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Metallocenyl-[2*H*]naphtho[1,2-b]pyrans: metal effect on the photochromic behaviour

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Previous studies have shown that the substitution by a ferrocenyl group in the 2-position of naphthopyrans has a specific and an original effect on the photochromic behaviour. In this work, the synthesis and the photochromic properties of new naphthopyrans substituted in the 2-position by three different metallocenyl groups (ferrocenyl, ruthenocenyl and osmocenyl) are presented. Whereas the ferrocenyl-substituted derivatives under UV irradiation show two absorption bands, the ruthenocenyl and osmocenyl derivatives are characterized by only one absorption band under the same condition. The photochromic behaviour of these compounds is compared with that of their parent alkyl or phenyl 2-substituted [2*H*]-naphtho[1,2-b]pyrans. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: [2*H*]Naphtho[1,2-b]pyrans; photochromism; ferrocenyl, osmocenyl, ruthenocenyl complexes

INTRODUCTION

The 2*H*-naphtho[1,2-b]pyrans (benzo[2*H*]chromenes) are an important class of photochromic materials.[1] Under UV irradiation they are converted into coloured photomerocyanine forms by cleavage of the C—O bond in the excited states[2] (Scheme 1). These photomerocyanines are highly conjugated forms and absorb in the visible range.

The reaction is reversible and the back closure process generally takes place by a thermal process and sometimes also by irradiation in the visible range. Photochromic materials are characterized by three main parameters:[3] the λ_{max} value of the opened form, the colourability A_{oo} under continuous irradiation (or A_0 by flash photolysis) and the thermal ring closure kinetic constant k_Δ.

Previous studies[4,5] have shown that the introduction of a ferrocenyl group in the 2-position of naphtho[1,2-b]pyrans modifies considerably the photochromic behaviour: *viz*. an extended wavelength absorption range in the visible spectrum with two absorption bands around 450 and 600 nm, an increase of the closure kinetic constants, and a good enough resistance to fatigue. The preparation of ferrocenyl-[3*H*]-naphtho[1,2-b]pyrans shows that the type of annellation has a great influence on the spectrokinetic parameters.

Thus we decided to check the influence of the metal and we prepared a series of metallocenyl-[2*H*]-naphtho[1,2-b]pyrans using metals of the d^8 series, as the corresponding metallocenes are stable.[6] In addition to ferrocene (Fc), ruthenocene (Rc) and osmocene (Oc) were used (Scheme 2).

The use of two substituents (methyl, phenyl) in the 2-position and two naphthols (naphth-1-ol and 3,4-dimethyl-naphth-1-ol) could allow the modulation of the spectrokinetic parameters.[6–8] The comparison of their photochromic parameters by reference to the parent 2-phenyl- and 2-methyl-naphtho[1,2-b]pyrans analogues should give some information on the metal effect (Table 1).

EXPERIMENTAL

Solvents were purified by distillation over P_2O_5 (CH_2Cl_2) or C_6H_5MgBr (THF). Column chromatography (CC): silica gel 60 *Merck* (0.063–0.200 mm). Melting points: *Electrothermal 9100* apparatus with capillary tubes. IR spectra: *Perkin Elmer 297* spectrophotometer. ^1H and ^{13}C NMR spectra: *Bruker-AC-250* spectrometer; ^1H 250 MHz, ^{13}C 62.8 MHz, chemical shifts δ downfield from $SiMe_4$, coupling constants *J* (Hz). Spectrokinetic parameters: *Beckman DU-7500* spectrophotometer, irradiation with an *Oriel* 150 W high-pressure xenon lamp and beam guided to the thermostated quartz cell via fibre optics. The photochromic solution ($C = 5 \times 10^{-4}$ mol l^{-1})

