Synthesis and Photochromic Behavior of Novel Annelated 2*H*-Chromenes Derived from Hydroxy-9*H*-xanthen-9-ones

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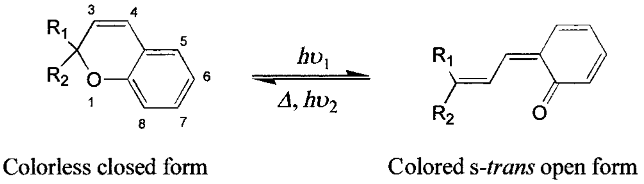
The synthesis of four novel pyrano-xanthenones derived from hydroxy-9*H*-xanthen-9-ones is described, and their photochromic properties in solution are reported. All compounds synthesized exhibit a good colorability, making them good potential dyes. The presence of the chromone system fused in the 7,8-position seems to lead to more stabilized colored forms.

Introduction. – In the last years, the 2*H*-chromenes (2*H*-1-benzopyran derivatives) have been largely studied on the basis of their industrial applicability in the field of the photochromic ophthalmic plastic lenses [1]. Similar to spiropyranes and spirooxazines, their photochromic activity is the result of their ability to undergo a reversible cleavage of the C–O bond, leading to a quasi-planar 'open form' with a distinct absorption spectrum (*Scheme 1*).

Scheme 1

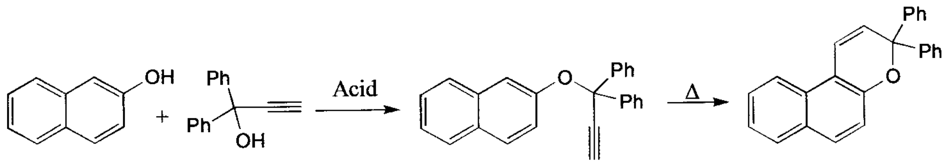


Spirooxazines and spiropyrans [2] are well-known compounds with excellent photochromic activity and photostability, but the 'open forms' normally show relatively narrow absorption bands with maxima above 500 nm. The absorption maxima of the 'open form' of the 2*H*-chromenes are usually in the range of 400–500 nm, which is complementary to those of the above-mentioned compounds. This feature, along with a good fatigue resistance, little temperature dependence, and reasonable activation and fading rates, makes 2*H*-chromenes particularly suitable to form mixtures that produce photochromic systems with a neutral activated color (significative absorption along all the visible spectrum), as is required for the commercial acceptability of ophthalmic lenses. This approach is limited, however, because the compounds of both series often show differences in behavior (kinetics, temperature dependence, fatigue proneness, colorability *etc.*). Ideally, only one class of photochromic pigments should be used.

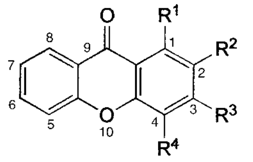
To improve the performance of photochromic systems, much attention has been devoted to the study of new photochromic molecules obtained by modification of 2*H*-1-benzopyrans, namely by heteroaromatic annelation [3]. In the present work, we describe the synthesis and characterization of novel 2*H*-chromenes derived from xanthone.

Results and Discussion. – *Synthesis.* There are several methods for the synthesis of 2*H*-chromenes [3]. One of the most versatile is based on a one-pot reaction of a phenol with an alkynol under acid catalysis (*Scheme 2*) [4–6]. The reaction is considered to proceed *via* a *Claisen* rearrangement of propargyl aryl ethers, formed by phenol *O*-alkylation, followed by enolization, [1,5] H-migration, and electrocyclic ring closure.

Scheme 2



According to this strategy, the preparation of 2*H*-chromenes, which contain the xanthone system, requires the availability of hydroxy-9*H*-xanthen-9-ones **1a**–**d**. 1-Hydroxy (**1a**) and 4-hydroxy-9*H*-xanthen-9-one (**1d**) were synthesized by improved procedures of reported methods [7][8].



