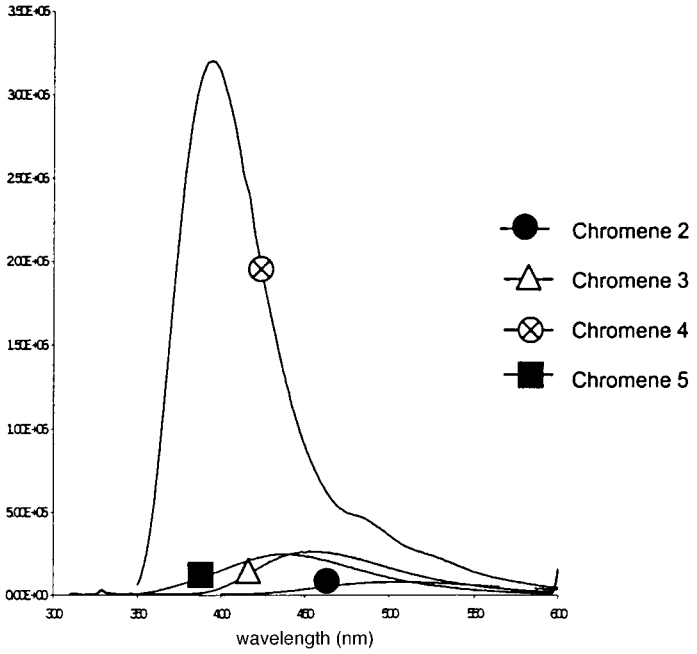


Fig. 2. *Fluorescent spectra of the chromenes* **2**–**5**

'colourability' (measured by the absorbance A_o immediately after the irradiation flash) [3][17], expressed by: $A_o = \varepsilon_{OF} \cdot \Phi_{col} \cdot k \cdot [CF]_o$ (at low concentration), where k depends on experimental conditions; ε_{OF} is the molar absorptivity of the open form at λ_{max}, Φ_{col} is the photocoloration quantum yield, and $[CF]_o$ is the initial concentration of the closed form.

From a general point of view, two features can be observed for all the compounds. Two phases in the kinetics of the fading rate occur, and two wide absorption bands are displayed (except for compound **3**). Regarding the absorption of the colored forms, the occurrence of two wide bands (except for **3**), similar to 2*H*-chromenes fused to five-membered heterocycles [17], is very interesting, because almost the whole visible range can be covered with a single dye. Instead of only one kinetic phase, as observed for the reference compounds, two phases in the kinetics of fading were observed, probably corresponding to two different isomers with different thermal stabilities in the open form. Taking into account the results of a recent NMR study performed on a structurally related naphthopyran [18], these isomers most likely possess two different configurations at the double bond attached to the naphthalene (or benzopyran) ring as shown in *Scheme 4* for a 5,6-annellated system. The fast fading-rate phase can be attributed to the transoid (*t*) *tZ*-isomer, which is usually of higher amplitude. This can be observed for both compounds **3** and **5**, but not for compounds **2** and **4**, for which the amplitudes of the two kinetic phases are similar.

Compounds **3** and **5**, both 5,6-annellated, but with reversed geometry, exhibit different photochromic behaviours. The open form of **3** displays only one absorption

Table 3. *Spectrokinetic Properties of* **2**–**5** *under Flash-Irradiation Conditions* (25 μM in toluene at 25°)

Compound	Type of annellation[a])	λ_1 [nm]	A_{01}	λ_2 [nm]	A_{02}	k_Δ (amplitude) (s^{-1}) (%)
2	7,8	420	0.90	512	0.41	0.17 (44) 0.014 (56)
3	5,6	491	1.05	–	–	2.20 (69) 0.02 (31)
4	6,7	432	0.95	563	0.45	4.50 (53) 0.03 (47)
5	5,6	429	0.26	562	0.11	20.00 (91) 0.03 (9)
Ref$_1$[b])	5,6	429	0.84	–	–	0.09
Ref$_2$[c])	7,8	403	1.08	481	1.62	0.002

[a]) With respect to the pyranone ring fused to the [1]benzopyrane moiety. [b]) 3,3-Diphenyl-3*H*-benzo[*f*][1]benzopyran. [c]) 2,2-Diphenyl-2*H*-benzo[*h*][1]benzopyran.