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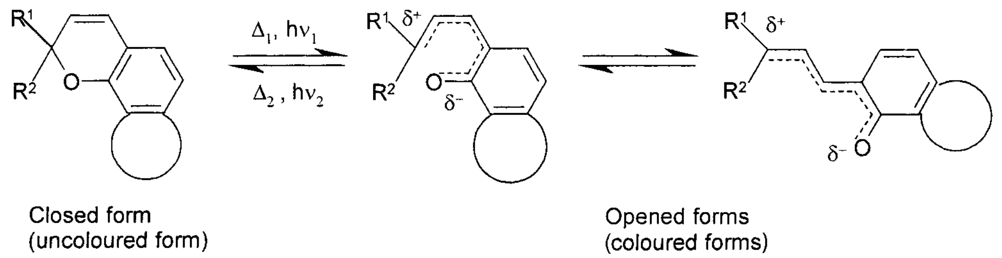
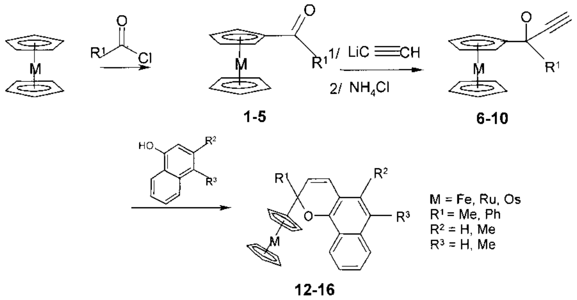


Scheme 1. General photochromic equilibrium.

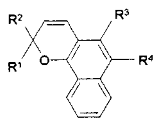


Scheme 2. Structure and synthesis of new 2-metallocenyl-naphtho[1,2-b]pyrans.

Table 1. Structure[a] of the [2H] naphtho [1,2-b] pyrans studied

Compound	R^1	R^2	R^3	R^4
12	Fc	Me	H	H
13	Fc	Ph	Me	Me
14	Rc	Me	H	H
15	Rc	Ph	Me	Me
16	Oc	Me	H	H
17	Ph	Me	H	H
18	Ph	Ph	Me	Me
19	Ph	Ph	H	H
20	Fc	Ph	H	H

[a]



were prepared in anhydrous toluene, acetonitrile and ethanol (*SDS France*).

Metallocenyl-ketones **1**, **2**, **3**, **4** and **5** were prepared according to Refs 9–11.

Ferrocenyl-methylketone (1)

Yield 79%. M.p. 86 °C (lit.[9] m.p. 83 °C). IR ($CHCl_3$, cm^{-1}) 2900, 1600. ^1H NMR ($CDCl_3$, ppm) $\delta = 2.45$ (3H, s), 4.1 (5H, s), 4.45 (2H, m), 4.7 (2H, m). ^{13}C NMR ($CDCl_3$, ppm) $\delta = 27.4$, 69.6, 69.8, 72.3, 79.2, 202.0.

Ferrocenyl-phenylketone (2)

Yield 68%. M.p. 105 °C (lit.[10] m.p. 107 °C). IR ($CHCl_3$, cm^{-1}) 1600. ^1H NMR ($CDCl_3$, ppm) $\delta = 4.2$ (5H, s), 4.5 (2H, d, *J* 1.8), 4.8 (2H, d, *J* 1.8), 7.4 (2H, m), 7.5 (1H, m), 7.8 (2H, dd, *J* 6.6 and 2.8). ^{13}C NMR ($CDCl_3$, ppm) $\delta = 70.2$, 72.1 72.9, 79.0, 127.3, 128.1, 133.6, 140.1, 198.2.

Ruthenocenyl-methylketone (3)

Yield 76%. M.p. 115 °C (lit.[11] m.p. 112 °C). IR ($CHCl_3$, cm^{-1}) 2900, 1670, 1280. ^1H NMR ($CDCl_3$, ppm) $\delta = 2.2$ (3H, s), 4.5 (5H, s), 4.7 (2H, m), 5.0 (2H, m). ^{13}C NMR ($CDCl_3$, ppm) $\delta = 27.0$, 71.2, 72.3, 73.9, 84.3, 200.2.

Ruthenocenyl-phenylketone (4)

Yield 55%. M.p. 116 °C (lit.[11] m.p. 123 °C). IR ($CHCl_3$, cm^{-1}) 1630, 1280. ^1H NMR ($CDCl_3$, ppm) $\delta = 4.5$ (5H, s), 4.7 (2H, m), 5.1 (2H, m), 7.4 (3H, m), 7.9 (2H, dd, *J* 7.1 and 1.5). ^{13}C NMR ($CDCl_3$, ppm) $\delta = 72.5$, 73.1, 73.9, 82.9, 128.2, 128.5, 128.6, 131.7, 139.4, 197.4.