1a R^1=OH R^2=R^3=R^4=H

1b R^1=R^3=R^4=H, R^2=OH

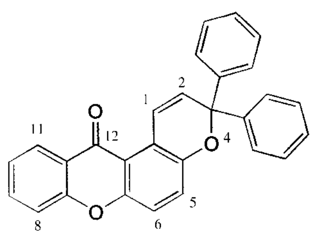
1c R^1=R^2=R^4=H, R^3=OH

1d R^1=R^2=R^3=H, R^4=OH

Thus, heating a mixture of salicylic acid, resorcinol, and $ZnCl_2$ for 6 h at 170° afforded **1a** in 30% yield. Microwave irradiation of a mixture of sodium 2-methoxyphenolate, sodium 2-chlorobenzoate, CuCl, and tris[2-(2-methoxyethoxy)-ethyl]amine gave 2-(2′-methoxyphenoxy)benzoic acid, which was then treated with polyphosphoric acid (PPA) to provide 4-methoxyxanthone in 41% yield. Demethylation with $AlCl_3$ gave **1d**. 2-Hydroxy- and 3-hydroxy derivatives **1b** and **1c**, respectively, were prepared according to known methods [9].

Condensation of 1,1-diphenylprop-2-yn-1-ol with hydroxy-9*H*-xanthen-9-ones **1b**–**d** under pyridinium p-toluenosulfonate (PPTS) catalysis gave the corresponding pyrano-xanthone derivatives **2**–**4** in 17–50% yield.

Under the same conditions, no reaction was observed with 1-hydroxyxanthone (**1a**). This lack of reactivity is probably due to the intramolecular H-bond between the OH and the C=O group. Thus, it was decided to reduce **1a** to 9*H*-xanthen-1-ol (**5**) [10], which was converted to the corresponding pyrano-xanthene **6** (*Scheme 3*). Oxidation of **6** by CrO_3/Py gave the pyrano-xanthenone **7** in good yield.



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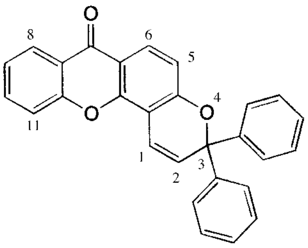

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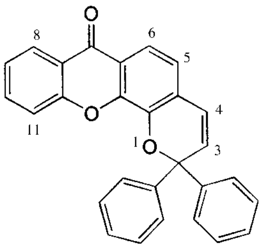

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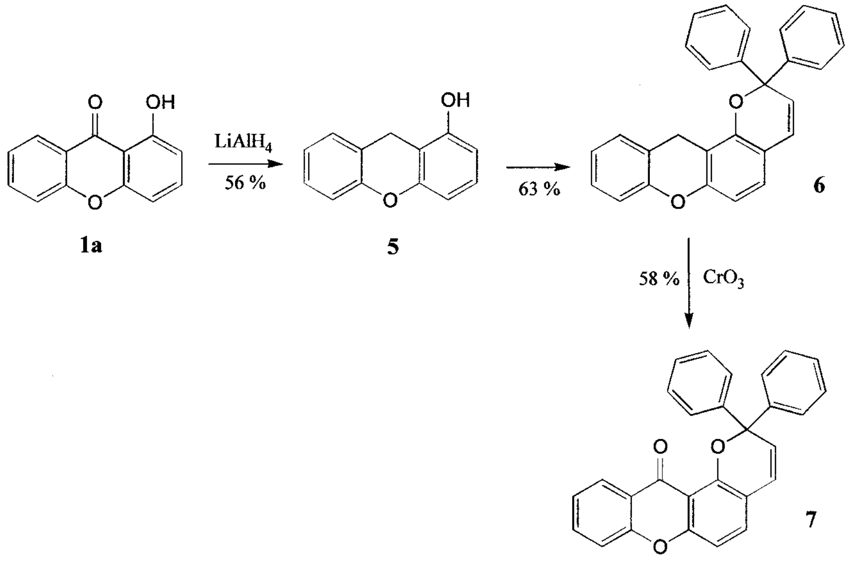
Scheme 3



