NEW FERROCENYL-NAPHTHOPYRANS WITH ORIGINAL PHOTOCHROMIC BEHAVIOUR

**Stéphane Anguille, Pierre Brun* and Robert Guglielmetti**
GCOPL ERS CNRS 158, Faculté des Sciences de Luminy
Case 901, F-13288 Marseille cedex 09, France

Abstract: The synthesis and the photochromic properties of a new family of naphthopyrans substituted in the -3 position by a ferrocenyl group are presented. The photochromic behaviour of these compounds is compared with the parent -3,3-diphenyl-naphthopyrans ones. It shows quite original photochromic properties: extended wavelength range in the visible absorption spectrum, sensitivity of the spectrokinetic parameters to the annellation type.

Introduction:

The 2*H*-benzopyrans (2*H*-chromenes) are known as an important class of photochromic materials (1). When exposed to UV irradiation they are converted into coloured merocyanine forms by cleavage of the C-O bond (Scheme 1). These photomerocyanines are highly conjugated forms and absorb in the visible range.

uncoloured form   coloured form
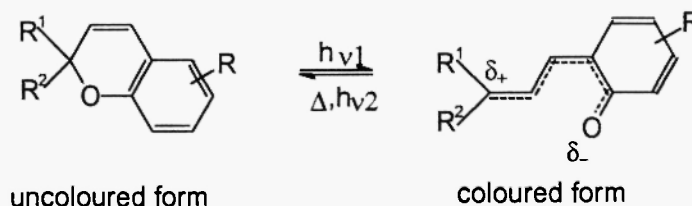
Scheme 1: *Photochromic equilibrium*

The reaction is reversible and the back cyclisation generally takes place by a thermal process and sometimes also by a photochemical process in the visible region. Photochromic materials are characterised by three main parameters: the λ_{max} of the opened form, the colourability A_{∞}, under continuous irradiation (or A_0 by flash photolysis) and the thermal ring closure kinetic constant k_Δ (2).

Previous works have shown that the introduction of conjugated substituents in the -2 position of 2*H*-chromenes or in the -3 position of naphthopyrans (R^1 and R^2) have interesting effects on the spectrokinetic parameters: decrease of the k_Δ, increase of the A_{∞} and important bathochromic shift of the λ_{max} (3, 4, 5).

Thus we have anticipated that substitution in this position by an aromatic organometallic group could give interesting effects on the photochromic properties. The ferrocenyl group was chosen because the sandwich type bicyclopentadienyl-iron complex is aromatic (6π electrons on each cyclopentadienyl moiety) and also because it is one of the most stable complex in the metallocene series (18 valence electrons)(6).

The only known application of such an approach was described with fulgides derivatives (7).

We describe here the synthesis of two ferrocenyl naphthopyrans 4 and 5, respectively, annellated in the 5-6 and 7-8 positions. The photochromic properties of these compounds are compared with those of the phenyl substituted parent naphthopyrans (4, 5).

Results and discussion:

Synthesis:

The two compounds 4 and 5 were synthesized using a three steps procedure. The starting compound, the ferrocenyl ketone 1 is prepared by a Friedel-Crafts reaction between ferrocene and benzoyl chloride (8) in the presence of $AlCl_3$. The yield in 1 is correct (59%) although it is much better with non aromatic acid chloride, i.e. 79% when the same reaction is performed with acetyl chloride. In this reaction, the Lewis acid reacts also as an oxidant and converts partly the ferrocene (Fe^{II}) into ferricinium (Fe^{III}) (9); this limits the yield of the ketone 1. In the second step propargylic alcohol 2 is prepared by condensation of an acetylide ion with ketone 1.

This reaction has been optimised. Indeed the basicity of the reaction medium induces a double condensation on the ketone and the propargylic diol 3 is formed at the expense of alcohol 2 (10) (Scheme 2).
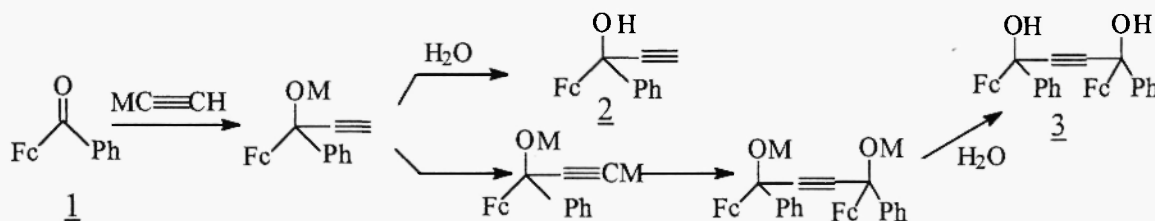