Osmocenyl-methylketone (5)

Yield 54%. M.p. 129 °C (lit.[11] m.p. 126 °C). IR ($CHCl_3$, cm^{-1}) 2900, 1660, 1270. ^1H NMR ($CDCl_3$, ppm) $\delta = 2.1$ (3H, s), 4.7 (5H, s), 4.9 (2H, m), 5.2 (2H, m). ^{13}C NMR ($CDCl_3$, ppm) $\delta = 26.8$, 63.8, 66.6, 66.9, 78.0, 198.1.

Preparation of metallocenyl propynols 6, 7, 8, 9 and 10[12]

To a solution of lithium acetylide (7.5 mmol) in 100 ml of anhydrous THF, cooled to 0 °C (ice bath), a solution of metallocenylketones **1**, **2**, **3**, **4** or **5** (1.5 mmol) in 100 ml of anhydrous THF was slowly added. The mixture was stirred for 2.5 h, and then hydrolysed with saturated aqueous NH_4Cl. The organic phase was filtered on Celite, washed with H_2O, dried with $MgSO_4$ and evaporated. The residue was rapidly chromatographed (silica gel, hexane/ether: 75/15).

3-Ferrocenyl-but-1-yn-3-ol (**6**)

Yield 51%. M.p. 47 °C. IR ($CHCl_3$, cm^{-1}) 3540, 3300. ^1H NMR ($CDCl_3$, ppm) $\delta = 1.7$ (3H, s), 2.7 (1H, s), 2.9 (1H, s), 4.1 (2H, m), 4.2 (5H, s), 4.3 (2H, m). ^{13}C NMR ($CDCl_3$, ppm) $\delta = 31.0$, 65.0, 66.5, 67.0, 68.5, 68.8, 70.8, 87.4, 95.7.

1-Ferrocenyl-1-phenylprop-2-ynol (**7**)

Yield 65%. M.p. 56 °C. IR ($CHCl_3$, cm^{-1}) 3560, 3300, 2100. ^1H NMR ($CDCl_3$, ppm) $\delta = 2.7$ (1H, s), 3.1 (1H, s), 4.1 (1H, m), 4.2 (2H, m), 4.2 (5H, s), 4.4 (1H, m), 7.2 (3H, m), 7.5 (2H, m). ^{13}C NMR ($CDCl_3$, ppm) $\delta = 65.3$, 68.5, 68.7, 69.3, 71.4, 71.5, 73.3, 87.0, 96.8, 125.7, 127.9, 128.3, 143.9.

3-Ruthenocenyl-but-1-yn-3-ol (**8**)

Yield 34%. M.p. 61 °C. IR ($CHCl_3$, cm^{-1}) 3540, 3300. ^1H NMR ($CDCl_3$, ppm) $\delta = 1.6$ (3H, s), 2.2 (1H, s), 2.4 (1H, s), 4.4 (2H, m), 4.5 (5H, s), 4.6 (1H, m), 4.8 (1H, m). ^{13}C NMR: $\delta = 30.8$, 67.9, 70.4, 70.6, 70.7, 71.0, 72.0, 73.6, 87.1, 101.2.

1-Ruthenocenyl-1-phenylprop-2-ynol (**9**)

Yield 39%. M.p. 56 °C. IR ($CHCl_3$, cm^{-1}) 3540, 3300. ^1H NMR ($CDCl_3$, ppm) $\delta = 2.5$ (1H, s), 2.7 (1H, s), 4.4 (1H, m), 4.5 (2H, m), 4.6 (5H, s), 4.9 (1H, m), 7.2 (3H, m), 7.6 (2H, m). ^{13}C NMR ($CDCl_3$, ppm) $\delta = 68.5$, 69.6, 70.6, 71.1, 71.5, 71.8, 72.4, 86.6, 102.3, 125.6, 127.7, 128.1, 128.2, 143.0.

3-Osmocenyl-but-1-yn-3-ol (**10**)

Yield 26%. M.p. 91 °C. IR ($CHCl_3$, cm^{-1}) 3300. ^1H NMR ($CDCl_3$, ppm) $\delta = 1.7$ (3H, s), 2.0 (1H, s), 2.4 (1H, s), 4.6 (2H, m), 4.7 (5H, s), 4.8 (1H, m), 5.1 (1H, m). ^{13}C NMR ($CDCl_3$, ppm) $\delta = 30.0$, 61.9, 63.9, 64.3, 64.7, 64.8, 64.9, 70.0, 86.8, 95.0.