Photochromic Properties. The introduction of a fused chromone group by heteroannelation in the 5,6- and 7,8-positions of the 2*H*-1-benzopyran moiety (*Scheme 1*) led to compounds **2**–**4** and **7** that exhibit photochromic behavior at room temperature in toluene. The relevant parameters used to characterize this behavior (spectrokinetic parameters [11]) are reported in the *Table*, in which we included two corresponding naphthopyrans (Ref1 and Ref2) as reference compounds [12] for comparison. Flash-photolysis equipment coupled to a fast-scan spectrometer was used for this purpose [13].

Maxima wavelengths of the colored form (λ_{max}) describe the color that can be achieved upon irradiation. The visible absorption spectra of the benzopyrans obtained do not follow a general pattern. From a general point of view, a global bathochromic shift can be observed when compared to the parameters concerning the corresponding naphthopyrans. However, compounds **2** (heteroannelation in the 5,6-positions of the naphthopyran) and **7** (heteroannelation in the 7,8-positions) display in toluene one single band, and compounds **3** (heteroannelation in the 5,6-positions) and **4**

Table. *Spectrokinetic Properties: Maxima Wavelengths of the Colored Form* (λ_1, λ_2), *Colorability* (A_{01}, A_{02}), *Bleaching Rate* (k_Δ)*, and Resistance towards Photodegradation* ($t_{A_0/2}$) *of 2*H*-Chromenes* **2**–**4** *and* **7**, *and Two Reference Compounds in Toluene Solutions* (2.5×10^{-5} M at 25°). Ref1 = 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran; Ref2 = 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran

Compound	Annelation	λ_1 [nm]	A_{01}	λ_2 [nm]	A_{02}	k_Δ (amplitude) [s^{-1}] [%]	$t_{A_0}/2$ [min]
2	5,6	484	1.50	–	–	7.70 (96) 0.10 (4)	917
3	5,6	428	1.30	515	0.70	8.20 (49) 0.03 (51)	36
4	7,8	436	1.10	522	1.00	0.66 (82) 0.02 (18)	35
7	7,8	467	1.80	–	–	0.31 (17) 0.02 (83)	6
Ref1	5,6	432	0.84	–	–	0.09	509
Ref2	7,8	403	1.08	481	1.62	0.002	

(heteroannelation in the 7,8-positions) display two bands, the first one located near 430 nm and the other one near 520 nm, covering a much larger range of wavelengths in the visible region. This behavior was observed in 2*H*-chromenes to which different five-membered rings were introduced in 5,6-positions [14], and it is markedly different from the behavior of the parent naphthopyran that shows a single absorption band with a maximum at 432 nm under the same experimental conditions. It is apparent that, when the geometry of the fused chromone group is reversed (*e.g.*, compound **2** to **3**, and **4** to **7**), a change of the electronic absorption spectra pattern occurs, leading to a splitting into two bands. The presence of a heteroatom in positions 5 and 8 of the chromene moiety seems to be important for this effect that results in a much larger coverage range of visible wavelengths, leading to compounds potentially interesting as orange-color-developing substances.

Thermal bleaching (ring closure) rate constants (k_Δ) provide a measure of how fast the system returns to its uncolored form and provides information on the stability of the colored open form at room temperature. All the new compounds described show two phases of kinetics of fading with variable amplitudes; this is different from the kinetics exhibited by the reference compounds. The slow fading rate can be attributed to the most stable s-*trans*-isomer. The thermal bleaching of compounds **2** and **3** has been found to be a very fast process, indicating a photogenerated form poorly stabilized. This is not suitable for application in variable optical-transmission materials. Compounds **4** and **7** show a relatively slower process of fading with interesting values. The presence of the chromone system fused in the 7,8-positions seems to lead to more stabilized colored open forms.