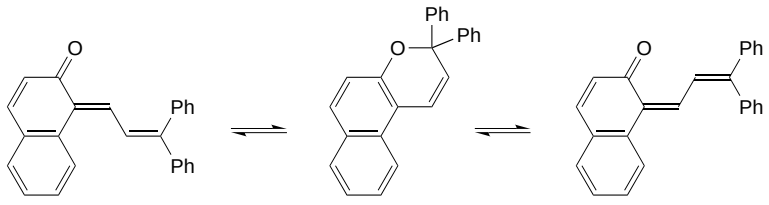
band centred at 491 nm, while that of compound **5** interestingly exhibits two extended absorption bands. The colorabilities observed for the open form of **5**, however, are modest, a fact that can be related to the fast rate of thermal bleaching, hindering the formation of colored species with a reasonable yield. The presence of the oxygen atom O(1) in the benzopyranone moiety of **5** (*Scheme 4*) seems to lead to an appreciable thermal instability of the open form.

By comparing the two 7,8-annellated compounds **2** with **Ref**$_2$, it can be inferred that replacing an annellated benzo group by a six-membered lactone modifies λ_{max}, the colorability as well as the thermal stability of the open form, whose major isomer after flash-irradiation is considerably more unstable.

The reference compound, to which **4** should be compared, is 2,2-diphenyl-2*H*-benzo[*g*][1]benzopyran, which is photochromic only at very low temperatures [19] [20] as a result of the loss of aromaticity in the naphthalene part upon irradiation. As it can be observed, **4** displays photochromic behaviour already at room temperature with an interesting coloration efficiency, although with fast bleaching, indicating that the open form is not particularly stable.

Fluorescence is a competing relaxation process that can negatively affect the photochromic performance of dyes. In the above compounds, the excited state,

Scheme 4



(*tE*)-Isomer (*tZ*)-Isomer

normally leading to C–O cleavage, can be deactivated by fluorescence [21][22]. All the described compounds however exhibit a modest to low fluorescence except for **4**, which shows a relevant emission band centred at 396 nm (*Fig. 1*) for excitation in the near-UV (340 nm). Under the experimental conditions of irradiation, fluorescence can be activated simultaneously during ring opening. Consequently, we would expect a negative influence on the photochromic behaviour of this compound. However, under the experimental conditions no clear effect was observed as reported for some fluorescent 2*H*-chromenes [23].

3. Conclusions. Five novel 2*H*-chromenes incorporating a fused pyranone moiety have been synthesized. Compounds **2**, **4**, and **5** displayed photochromic behaviour in solution at ambient temperature, absorbing throughout the visible range. These compounds may be interesting for applications such as photochromic ophthalmic lenses. The presence of the endocyclic O-atom in the coumarin system promotes a significant thermal instability of the open form upon irradiation. Compound **4**, despite of fast bleaching, exhibited an interesting coloration efficiency. Apparently, the fluorescence characteristics of these compounds have no negative effect on their photochromic behaviour in contrast to related chromenes [23].