3,4-Methylnaphth-1-ol (**11**)[13]

To a solution of 2,3-dimethylfurane (10 mmol) in anhydrous THF was added 12 mmol of magnesium. The mixture was heated to reflux and 10 mmol of 1-bromo-2-fluorobenzene in anhydrous THF (10 ml) was added. The mixture was stirred and heated to reflux over 2 h. The organic phase was washed with a saturated solution of NH_4Cl and with H_2O, dried and reduced under vacuum. The residue was chromatographed (silica gel). Yield 78%. M.p. 120 °C. ^1H NMR ($CDCl_3$, ppm) $\delta = 2.3$ (3H, s), 2.4 (3H, s), 5.1 (1H, s), 6.6 (1H, m), 7.4 (2H, m), 7.8 (1H, d, *J* 8.7), 8.1 (1H, d, *J* 8.7). ^{13}C NMR ($CDCl_3$, ppm) $\delta = 14.0$ (CH_3), 20.8, 111.9, 121.9, 123.7, 123.8, 123.9, 126.4, 134.2, 135.1, 149.6, 190.2.

Preparation of metallocenyl-[2*H*]-naphtho[1,2-b]pyrans 12, 13, 14, 15 and 16

A solution of the appropriate propargylic alcohol **6**, **7**, **8**, **9** or **10** (1 mmol) in a minimum of CH_2Cl_2 was added to a solution of the naphthol (5 mmol) in a minimum of CH_2Cl_2. The mixture was stirred until total consumption of the propargylic alcohol. The organic phase was washed with H_2O, dried and reduced under vacuum. The residue was chromatographed (silica gel, 100% hexane).

2-Ferrocenyl-2-methyl-[2H]-naphtho[1,2-b]pyran (**12**)

Yield 15%. M.p. 131 °C. UV (acetonitrile, nm) 328, 338, 354. ^1H NMR ($CDCl_3$, ppm) $\delta = 1.7$ (3H, s), 4.05 (2H, m), 4.1 (5H, s), 4.15 (1H, m), 4.2 (1H, m), 6.2 (1H, d, *J* 10.0), 6.4 (1H, d, *J* 10.0), 7.1 (1H, m), 7.3 (3H, m), 7.6 (1H, m), 8.1 (1H, m). ^{13}C NMR ($CDCl_3$, ppm) $\delta = 28.5$, 65.3, 66.5, 68.0, 68.3, 69.0, 77.9, 94.3, 115.0, 119.9, 122.1, 122.2, 124.7, 124.9, 125.4, 126.2, 127.8, 128.3, 134.7, 148.3. Anal. Found: C, 76.2; H, 5.8. Calc. for $C_{29}H_{22}FeO$: C, 75.8; H, 5.3%.

2-Ferrocenyl-2-phenyl-5,6-dimethyl-[2H]-naphtho[1,2-b]pyran (**13**)

Yield 56%. M.p. 167 °C. UV (acetonitrile, nm) 335, 350. ^1H NMR ($CDCl_3$, ppm) $\delta = 2.35$ (3H, s), 2.45 (3H, s), 4.0 (5H, s), 4.1 (3H, m), 4.4 (1H, m), 6.3 (1H, d, *J* 10.0), 6.9 (1H, d, *J* 10.0), 7.0 (3H, m), 7.4 (4H, m), 7.8 (1H, m), 8.4 (1H, m). ^{13}C NMR ($CDCl_3$, ppm) $\delta = 14.5$, 15.9, 65.8, 66.3, 67.8, 67.9, 68.9, 79.4, 94.5, 108.2, 120.2, 122.2, 122.9, 123.0, 123.9, 124.3, 125.3, 126.1, 126.6, 127.0, 127.7, 128.1, 129.5, 138.8, 146.2. Anal. Found: C, 79.1; H, 7.4. Calc. for $C_{29}H_{22}FeO$: C, 79.1; H, 7.2%.