Scheme 2: *Formation of alcohols 2 and diol 3*

In order to limit this side reaction, the condensation has to be performed under high dilution conditions, at low temperature and with the less basic acetylide ion. We thus used lithium acetylide as it is the less basic available one. Indeed the yield in alcohol 2 increases from 16% to 51% when lithium acetylide was used instead of sodium one. Propargylic alcohol 2 is then reacted with naphthol in the presence of *p*-toluene sulfonic acid. The acid catalyses the formation of the corresponding ether (11). The mechanism of the cyclisation involves a series of pericyclic reactions leading to the naphthopyran systems (12) (Scheme 3).
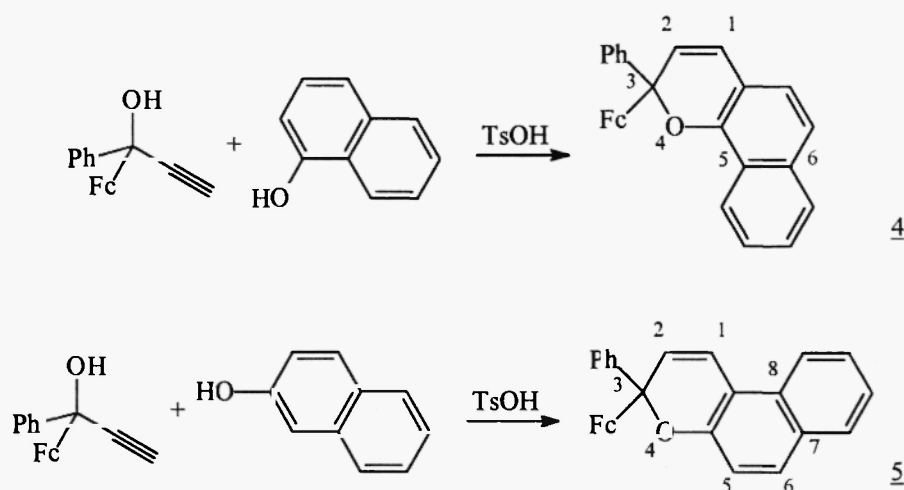
Scheme 3: *Formation of the naphthopyrans 4 and 5*

In these conditions naphthopyran 5 is obtained in 60% yield while compound 4 is formed in only 13%. It has to be noted that propargylic alcohol 2 is not very stable in acidic medium. Under these conditions, it is very easily converted to an α-β ethylenic aldehyde 6 by a Meyer-Schuster reaction (13) (Scheme 4).
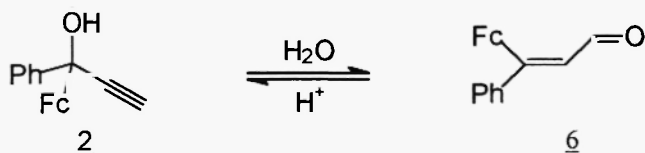
Scheme 4: *Meyer-Schuster reaction of alcohol 2*

Owing to the acidic character of naphth-1-ol and naphth-2-ol (pKa are 9.34 and 9.51 respectively) (14), we performed the same reaction in the absence of *p*-TsOH. The yields are improved to 79% for 5 and to 25% for naphthopyran 4.

The observed difference for the formation of 4 and 5 is mainly due to the fact that the electronic density is higher on carbon-1 of naphth-2-ol than on carbon-2 of naphth-1-ol (5) : the cyclisation process is thus favoured in the case of 5. Furthermore the acidity of the medium favours the competitive Meyer-Schuster reaction.