'*Colorability*' (A_0; absorbance measured just after the flash) is the photocoloration efficiency, and a function of the quantum yield of the photocoloration process and the molar absorptivity of the colored species. All the compounds synthesized exhibit a good colorability, rendering them good potential dyes.

Fatigue resistance ($t_{A_0/2}$; time necessary to observe a decrease of half of the colorability) measures the tendency of the system to photodegradation under the experimental conditions considered [15]. From the results in the *Table*, it is noteworthy that compound **2** shows a good fatigue resistance, which may not indicate, however, an unusual photodegradation resistance, as this process has its main origin in the open form [16]. The open form of **2** seems to have a very short lifetime, as indicated by the high bleaching-rate value that covers almost all the ring closure process. Compounds **3**, **4** and **7** undergo photodegradation very easily.

Conclusion. – The synthesis of 2*H*-chromenes with a fused chromone group (pyrano-xanthenones) was achieved by usual methods. Particularly remarkable is the result that only 'angular' 2*H*-chromenes were obtained from 2-hydroxy- and 3-hydroxy-9*H*-xanthen-9-ones. The photochromic compounds described exhibit improved colorabilities, and, for compounds **3** and **4**, a marked broadening of visible absorption spectra is observed that makes these 9*H*-xanthen-9-one derivatives potentially interesting for photochromic applications.

Experimental Part

General. Column chromatography (CC): silica gel *60* (70–230 mesh). Photochromic measurements were performed in 2.5×10^{-5} M toluene soln. at 25° with a *Warner & Swasey* spectrometer (cell pathlength 10 cm); flash energy 60 J. Resistance towards photodegradation was measured in 0.5×10^{-5} toluene soln. at 25° (cell pathlength 5 cm); lamp *XBO 250 W + Schott filters WG295* and *IR 114*; flash energy 150 J. M.p.: uncorrected. IR Spectra: *Perkin-Elmer FTIR-1600* spectrometer, wave numbers in cm^{-1}. ^{1}H-NMR Spectra: in $CDCl_3$ (except if otherwise stated) on a *Varian Unity Plus* at 300 MHz. ^{13}C-NMR Spectra: in $CDCl_3$ in a *Varian Unity Plus* at 75.4 MHz. NMR Assignments were based on irradiation experiments. MS: *AutoSpecE* spectrometer. Elemental analyses were carried out with a *LECO 932 CHNS* analyzer.

*1-Hydroxy-9*H*-xanthen-9-one* (**1a**). A mixture of salicylic acid (3.00 g, 21.7 mmol), resorcinol (1.00 g, 9.09 mmol), and anh. $ZnCl_2$ (1.00 g, 9.8 mmol) was heated at 170° for 6 h. After cooling, the mixture was dissolved in AcOEt (50 ml), and silica gel (5 g) was added. Evaporation afforded a residue, which was purified by CC (hexane/AcOEt 99.5 : 0.5) to yield **1a** (0.572 g, 30%). Yellow needles. M.p. 142–144° ([17]: 148°). ^{1}H-NMR: 12.67 (*s*, OH); 8.30 (*dd*, *J* = 7.3, 1.8, H–C(8)); 7.78 (*ddd*, *J* = 1.8, 6.9, 8.4, H–C(6)); 7.61 (*t*, *J* = 8.4, H–C(3)); 7.50 (*dd*, *J* = 0.7, 8.4, H–C(5)); 7.42 (*t*, *J* = 7.3, H–C(7)); 6.96 (*d*, *J* = 8.4, H–C(4)); 6.82 (*d*, *J* = 8.4, H–C(2)).