Experimental Part

1. *General.* Petroleum ether: b.p. 40–60°. Column chromatography (CC): *Silica Gel 60* (*70–230 mesh*). M.p.: uncorrected. UV-Spectra: in MeOH on a *JASCO 7850*; λ_{max} (log ε [$dm^3\,mol^{-1}\,cm^{-1}$]. Fluorescence spectra: in MeOH on a *SPEX FLUOLOG-2* analyzer, with a double monochromator and an emission xenon lamp (450 W). FT-IR Spectra: *Bomen*, *MB Series*; in cm^{-1}. ^{1}H-NMR Spectra: in $CDCl_3$ (if not stated otherwise) on a *Varian Unity Plus* (300 MHz); δ in ppm rel. to Me_4Si (= 0 ppm), *J* in Hz. ^{1}H-NMR assignments were based on irradiation experiments. ^{13}C-NMR Spectra: in $CDCl_3$ on a *Varian Unity Plus* (75.4 MHz). MS: *AutoSpecE Spectrometer*; *m*/*z* (%). Elemental analyses: *LECO 932 CHNS Analyser*.

2. *Spectrokinetic Measurements.* For the determination at 25° of λ_1, λ_2, A_{01}, A_{02}, and k_Δ, 25 μM of **1**–**5** in toluene were used. The flash-photolysis apparatus was coupled to a *Warner and Swasey* rapid spectrometer, to allow recording of absorption spectra of the coloured forms in the visible 400–700 nm range (acquisition time: 1 ms, repetitivity: 1.25 ms) [3][16]. Flashes (duration: 50 μs) were generated by two xenon tubes with a quartz envelope. The energy of the flashes was 60 J for the whole polychromatic emission spectrum. For measurements, thermostated (25°C) 100 mm cells were used. The light from the analysis lamp (50 W, quartz-iodide) was filtered using a *Schott GG400* high-pass filter. In a preliminary experiment, both the visible absorption spectrum and λ_1 and λ_2 of the open form were determined. In a second experiment, the initial absorbances A_{01} and A_{02} were measured, followed by the decrease in absorbance with time. The rate constants were calculated using a bi-exponential model.

3. *Syntheses. – 2-Hydroxy-6-methoxybenzaldehyde:* A soln. of 3-methoxyphenol (1.8 ml, 16.11 mmol) in CH_2Cl_2 (40 ml) was added dropwise to a soln. of BuLi in hexanes (1.6M, 40 ml, 64.12 mmol) at 0° under stirring. The mixture was left at r.t. for 12 h, while colorless crystals separated. Then, a soln. of methyl(phenyl)formamide (2 ml, 16.11 mmol) in Et_2O was added dropwise (20 min). The mixture was refluxed for 30 min and poured into a soln. of 1M aq. H_2SO_4 at 0°. The org. layer was extracted with Et_2O, the combined extracts were dried ($MgSO_4$), and the solvent was removed *in vacuo*, providing a brown oil, which was purified by CC (SiO_2; petroleum ether/Et_2O). Yellow solid (1.5 g, 61%). M.p. 74–76° (Lit. 75° [24]). ^{1}H-NMR: 3.91 (*s*, MeO); 6.39 (*d*, *J* = 8.4, H–C(3)); 6.54 (*d*, *J* = 8.4, H–C(5), 7.42 (*t*, *J* = 8.4, H–C(4)); 10.35 (*s*, CHO), 12.0 (*s*, HO).

General Procedure for the Synthesis of **1b**, **1d**, *and* **1e**. A mixture of 2-hydroxybenzaldehyde (18.1 mmol) and ethyl (triphenylphosphoranylidene)acetate (7.6 g, 21.72 mmol) in *N*,*N*-diethylaniline (50 ml), was refluxed under N_2 for the length of time indicated below. The reaction mixture was diluted with 5% aq. HCl soln., extracted with Et_2O, and concentrated *in vacuo*. The remainder was purified by CC (petroleum ether/Et_2O).

*6-Hydroxy[1]benzopyran-2(2*H*)-one ('6-Hydroxycoumarin')* (**1b**): 6 h reflux; gray solid (85%). M.p. 252–254° (Lit. 252–254° [24]). ^{1}H-NMR ($(CD_3)_2CO$): 6.38 (*d*, *J* = 9.6, H–C(3)); 7.04–7.11 (*m*, H–C(7)); 7.13 (*d*, *J* = 3, H–C(5)); 7.21 (*d*, *J* = 8.7, H–C(8)); 7.89 (*d*, *J* = 9.6, H–C(4)); 8.6 (*s*, HO).