Spectrokinetic parameters:

We have measured the spectrokinetic parameters of compounds 4, 5, 7 and 8 (Scheme 5 and Figures 1 and 2) under the same conditions, with a Beckman DU-7500 spectrophometer.
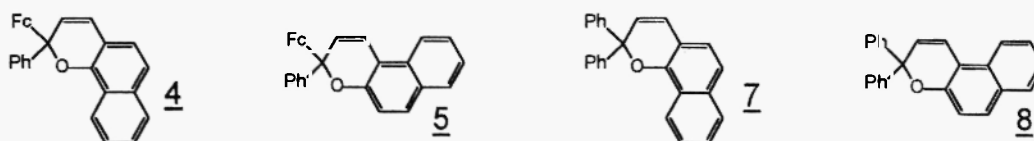
Scheme 5: *Naphthopyrans studied*

Under irradiation, in toluene solution, in the UV-visible range, compounds $\underline{4}$ and $\underline{5}$ are opened and the λ_{max} is shifted to higher values (see Table I). The colourability A_∞ and the closure kinetic rate constant k_Δ were measured under continuous irradiation conditions (15). When the photostationary equilibrium state is reached (equilibrium between opened and closed forms) the colourability is determined. It corresponds to the value of the optical density at the photostationary state. Thermal bleaching kinetic constants k_Δ (a fast one $k_{\Delta 1}$ and a slow one $k_{\Delta 2}$) are determined by plotting the variation of the O.D. versus time, when the irradiation is stopped (Figures 1 and 2).
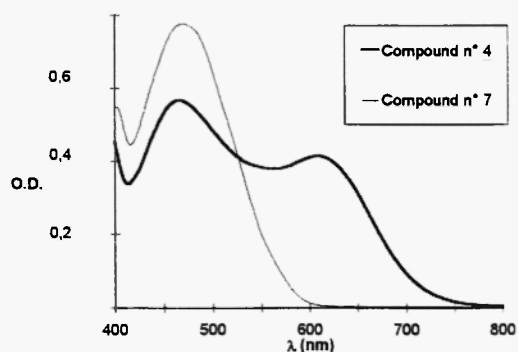
Fig. 1: *Spectra of irradiated compounds $\underline{4}$ and $\underline{7}$*
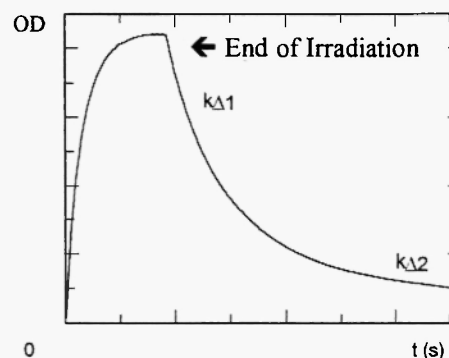
Fig. 2: *DO variation during and after irradiation*

The results are reported in the Table I.

Table I: *Spectrokinetic parameters for compounds $\underline{4}$, $\underline{5}$, $\underline{7}$ and $\underline{8}$*

toluene, 25 °C	4		5		7	8
λ_{max} (nm)	467	600	450	602	469	432
A_∞	0.26	0.18	0.03	0.01	0.8	0.04
$k_\Delta 1$ ($10^{-3}.s^{-1}$)	2.0		208.3		1.7	91.2
$k_\Delta 2$ ($10^{-3}.s^{-1}$)	<0.1		3.0		0.6	2.0

The examination of the data indicates strong modifications when a phenyl group is replaced by a ferrocenyl one. The most important and interesting effect is observed in the visible absorption spectra of $\underline{4}$ and $\underline{5}$. These compounds present two λ_{max} centred respectively on 467, 600 nm and 450, 602 nm while naphthopyrans $\underline{7}$ and $\underline{8}$ exhibit only one absorption centred respectively on 469 and 432 nm.

Photomerocyanines forms of 4 and 5 are grey-blue while 7 and 8 ones are yellow. The colourability of ferrocenyl derivatives is lower than that of compounds 7 and 8. It has to be noted that the annellation type induces the same modification trend in the two series 4-5 and 7-8 (5).

The introduction of a ferrocenyl group changes also the k_Δ. The kinetics are much faster for the ferrocenyl compounds. All these compounds present two kinetics, one fast and the second slow. In the case of compound 4 the second k_Δ could not be determined accurately as it has a very small value. For that compound we checked that the thermal bleaching rate constants were identical when measured at the two wavelength maxima.

Conclusion:

Ferrocenyl naphthopyrans are new photochromic organometallic materials. They are relatively easy to prepare. They present interesting and original photochromic properties with an extended absorption in the visible area. Further work is actually in progress in order to study the influence of annellation type, steric effects on the spectrokinetic parameters and also to study the excited states and their involvement in the photocolouration process.