2-Ruthenocenyl-2-methyl-[2H]-naphtho[1,2-b]pyran (**14**)

Yield 14%. M.p. 146 °C. UV (acetonitrile, nm) 319, 350, 363. ^1H NMR ($CDCl_3$, ppm) $\delta = 1.8$ (3H, s), 4.5 (2H, m), 4.6 (5H, s), 4.7 (1H, m), 4.9 (1H, m), 6.2 (1H, d, *J* 10.1), 6.8 (1H, d, *J* 10.1), 7.2 (1H, m), 7.4 (3H, m), 7.7 (1H, m), 8.3 (1H, m). ^{13}C NMR ($CDCl_3$, ppm) $\delta = 28.4$, 69.4, 69.6, 70.1, 70.3, 71.4, 79.6, 94.3, 115.0, 119.8, 122.3, 122.7, 124.7, 124.9, 125.6, 126.4, 127.9, 128.3, 134.7, 147.9. Anal. Found: C, 67.6; H, 11.1. Calc. for $C_{29}H_{22}ORu$: C, 67.8; H, 10.1%.

2-Ruthenocenyl-2-phenyl-5,6-dimethyl-[2H]-naphtho[1,2-b]pyran (**15**)

Yield 28%. M.p. decomposition at 160 °C. UV (acetonitrile, nm) 326, 339, 355. ^1H NMR ($CDCl_3$, ppm) $\delta = 2.3$ (3H, s), 2.4 (3H, s), 4.3 (5H, s), 4.35 (1H, m), 4.4 (2H, m), 4.65 (1H, m), 6.1 (1H, d, *J* 10.0), 6.7 (1H, d, *J* 10.0), 7.1 (3H, m), 7.3 (2H, m), 7.4 (2H, m), 7.8 (1H, m), 8.3 (1H, m). ^{13}C NMR ($CDCl_3$, ppm) $\delta = 14.5$, 15.6, 69.4, 69.6, 70.1, 70.3, 71.4, 79.1, 98.7, 114.9, 120.5, 122.4, 123.3, 123.5, 123.8, 124.3, 126.0, 126.1, 127.2, 127.4, 127.6, 129.2, 133.4, 145.3, 146.4. Anal. Found: C, 72.0; H, 6.7. Calc. for $C_{29}H_{22}ORu$: C, 72.2; H, 6.6%.

2-Osmocenyl-2-methyl-[2H]-naphtho[1,2-b]pyran (**16**)

Yield 11%. M.p. 82 °C. UV (acetonitrile, nm) 328, 358. ^1H NMR ($CDCl_3$, ppm) $\delta = 1.7$ (3H, s), 4.6 (2H, m), 4.7 (5H, s), 4.8 (1H, m), 4.9 (1H, m), 6.2 (1H, d, *J* 10.1), 6.8 (1H, d, *J* 10.1), 7.2 (1H, m), 7.4 (3H, m), 7.7 (1H, m), 8.3 (1H, m). ^{13}C NMR ($CDCl_3$, ppm) $\delta = 29.3$, 62.7, 64.7, 64.9, 65.6, 65.7, 79.9, 95.3, 115.0, 119.9, 122.1, 122.2, 124.7, 124.9, 125.6, 126.2, 127.9, 128.3, 134.7, 148.4. Anal. Found: C, 47.4; H, 7.9. Calc. for $C_{29}H_{22}OOs$: C, 47.7; H 7.6%.

2,2-Diphenyl-5,6-dimethyl-[2*H*]-naphtho[1,2-b]pyran (18)

A solution of 2-phenylprop-3-yn-2-ol (1 mmol) in a minimum amount of CH_2Cl_2 was added to a solution of 3,4-dimethylnaphth-1-ol (5 mmol) with a catalytic amount of

Table 2. Yield and experimental conditions for the metallocenyl-ketones

R^1, metal		Yield (%)	T (°C)	t (h)
Me, Fe[9]	**1**	79	0	1
Ph, Fe[10]	**2**	67	0	1
Me, Ru[11]	**3**	76	37	3
Ph, Ru[11]	**4**	55	37	3
Me, Os[11]	**5**	61	37	5

para-toluenesulfonic acid in a minimum amount of CH_2Cl_2. The mixture was stirred until total consumption of propargylic alcohol. The organic phase was washed with H_2O, dried and reduced under vacuum. The residue was chromatographed (silica gel, 100% hexane).