*8-Hydroxy[1]benzopyran-2(2*H*)-one* (**1d**): 8 h reflux; gray solid (50%). M.p. 148–150° (Lit. 160° [24]). ^{1}H-NMR: 6.13 (*s*, HO); 6.44 (*d*, *J* = 9.6, H–C(3)); 6.88–7.30 (*m*, H–C(5,6,7)); 7.74 (*d*, *J* = 9.6, H–C(4)).

*5-Methoxy[1]benzopyran-2(2*H*)-one* (**1e**): 8 h reflux, yellow solid (31%). M.p. 78–80° (Lit. 78–80° [24]). ^{1}H-NMR: 3.93 (*s*, MeO); 6.33 (*d*, *J* = 9.6, H–C(3)); 6.71 (*d*, *J* = 8, H–C(6) or H–C(8)); 6.91 (*d*, *J* = 8, H–C(8), or H–C(6)); 7.43 (*t*, *J* = 8, H–C(7)); 8.08 (*d*, *J* = 9.6, H–C(4)).

*5-Hydroxy[1]benzopyran-2(2*H*)-one* (**1a**): Compound **1e** (0.4 g, 2.0 mmol) was dissolved in anh. CH_2Cl_2 under stirring. A soln. of BBr_3 (6 ml, 1M in CH_2Cl_2) was added dropwise at −60°. The mixture was stirred at r.t. under N_2 for 24 h. The soln. was treated with H_2O (40 ml), extracted with Et_2O (3 × 20 ml), and the organic layers were combined and dried (Na_2SO_4). Evaporation gave a red solid which was purified by CC (petroleum ether/Et_2O): 0.23 g (69%). M.p. 231–232° (Lit. 221–223° [24]). ^{1}H-NMR: 5.76 (*s*, HO); 6.37 (*d*, *J* = 9.9, H–C(3)); 6.66 (*dd*, *J* = 8.4, 0.6, H–C(6)); 6.92 (*d*, *J* = 8.4, H–C(8)); 7.34 (*t*, *J* = 8.1, H–C(7)); 8.10 (*d*, *J* = 9.6, H–C(4)).

General Procedure for the Synthesis of **2**–**5** (Method A). *p*-Tolylsulfonic acid (PTS, 0.154 g, 0.80 mmol) and the corresponding benzopyrane **1** (6.17 mmol) were added to a soln. of 1,1-diphenylprop-2-yn-1-ol (2 g, 9.26 mmol) in anh. solvent (50 ml). The suspension was refluxed under Ar and (after cooling) was poured on H_2O. The aq. phase was extracted with $CHCl_3$ (4 × 30 ml). The combined org. layers were washed with 10% aq. NaOH soln. (4 × 30 ml), dried (Na_2SO_4), and evaporated. The remaining yellow oils were purified by CC (petroleum ether/Et_2O).

*2,8-Dihydro-2,2-diphenylpyrano[2,3-*f*]benzopyran-8-one* (**2**): 24 h reflux in CH_2Cl_2; light yellow solid (26%). M.p. 192–193°. UV: 224 (4.46), 255 (4.19), 264 (4.23), 290 (4.28). FT-IR (Nujol): 1719 (C=O), 1594, 1493, 1367, 1237, 1173, 1103. ^{1}H-NMR: 6.14 (*d*, *J* = 10, H–C(3) or H–C(4)); 6.55 (*d*, *J* = 9.6, H–C(9)); 6.50 (*d*, *J* = 10, H–C(4) or H–C(3)); 6.82 (*d*, *J* = 8.6, H–C(6)); 7.18 (*d*, *J* = 8.6, H–C(5)); 7.29–7.42 (*m*, 10 arom. H, Ph); 8.15 (*d*, *J* = 9.6, H–C(10)). ^{13}C-NMR: 84.04 (C(2)); 109.04 (*d*); 115.13 (*d*); 116.48 (*s*); 122.35 (*d*); 126.79 (4*d*, Ph); 127.65 (*s*); 127.89 (C(4′,4″)); 128.29 (4*d*, Ph); 129.45 (*d*); 137.80 (*d*); 144.03, 148.93, 154.59 (3*s*); 160.57 (C=O). The signal of one C-atom was probably buried under another signal. MS: 353 (25, $[M+1]^+$), 352 (100, M^+), 323 (6), 276 (19), 275 (85), 247 (10), 191 (11), 189 (10), 165 (8). Anal. calc. for $C_{24}H_{16}O_3$ (352): C 81.82, H 4.54; found: C 81.47, H 4.806.