Experimental Part:

General: Solvents were dried by distillation over P_2O_5 (CH_2Cl_2), RMgBr (THF). Column chromatography (CC): silica gel 60 *Merck* (0.063-0.200 mm). Melting points: *Electrothermal 9100* apparatus with capillary tubes. IR spectra in $CHCl_3$: *Perkin Elmer 297* spectrophotometer. ^{1}H and ^{13}C NMR Spectra in $CDCl_3$: *Bruker-AC-250* spectrometer; chemical shifts δ in ppm downfield from $SiMe_4$, coupling constants J in Hz. Spectrokinetic parameters: *Beckman DU-7500* spectrophotometer, irradiation with *Oriel 150 W* hight pressure xenon lamp, bright flux was ruled at 115 $W.m^{-2}$ and guide to the quartz cell by an optical fiber, the photochromic solution (C = 1.10^{-4} $mol.L^{-1}$) were prepared in anhydrous toluene (*SDS France*).

ferrocenyl-phenyl ketone 1 was prepared acording to ref. 8. To a solution of ferrocene (4.65g, 24.75 mmol) in dry CH_2Cl_2 (100mL) was added a mixture of benzoylchloride (3.53g, 24.75 mmol)-$AlCl_3$ (3.3g, 24.75 mol) in dry CH_2Cl_2 (50mL). The mixture was stirred during 1 h and poured into cold H_2O and the organic phase was washed with H_2O until neutral pH. The organic phase was dried ($MgSO_4$), evapored and the residue chromatographied (silica gel, hexane/ether : 80/20) ; Yield: 59%; ^{1}H-NMR (250 MHz): 4.2 (s, 5H), 4.5 (dd, J=1.8,1.8, 2H), 4.8 (dd, J=1.8,1.8, 2H), 7.4 (m, 2H), 7.5 (m, 1H), 7.8 (dd, J=6.6, 2.8, 2H); ^{13}C-NMR (62.8 MHz): 70.2 (CH), 72.1 (CH), 72.9 (CH), 79.0 (C), 127.3 (CH), 128.1 (CH), 133.6 (CH), 140.1 (C), 198.2 (C); IR: 2900, 1600 cm^{-1}; M.p.: 105°C (litt.: (8) 108-109°C)

1-ferrocenyl-1-phenylprop-2-ynol 2: To a solution of lithium acetylide (0.690g, 7.5mmol) in 100mL of anhydrous THF, cooled to 0° (ice bath), 1 (0.435g, 1.5mmol in 100ml of anhydrous THF) was slowly added. The mixture was stirred for 2h30 then hydrolyzed with sat. aqueous NH_4Cl. The organic phase was washed with H_2O, dried with $MgSO_4$ and evaporated. The residue was rapidly chromatographied (silica gel, hexane/ether : 75/15) in order to avoid the formation of 6 by a Meyer-Schuster transposition) ; yield: 65%; ^{1}H-NMR (250 MHz): 2.7 (s, 1H), 3.1 (s, 1H), 4.1 (m, 1H), 4.2 (m, 2H), 4.2 (s, 5H), 4.4 (m, 1H), 7.2 (m, 3H), 7.5 (m, 2H); ^{13}C-NMR (62.8 MHz): 65.3 (CH), 68.5(CH), 68.7 (CH), 69.3 (CH), 71.4 (C), 71.4 (C), 73.3 (CH), 87.0 (C), 96.8 (C_4), 125.7 (CH), 127.9 (CH), 128.3 (CH), 143.9 (C); IR: 3560, 3300, 2100 cm^{-1}; M.p.: 56°C.

1,4-diferrocenyl-1,4-diphenylbut-2-yn-1,4-diol 3 (by-product): ^{1}H-NMR (250 MHz): 3.1 (s, 1H), 4.1 (s, 5H), 4.2 (m, 2H), 4.3 (m, 2H), 7.2 (m, 3H), 7.6 (d, J=7.0, 2H); ^{13}C-NMR (62.8 MHz): 65.3 (CH), 68.4 (CH), 68.7 (CH), 68.8 (CH), 69.1 (CH), 71.3 (C), 88.1 (C), 97.3 (C), 125.6 (CH), 127.8 (CH), 128.3 (CH), 144.4 (C); IR: 3540, 1210 cm^{-1}; M.p.:163.5°C.