*4-Hydroxy-9*H*-xanthen-9-one* (**1d**). A mixture of sodium 2-chlorobenzoate (5.00 g, 28.1 mmol), sodium 2-methoxyphenolate (5.00 g, 34.2 mmol), CuCl (350 mg, 4 mmol), and tris[2-(2-methoxyethoxy)ethyl]amine (0.2 ml) were suspended in dioxane (15 ml) and submitted to microwave irradiation for 40 min (1100 W). The residue was treated with H_2O (100 ml) and filtered. The soln. thus obtained was acidified with 2M HCl and extracted with AcOEt (3 × 50 ml). The org. phase was washed with H_2O and dried (Na_2SO_4). The crude product was dissolved in polyphosphoric acid (15 ml), stirred 1 day at 60°, quenched with H_2O, and extracted three times with AcOEt. The combined org. extracts were dried (Na_2SO_4). After evaporation, the crude product was purified by CC (hexane/AcOEt) to yield 4-methoxy-9*H*-xanthen-9-one (2.58 g, 41%). Yellow solid. M.p. 118–120°. ^{1}H-NMR: 8.36 (*dd*, *J* = 7.8, 1.8, H–C(8)); 7.93 (*dd*, *J* = 7.8, 1.8, H–C(1)); 7.76 (*ddd*, *J* = 8.7, 7.5, 1.8, H–C(6)); 7.63 (*dd*, *J* = 8.7, 1.2, H–C(5)); 7.41 (*ddd*, *J* = 7.8, 7.5, 1.2, H–C(7)); 7.33 (*t*, *J* = 7.8, H–C(2)); 7.27 (*dd*, *J* = 7.8, 1.8, H–C(3)); 4.06 (*s*, MeO). To a soln. of 4-methoxy-9*H*-xanthen-9-one (0.830 g, 3.67 mmol) in anh. benzene (30 ml) was added $AlCl_3$ (4 g, 30.0 mmol) under an Ar atmosphere. The mixture was stirred under reflux for 1 h and then acidified with 10% HCl. The aq. phase was extracted with Et_2O (3 × 100 ml). The org. phase was washed with H_2O, dried (Na_2SO_4), and the solvent was evaporated under reduced pressure leaving the crude **1d**. Recrystallization from MeOH gave pure **1d** (0.690 g, 89%). Colorless needles. M.p. 233–236° ([18]: 230–233°). ^{1}H-NMR ((D_6)Acetone): 9.15 (*s*, OH); 8.29 (*dd*, *J* = 7.8, 1.8, H–C(8)); 7.89 (*ddd*, *J* = 8.0, 7.5, 1.8, H–C(6)); 7.76 (*dd*, *J* = 7.8, 2, H–C(1)); 7.66 (*dd*, *J* = 8.0, 1.2, H–C(5)); 7.50 (*ddd*, *J* = 7.8, 7.5, 1.2, H–C(7)); 7.40 (*dd*, *J* = 7.8, 2, H–C(3)); 7.32 (*t*, *J* = 7.8, H–C(2)).

Preparation of Pyrano-xanthenones. General Procedure. To a mixture of hydroxy-9*H*-xanthen-9-one **1** (212 mg, 1.00 mmol), 1,1-diphenylprop-2-yn-1-ol (312 mg, 1.50 mmol), and PPTS (25 mg), 30 ml of dry $CHCl_3$

were added. The suspension was refluxed for 3 days under Ar. The suspension was then treated with H_2O, and the aq. phase was extracted with $CHCl_3$ (3 × 30 ml). The org. phase was then washed with 5% NaOH soln. (3 × 20 ml) and dried (Na_2SO_4). Solvent evaporation gave a yellow oil, which was purified by CC (silica gel; hexane/AcOEt 90:10). Recrystallization from pentane/CH_2Cl_2 gave a crystalline material.