Yield 67%. M.p. 137 °C. UV (acetonitrile, nm) 350, 363. ^1H NMR ($CDCl_3$, ppm) $\delta = 2.3$ (3H, s), 2.4 (3H, s), 6.1 (1H, d, J 9.9), 6.9 (1H, d, J 9.9), 7.1 (6H, m), 7.4 (2H, m), 7.5 (4H, m), 7.8 (1H, m), 8.3 (1H, m). ^{13}C NMR ($CDCl_3$, ppm) $\delta = 14.6$, 15.9, 98.7, 115.8, 121.9, 122.5, 123.8, 123.9, 124.4, 126.4, 126.9, 127.5, 127.6, 128.2, 129.4, 131.2, 134.3, 145.4, 146.7. Anal. Found: C, 89.1; H 6.6. Calc. for $C_{27}H_{22}O$: C, 89.4; H 6.1%.

RESULTS AND DISCUSSION

Synthesis

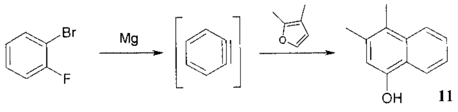
The new metallocenyl-naphthopyrans are synthesized in three steps from Fc, Rc and Oc (Scheme 2 and Table 1).

The first step is the synthesis of the metallocenyl-ketones.[9–11] Five metallocenyl-ketones were synthesized (Table 2). Taking into account the yield and the experimental conditions, it can be seen that the reactivity of the d^8 series metallocene decreases in the order: Fc > Rc > Oc, in agreement with the literature.[11]

The second step is the synthesis of propargylic alcohols[4,12] by condensation of lithium acetylide on the metallocenyl-ketones **1**, **2**, **3**, **4** and **5**. The results are reported in Table 3. For the same type of substitution (compounds **6**, **8** and **10**), a decrease of the yield is observed, correlating to the increase of the molar mass of metallocene. This result could have two courses: (i) the increase of the metallocene's steric hindrance[13] inhibits the approach of the acetylide on the carbonyl function; and (ii) the electrophilic character of the sp^2 carbon atom (carbonyl function) decreases when the metal is less electronegative.

Table 3. Yield of metallocenyl-propargylic alcohols

Compound	R^1	Metal	Yield (%)
6	Me	Fe	51
7[4]	Ph	Fe	65
8	Me	Ru	34
9	Ph	Ru	39
10	Me	Os	26



Scheme 3. Synthesis of 3,4-dimethylnaphth-1-ol.

Table 4. Yield of the new 2-metallocenyl-naphtho[1,2-b]pyrans

Compound	R^1, metal	R^2,R^3	Yield (%)
12	Me, Fe	H, H	15
13	Ph, Fe	Me, Me	56
14	Me, Ru	H, H	14
15	Ph, Ru	Me, Me	28
16	Me, Os	H, H	11

The synthesis of metallocenyl-naphthopyrans is the third step. These compounds are obtained by acid-catalysed condensation of the metallocenyl-propargylic alcohols with appropriate naphthols.[3] Two naphthols were used: the commercially available naphth-1-ol and the 3,4-dimethylnaphth-1-ol (**11**) synthesized from 1-bromo-2-fluorobenzene and 2,3-diethylfurane[14] (Scheme 3). Five 2-metallocenyl-naphthopyrans were thus obtained (Table 4). In Table 4, two remarks can be made: the yields are better with the 3,4-dimethylnaphth-1-ol and the yields decrease when the molar mass of the metallocene increases.

Three analogues were used for comparing the metallocene effect and the phenyl effect through the photochromic behaviour: compounds **17** and **19**[15,16] for **12**, **14**, **16** and

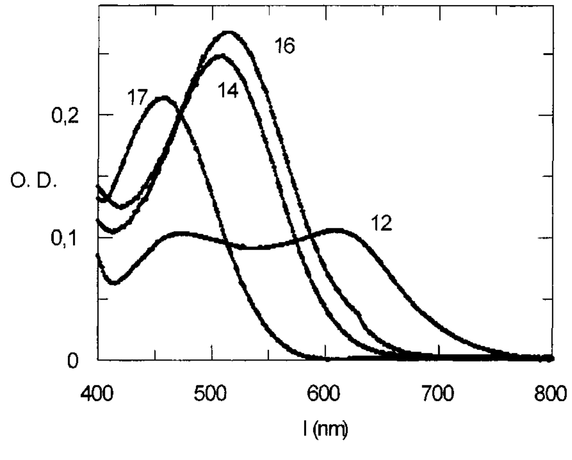


Figure 1. Visible spectra of metallocenyl(Fe, Ru, Os)-methylnaphthopyrans (**12**, **14**, **16**) and the phenyl homologue (**17**)