*3,8-Dihydro-8,8-diphenylpyrano[3,2-*f*][1]benzopyran-3-one* (**3**): 40 h reflux in MeCN; yellow crystals (20%). M.p. 226–227° (EtOH). UV: 222 (4.65), 290 (4.27), 302 (4.27). FT-IR (KBr): 1719 (C=O), 1565, 1271, 1196, 1119. ^{1}H-NMR: 6.38 (*d*, *J* = 10, H–C(9) or H–C(10)); 6.41 (*d*, *J* = 9.6, H–C(2)); 6.96 (*d*, *J* = 10, H–C(10) or H–C(9)); 7.11/7.14/7.15/7.18 (*AB*, *J* = 9, H–C(5), H–C(6)); 7.24–7.42 (*m*, 10 arom. H, Ph); 7.92 (*d*, *J* = 9.6, H–C(1)). ^{13}C-NMR: 82.57 (C(8)); 114.41 (*s*); 116.79 (*d*); 117.01 (*s*); 117.37 (*d*); 117.81 (*d*); 120.87 (*d*); 126.91 (4*d*, Ph); 127.85 (C(4′,4″); 128.24 (4*d*, Ph); 131.86 (*d*); 138.41 (*d*); 143.89, 148.69, 149.01 (3*s*); 160.58 (C=O). MS: 353 (18, $[M+1]^+$), 352 (72, M^+), 276 (20), 275 (100), 247 (8), 191 (6), 189 (5), 165 (8). Anal. calc. for $C_{24}H_{16}O_3$: C 81.82, H 4.54; found: C 81.78, H 4.69.

*2,8-Dihydro-2,2-diphenylpyrano[3,2-*g*][1]benzopyran-8-one* (**4**): 48 h reflux in toluene; yellowish solid (25%). Recrystallization from $CHCl_3$/petroleum ether yielded colourless crystals (14%). M.p. 190–193°. UV: 222 (4.46), 267 (4.40), 339 (4.08), 347 (4.10). FT-IR (Nujol): 1740 (C=O), 1721, 1650, 1627, 1564, 1366, 1275, 1140. ^{1}H-NMR: 6.23 (*d*, *J* = 9.3, H–C(7)); 6.27 (*d*, *J* = 10, H–C(3) or H–C(4)); 6.66 (*d*, *J* = 10, H–C(4), or H–C(3)); 6.89 (*s*, H–C(10)); 7.11 (*s*, H–C(5)); 7.26–7.44 (*m*, 10 arom. H, Ph); 7.57 (*d*, *J* = 9.3, H–C(6)). ^{13}C-NMR: 83.76 (C(2)); 104.69 (*d*); 113.18 (*s*); 113.45 (*d*); 118.38 (*d*); 121.78 (*s*); 125.16 (*s*); 126.87 (4*d*, Ph); 127.87 (C(4′,4″)); 128.27 (4*d*, Ph); 129.45 (*d*); 143.15 (*d*); 143.96 (*d*); 155.51 (*s*); 156.09 (*d*); 160.86 (C=O). MS: 353 (27, $[M+1]^+$), 352 (100, M^+), 323 (8), 276 (10), 275 (55), 247 (10), 191 (9), 189 (5), 165 (5). Anal. calc. for $C_{24}H_{16}O_3$: C 81.81, H 4.54; found: C 81.60, H 4.77.