3,3-Diphenyl-3H-pyrano[3,2-a]xanthen-12(12H)-one (**2**): 41%. M.p. 227–228°. IR: 3050, 1648, 1610, 1579, 1467, 1454, 1307, 1243, 1216, 1145, 1066, 970, 759. ^{1}H-NMR ((D_6)Acetone): 8.47 (*dd*, *J* = 10.2, 0.6, H–C(1)); 8.24 (*dd*, *J* = 8.1, 1.5, H–C(11)); 7.84 (*ddd*, *J* = 9.0, 7.2, 1.5, H–C(9)); 7.56 (*m*, 6 H); 7.49 (*d*, *J* = 9.0, H–C(8)); 7.46 (*ddd*, *J* = 8.1, 7.2, 1.5, H–C(10)); 7.42–7.26 (*m*, 6 H); 6.64 (*d*, *J* = 10.2, H–C(2)). ^{13}C-NMR: 179.08 (C=O); 155.31; 152.15; 148.54; 144.18; 134.41; 131.03; 128.09; 127.60; 127.08; 126.53; 124.44; 123.60; 122.50; 122.21; 120.22; 118.65; 117.44; 116.35; 81.86 (C(3)). MS: 402 (100, M^+), 401 (15), 385 (12), 325 (90), 239 (13), 191 (15), 165 (16), 77 (10). Anal. calc. for $C_{28}H_{18}O_3$: C 83.58, H 4.48; found: C 83.38, H 4.75.

3,3-Diphenyl-3H-pyrano[2,3-c]xanthen-7(7H)-one (**3**): 48%. M.p. 194–195°. IR: 3080, 1650, 1635, 1618, 1465, 1438, 1261, 1072, 754, 700. ^{1}H-NMR ((D_6)Acetone): 8.24 (*dd*, *J* = 8.1, 1.5, H–C(8)); 8.17 (*d*, *J* = 9, 1 H); 7.86 (*ddd*, *J* = 8.7, 7.2, 1.5, H–C(10)); 7.70 (*dd*, *J* = 8.7, 1.2, H–C(11)); 7.55 (*m*, 4 H); 7.48 (*ddd*, *J* = 8.1, 7.2, 1.2, H–C(9)); 7.45–7.26 (*m*, 7 H); 7.15 (*d*, *J* = 9, H–C(5)); 6.64 (*d*, *J* = 10.2, H–C(2)). ^{13}C-NMR: 175.83 (C=O); 158.45; 156.79; 145.23; 135.56; 129.95; 129.13; 128.65; 128.19; 127.53; 127.39; 126.93; 125.09; 122.46; 118.82; 117.09; 117.02; 114.80; 110.48; 84.50 (C(3)). MS: 402 (55, M^+), 401 (15), 325 (100), 239 (12), 191 (13), 165 (14). Anal. calc. for $C_{28}H_{18}O_3$: C 83.58, H 4.48; found: C 83.51, H 4.53.

2,2-Diphenyl-2H-pyrano[3,2-c]xanthen-7(7H)-one (**4**): 17%. M.p. 204–206°. IR: 3080, 1656, 1637, 1606, 1461, 1446, 1326, 1224, 960, 744. 700. ^{1}H-NMR ((D_6)Acetone): 8.33 (*dd*, *J* = 7.8, 1.5, H–C(8)); 7.84 (*d*, *J* = 8, H–C(6)); 7.74 (*ddd*, *J* = 8, 6.9, 1.5, H–C(10)); 7.63 (*d*, *J* = 8, H–C(11)); 7.53 (*m*, 4 H); 7.42–7.26 (*m*, 7 H); 7.05 (*d*, *J* = 8, H–C(5)); 6.75 (*d*, *J* = 10, 1 H); 6.64 (*d*, *J* = 10, 1 H). ^{13}C-NMR: 176.83 (C=O); 156.13; 145.61; 144.01; 140.83; 134.65; 131.98; 128.28; 127.89; 126.89; 126.63; 126.03; 123.93; 123.00; 122.64; 121.64; 121.38; 118.38; 118.26; 83.36 (C(2)). MS: 402 (100, M^+), 401 (30), 385 (7), 325 (90), 239 (15), 191 (10), 165 (15), 77 (5). Anal. calc. for $C_{28}H_{18}O_3$: C 83.58, H 4.48; found: C 83.15, H 4.55.