Table 5. Spectrokinetic parameters ($T = 25\,°C$)

	Toluene		Acetonitrile		Ethanol	
Compound	λ_{max} (nm)	k_{Δ} (s^{-1})	λ_{max} (nm)	k_{Δ} (s^{-1})	λ_{max} (nm)	k_{Δ} (s^{-1})
12	*473*	**0.9×10^{-4}**	*472*	**1.1×10^{-2}**	*396*	0 (396)
	608		609	4.2×10^{-3}	425, *609*	**1.4×10^{-3}**
13	*470*	**2.8×10^{-4}**	*470*	**2.3×10^{-2}**	*470*	**6.1×10^{-3}**
	582		602	1.2×10^{-3}	592	2.0×10^{-4}
14	*493*	**1.9×10^{-1}**	*496*	**1.2×10^{-3}**	*512*	**2.9×10^{-3}**
		1.1×10^{-3}		9.0×10^{-4}		3.3×10^{-3}
15	*505*	**3.9×10^{-2}**	*506*	**8.0×10^{-2}**	*515*	**4.6×10^{-2}**
		6.0×10^{-4}		6.0×10^{-4}		1.7×10^{-3}
16	*503*	**8.9×10^{-2}**	*500*	**2.1×10^{-3}**	*520*	**1.1×10^{-2}**
		2.5×10^{-3}				
17	*450*	**1.5×10^{-2}**	*458*	**2.2×10^{-2}**	*461*	**5.6×10^{-3}**
		5.0×10^{-5}		1.1×10^{-3}		8.0×10^{-4}
18	*474*	**3.6×10^{-3}**	*476*	**7.0×10^{-3}**	*481*	**3.8×10^{-3}**
		4.0×10^{-4}		8.0×10^{-4}		
19	*472*	**5×10^{-4}**	*471*	**4.0×10^{-4}**	*490*	**5×10^{-4}**
20	*457*	**2×10^{-3}**	*450*	**1.2×10^{-2}**	*469*	**1.9×10^{-3}**
	600	1×10^{-4}	*602*	**10^{-5}**	618	

20,[17] and compound **18** for **13** and **15**. Compound **18** was obtained from 2-phenylprop-3-yn-2-ol and 3,4-dimethylnaphth-1-ol (**11**) under acid catalysis (*para*-toluenesulfonic acid; yield 67%).

Photochromic parameters of the new metallocenyl-naphthopyrans

These studies were performed under continuous irradiation with a xenon lamp (150 W).[18] A UV–visible spectrophotometer was used for the determination of the λ_{max} values of the photomerocyanine and the decrease of the optical density when the irradiation is stopped. From these results, the bleaching kinetic constants k_{Δ} were calculated using PC software (Grafit 3.0). The studies were realized in three different solvents: toluene, acetonitrile and ethanol at 25 °C to determine solvatochromic effects.[19] In order to quantify the effect of the metallocenyl substituent, the photochromic properties were compared with those of the three corresponding analogues (**17, 18** and **19**).

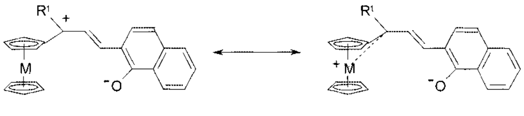
The results concerning the spectrokinetic parameters are reported in Table 5. For the ferrocenyl compounds (**12, 13** and **20**), k_{Δ} value, were determined at the λ_{max} values given in italics. k_{Δ} values in bold-faced type represent the maximum amplitude of the thermal bleaching.