*2,8-Dihydro-8,8-diphenylpyrano[2,3-*f*][1]benzopyran-2-one* (**5**): 48 h reflux in toluene; white solid (4%). M.p. 229–230°. FT-IR (Nujol): 1731 (C=O), 1599, 1259, 1111. UV: 237 (4.18), 284 (4.00), 292 (4.03), 330 (3.87), 347 (3.73). ^{1}H-NMR: 6.23 (*d*, *J* = 9, H–C(3)); 6.29 (*d*, *J* = 10, H–C(9) or H–C(10)); 6.88 (*d*, *J* = 8, H–C(6)); 7.20 (*d*, *J* = 10, H–C(10) or H–C(9)); 7.24 (*d*, *J* = 8, H–C(5)); 7.25–7.46 (*m*, 10 arom. H, Ph); 7.58 (*d*, *J* = 9, H–C(4)). ^{13}C-NMR: 83.66 (C(8)); 109.47 (*s*); 112.97 (*d*); 112.99 (*s*); 113.59 (*d*); 116.24 (*d*); 126.92 (4*d*, Ph); 127.84 (C(4′,4″)); 128.17 (*d*); 128.22 (4*d*, Ph); 129.13 (*d*); 143.74 (*d*); 143.97, 150.15, 155.53 (3*s*); 160.74 (C=O). MS: 353 (16, $[M+1]^+$), 352 (60, M^+), 275 (70), 247 (14), 167 (21), 164 (42), 149 (58), 119 (100). Anal. calc. for $C_{24}H_{16}O_3$ (352): C 81.81; H 4.54; found: C 82.15, H 4.33.

*2,9-Dihydro-2,2-diphenylpyrano[3,2-*h*]benzopyran-2-one* (**6**) (Method B). To a soln. of **1d** (0.3 g, 1.54 mmol) in anh. toluene (20 ml) a soln. of $(EtO)_4Ti$ (0.3 ml, 1.54 mmol) in anh. toluene (20 ml) was added over a period of 20 min. After the mixture had been refluxed for 1 h, the EtOH formed was slowly distilled off and the mixture was cooled to r.t. Then, 3,3-diphenylprop-2-enal (β-phenylcinnamaldehyde) was added (0.32 g, 1.54 mmol), and the mixture was refluxed for 30 h under Ar. After cooling, a 2M soln. of aq. NaOH (50 ml) was added, the mixture was extracted with CH_2Cl_2 (4×30 ml), the org. layers were combined, dried ($MgSO_4$), and concentrated *in vacuo*. The resulting product was purified by CC to yield an oily brown solid (2 mg). ^{1}H-NMR: 6.15 ($d, J = 10$, H–C(3) or H–C(4)); 6.36 ($d, J = 9.6$, H–C(8)); 6.45 ($d, J = 10$, H–C(4) or H–C(3)); 6.82 ($d, J = 8.5$, H–C(5) or H–C(6)); 7.18 ($d, J = 8.5$, H–C(6) or H–C(5)); 7.26–7.50 (m, 10 arom. H,Ph); 8.16 ($d, J = 9.6$, H–C(7)). MS: 353 (24, $[M+1]^+$), 352 (100, M^+), 323 (5), 276 (14), 275 (72), 247 (7), 191 (8), 189 (5), 165 (5). HR-MS: 352.1092 (M^+, $C_{24}H_{16}O_3$; calc. 352.1099).