9H-Xanthen-1-ol (**5**). To a soln. of **1a** (300 mg) in benzene (15 ml), a soln. of $LiAlH_4$ (80 mg, 2.1 mmol) in dry Et_2O (15 ml) was added under Ar, and the mixture was heated under reflux for 2 h. After treatment with hydrated Na_2SO_4, the mixture was poured into H_2O (50 ml) and extracted with Et_2O (3 × 20 ml). The org. phase was dried (Na_2SO_4). Evaporation afforded a residue, which was purified by CC (AcOEt/hexane 99:1). Evaporation gave **5** (0.180 g, 56%), which crystallized as colorless needles. M.p. 142–144°. ^{1}H-NMR: 7.20 (*m*, 2 H); 7.04 (*m*, 3 H); 6.65 (*d*, *J* = 8.4, 1 H); 6.49 (*d*, *J* = 8.4, 1 H); 3.99 (*s*, 2 H).

2,2-Diphenyl-2H-12H-pyrano[2,3-a]xanthene (**6**): 63%. IR: 3100, 2980, 1639, 1612, 1479, 1261, 1072, 802, 698. ^{1}H-NMR: 7.48 (*m*, 4 H); 7.4–7.25 (*m*, 6 H); 7.23 (*m*, 2 H); 7.02 (*m*, 2 H); 6.88 (*d*, *J* = 8.1, 1 H); 6.60 (*d*, *J* = 9.9, 1 H); 6.56 (*d*, *J* = 8.1, 1 H); 6.03 (*d*, *J* = 9.9, 1 H); 4.08 (*s*, 2 H). ^{13}C-NMR: 152.44; 151.26; 150.33; 145.08; 129.33; 128.12; 127.59; 127.50; 126.82; 125.97; 125.08; 123.28; 122.93; 119.55; 116.38; 115.60; 108.70; 108.64; 82.96 (C(2)); 22.57 (C(12)). MS: 388 (100, M^+), 311 (30).

2,2-Diphenyl-2H-pyrano[2,3-a]xanthen-12(12H)-one (**7**). To a soln. of **6** (0.367 g, 0.946 mmol) in pyridine (5 ml), CrO_3 (0.400 g) was added. After stirring for 4 h at r.t., the mixture was poured into 5% aq. HCl (50 ml). The aq. layer was extracted with Et_2O (3 × 100 ml). The org. phase was washed with H_2O, dried (Na_2SO_4), and the solvent was evaporated under reduced pressure, leaving the crude product, which was purified by CC (silica gel; hexane/AcOEt 95:5): 220 mg (58%) of **7**. M.p. 211–214°. ^{1}H-NMR: 8.35 (*dd*, *J* = 8.1, 1.5, H–C(11)); 7.66 (*m*, 5 H); 7.41–7.19 (*m*, 9 H); 6.93 (*d*, *J* = 8.7, 1 H); 6.66 (*d*, *J* = 9.6, 1 H); 6.39 (*d*, *J* = 9.6, 1 H). ^{13}C-NMR: 176.04 (C=O); 157.40; 155.22; 153.69; 144.90; 134.20; 132.13; 128.26; 127.57; 127.34; 126.78; 126.49; 123.77; 123.03; 122.94; 117.38; 117.06; 112.60; 109.75; 83.42 (C(2)). MS: 402 (100, M^+), 385 (13), 325 (90), 297 (11), 239 (12), 191 (14), 165 (14). MS: 402 (100, M^+), 401 (10), 385 (12), 325 (90), 297 (12), 239 (15), 201 (13), 191 (15), 165 (15). Anal. calc. for $C_{28}H_{18}O_3$: C 83.58, H 4.48; found: C 83.72, H 4.69.

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