Spectroscopic results

First, it must be noted that the ferrocenyl-substituted naphthopyrans **12**, **13** and **20** show a unique behaviour: two absorption bands are observed for the opened forms, whereas only one is observed for the parent compounds **17**, **18** and **19**. Furthermore, when compound **12** is irradiated in ethanol a third absorption band is observed and the corresponding opened form does not cyclize back to the closed form when irradiation is stopped. This is not observed when another metal replaces the iron atom or when a methyl group is replaced by a phenyl one and thus, this could be considered as quite specific.

Because of the peculiar behaviour of the ferrocenyl series, their absorption bands between 450 and 473 nm, in toluene and acetonitrile, will be taken into account for comparison purposes. It can be seen that, when a phenyl group in **17** is replaced by a metallocenyl one, a bathochromic effect is observed, with an increasing effect in the Fc, Rc, Oc series. The same trend is observed in the dimethyl-substituted series when Rc (**13** and **15**) replaces Fc. The bathochromic effect results from a decrease of the open form's energy level; the origin of this decrease could be the metallocenyl's stabilization of the zwitterionic photomerocyanine by electron donation (Scheme 4). The increasing stabilization when the metal's electronic density increases[20] can explain the increasing bathochromic effect.

The replacement of a phenyl group by a ferrocenyl one (**18**



Scheme 4. Zwitterionic photomerocyanine stabilization by metallocenyl group.

to **13**) does not change the observed λ_{max} values. The same absence of effect is observed between **18** and **19**: dimethyl substitution does not have an effect on the λ_{max} values. However, a small bathochromic effect is observed when **20** is compared with **13**.

Kinetic results

Generally, two bleaching kinetic constants can be measured. This reflects the fact that, after opening of the starting compounds, two or more isomers of the photomerocyanine are formed. These stereoisomers differ by the relative stereochemistry of the polyenic system formed.

In this discussion, the main bleaching kinetics constants (bold-faced type in Table 5) will be compared. Two remarks for the ferrocenyl compounds can be made: the k_Δ values are almost similar for **12, 13** and **20**;[4] for compound **12**, in toluene, only the slow bleaching kinetic constant is observed because the photochromic equilibrium cannot be reached.

It appears from Table 5 that the k_Δ value depends on the nature of the solvent and that very often acetonitrile has a specific effect. When a phenyl group in **17** is replaced by Fc (**12**) the k_Δ value decreases in toluene and ethanol, whereas it remains very similar in acetonitrile. With Rc and Oc groups (**14** and **16**) the k_Δ values increase in toluene and ethanol, whereas in acetonitrile they are smaller than those of **12** and **17**.

For the 2-phenyl-5,6-dimethylnaphtho[1,2-b]pyran structures (compounds **13, 15** and **18**), the presence of the metallocenyl group increases the k_Δ values in all solvents compared with the reference (phenyl group). The same effect is observed when **19** is compared with **18**. This increase is due to the steric effects introduced by the presence of the methyl groups in the opened form.

In toluene, acetonitrile and ethanol the metallocenyl compounds have a bleaching kinetic constant higher than those of the phenyl naphthopyrans. In ethanol, for the 2-ferrocenyl-2-methylnaphtho[1,2-b]pyran (compound **12**), a third λ_{max} absorption (396 nm) is observed with no bleaching kinetics ($k_\Delta = 0$), which is attributed to complex formation between the cisoid opened form and the protic solvent.

CONCLUSION

We have described the synthesis of five new 2-metallocenyl-[2*H*]naphtho[1,2-]pyrans. In most cases, these compounds are prepared in three steps in relatively good yields. We have shown the influence of the metal on the synthetic point of view.

We have also synthesized the 3,4-dimethylnaphth-1-ol used to prepare two metallocenyl compounds and the 2,2-diphenyl-5,6-dimethylnaphtho[1,2-b]pyran.

Studies of the photochromic properties have shown original spectrokinetic behaviour for these 2-metallocenyl-[2*H*]naphtho[1,2-b]pyrans: the 2-ferrocenyl-[2*H*]naphtho [1,2-b]pyrans are mainly characterized by two absorption bands (three in ethanolic solution and for a specific substitution), whereas the ruthenocenyl-and osmocenyl-naphtho[1,2-b]pyrans present just one absorption band in the neighbourhood of 500 nm.

Bathochromic effects have shown the participation of the metallocene's metal on the that decreasing of the energy level of the zwitterionic open form. Finally, we have shown the increase of the bleaching kinetics by the metallocene in the majority of cases.

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