3-ferrocenyl-3-phenylprop-2-enal 6 (by-product): ^{1}H-NMR (250 MHz): 4.1 (s, 5H), 4.2 (m, 2H), 4.3 (m, 2H), 6.5 (d, J=11, 1H), 7.4 (m, 5H), 9.1 (d, J=11, 1H); ^{13}C-NMR (62.8 MHz): 69.2 (CH),70.3 (C), 70.5 (CH), 72.0 (CH), 82.0 (C), 124.2 (CH), 128.2 (CH), 129.0 (CH), 129.5 (CH), 136.5 (C), 193.0 (CH); IR: 3100, 1650, 1210 cm^{-1}; M.p.: 102.1 °C.

3-ferrocenyl-3-phenyl-(3H)-naphtho(1,2-b)-pyran 4: A solution of the alcohol 2 (0.317g, 1 mmol) in minimum of CH_2Cl_2 was added to a solution of naphth-1-ol (0.576g, 4 mmol) in minimum of CH_2Cl_2. The mixture was stirred 7 days, until total consumption of alcohol 2. The organic phase was washed with H_2O, dried and evapored. The residue was chromatographied (silica gel, 100% hexane) : yield: 25%; ^{1}H-NMR (250 MHz): 4.0 (s, 5H), 4.1 (m, 3H), 4.4 (m, 1H), 6.2 (d, J=8.8, 1H), 6.6 (d, J=8.8, 1H), ^{13}C-NMR (62.8 MHz): 66.0 (CH), 66.5 (CH), 68.0 (CH), 69.1 (CH), 96.8 (C), 122.4 (CH), 128.0 (CH); IR: 3100, 1210 cm^{-1}; M. p.: 131°C; Anal. calc. for $C_{29}H_{22}OFe$: C 78.74, H 5.01; found: C 78.71, H: 5.04.

3-ferrocenyl-3-phenyl-(3H)-naphtho(2,1-b)-pyran 5: The same experimental process was used for 4 : yield: 75%; ^{1}H-NMR (250 MHz): 4.05 (m, 1H), 4.05 (s, 5H), 4.1 (m, 2H), 4.3 (m, 1H), 6.4 (d, J=10.1, 1H), 7.2 (d, J=10.1, 1H); ^{13}C-NMR (62.8 MHz): 66.6 (CH), 68.1 (CH), 69.1 (CH), 80.0 (C), 95.0 (C), 121.3 (CH), 123.5 (CH), 127.3 (CH); IR: 3100, 1210 cm^{-1}; M.p.: 149°C ; Anal. calc. for $C_{29}H_{22}OFe$: C 78.74, H 5.01; found: C 78.75, H: 5.04.

References:

(1)   R.S. Becker, U.S. Patent 3567605 (1971).

(2)   V. Pimienta, D. Lavabre, G. Levi, A. Samat, R. Guglielmetti and J. C. Micheau, J. Phys. Chem , 100, 4485 (1996).

(3)   M. Harfenist, E. Thom, J. Org. Chem., 37, 841 (1972).

(4)   B.Van Gemert, M. Bergomi, D. Knowles, Mol. Crist. Liq.Crist., 246 , 67 (1994).

(5)   J.L. Pozzo, Thèse en Science, Aix-Marseille II (1994).

(6)   T.J. Kealy and P. L. Pauson, Nature, London, 168, 1039 (1951).

(7)   R. W. McCabe, D. E. Parry, S. P. Sabari, J. Chem.Soc. Perkin Trans. I, 1023 (1993).

(8)   N. Weliky and E. S. Gould, J. Amer. Chem. Soc., 79, 2742 (1957).

(9)   M. Rosenblum, « Chemistry of Iron Group Metallocenes », Wiley, New York, 1965.

(10)   L. Brandsma, in « Preparative Acetylenic Chemistry, Study in Organic Chemistry », 2^e Ed. Elsevier, Amsterdam, 2, 1981, pp. 79-96.

(11)   I. Iwai, I. Ide, Chem. Pharm. Bull., 11, 1042 (1963).

(12)   J. Zsindely, H. Schmid, Helv.Chim. Acta., 51, 1510 (1968).

(13)   K. H. Meyer, K. S. Schuster, Chem. Ber., 55, 819 (1922).

(14)   D.R. Lide in « Handbook of Chemistry and Physics », Ed. 71, CRC Press, Boston, 1990, pp 8-36.

(15)   B. Luccioni-Houzé, M. Campredon, R. Guglielmetti, G. Giusti, Mol. Cryst. Liq. Cryst., 297, 161, (1997).