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REFERENCES

[1] 'Organic Photochromic and Thermochromic Compounds', Eds. J. Crano and R. Guglielmetti, Plenum Publishing Corporation, N.Y. 1998, 1999, Vols. 1–2.
[2] K. Ichimura, in 'Photochromism: Molecules and Systems', Eds. H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990, Chap. 26.
[3] J. L. Meyer, P. Levoir, R. Dubest, *Analyst* **1995**, *120*, 447.
[4] J. C. Crano, T. Flood, D. Knowles, A. Kumar, B. Van Gemert, *Pure Appl. Chem*. **1996**, *68*, 1395.
[5] A. M. F. Oliveira-Campos, M. M. Oliveira, L. H. M. Carvalho, C. Moustrou, A. Samat, R. Guglielmetti, J. Seita, Colour Science 98 Proceedings, Vol. 1, 'Dye and Pigment Chemistry', Leeds, 1999, 26.
[6] M. M. Oliveira, L. M. Carvalho, C. Moustrou, A. Samat, R. Guglielmetti, A. M. F. Oliveira-Campos, *Helv. Chim. Acta* **2001**, *84*, 1163.
[7] P. J. Coelho, L. M. Carvalho, J. C. Silva, A. M. F. Oliveira-Campos, A. Samat, R. Guglielmetti, *Helv. Chim. Acta* **2001**, *84*, 117.
[8] I. Iwai, J. Ide, *Chem. Pharm. Bull*. **1963**, *11*, 1042.
[9] J. L. Pozzo, V. Lokshin, A. Samat, R. Guglielmetti, R. Dubest, J. Aubard, *J. Photochem. Photobiol.*, *A* **1998**, *111*, 185.
[10] J. L. Pozzo, Ph.D. Thesis, Université de la Méditerranée, Marseille, France, 1994.
[11] T. Harayama, K. Katsuno, H. Nishioka, M. Fujii, Y. Nishita, H. Ishii, Y. Kaneko, *Heterocycles* **1994**, *39*, 613.
[12] T. Harayama, K. Katsuno, H. Nishioka, K. Murakani, N. Hayashida, H. Ishii, *Chem. Pharm. Bull*. **1994**, *42*, 2170.
[13] H. Gilman, J. W. Morton Jr., Organic Reactions, 1975, Vol. 8, 288.
[14] J. F. Mcomie, M. L. Watts, D. E. West, *Tetrahedron* **1968**, *24*, 2289.
[15] J. V. Morris, M. A. Mahaney, J. R. Huber, *J. Phys. Chem*. **1976**, *80*, 969.
[16] E. Pottier, R. Dubest, R. Guglielmetti, P. Tardieu, A. Kellmann, F. Tfibel, P. Levoir, J. Aubard, *Helv. Chim. Acta* **1990**, *70*, 303.
[17] J. L. Pozzo, A. Samat, R. Guglielmetti, V. Lokshin, V. Minkin, *Can. J. Chem.* **1996**, *74*, 1649.
[18] S. Delbaere, B. Luccioni, C. Bochu, Y. Teral, M. Campredon, G. Vermeersch, *J. Chem. Soc., Perkin Trans. 2* **1998**, 1153.
[19] B. Van Gemert, in 'Organic Photochromic and Thermochromic Compounds', Eds. J. Crano and R. Guglielmetti, Plenum Publishing Corporation, N.Y., 1999, Vol. 1, Chap. 3.
[20] R. S. Becker, J. Michl, *J. Am. Chem. Soc*. **1966**, *88*, 5931.
[21] T. Yamamoto, H. Hagashi, *J. Polym. Sci., Part A: Polymer Chem.* **1997**, *35*, 463.
[22] N. Dicesare, M. Belletete, C. Marano, M. Leclerc, G. Durocher, *J. Phys. Chem*. **1999**, *103*, 802.
[23] S. Coen, C. Moustrou, M. Frigoli, M. Julliard, A. Samat, R. Guglielmetti, *J. Photochem. Photobiol., A* **2001**, *139*, 1.
[24] 'Dictionary of Organic Compounds', 4th edn., Eyre and Spottiswoode Ltd., 1965, Vol. 3, p. 1666.

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