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Regioselective complexation in the 2*H*-chromene series and studies of their photochromic properties

Patrick Hannesschlager and Pierre Brun
Laboratoire de Synthèse Organique Sélective, GCOPL, ESA 6114, Université de la Méditerranée, 163 Av. de Luminy, 13288 Marseille Cedex 9, France

The regioselectivity of the complexation of chromenes with tricarbonyl(trispyridine)chromium [$Cr(CO)_3Py_3$] can be controlled by the addition of $BF_3{\cdot}Et_2O$ boron trifluoride etherate. Depending on the molar ratio of the Lewis acid, different complexes can be prepared. The spectrokinetic properties of the so-formed complexes were studied and it was shown that the thermal bleaching constants are either more or less reduced, depending on the position of the chromium tricarbonyl moiety. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: 2*H*-chromene; photochromism; tricarbonyl chromium complexes; tricarbonyl(trispyridine)chromium

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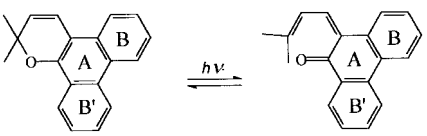
INTRODUCTION

2*H*-Chromenes and benzochromenes[1] are known as photochromic compounds. Under UV irradiation, cleavage of the C—O bond leads to coloured open forms (Fig. 1), which can cyclize back to the closed form when irradiation is stopped. In previous studies we have shown that the complexation of these compounds with a chromium tricarbonyl moiety on the A, B or B′ aromatic ring stabilizes the open forms and thus reduces the thermal bleaching kinetic constant (Eqn [1]).[2,3]



[1]

In this work we present regioselective syntheses of the same type of substrates in which the chromium tricarbonyl group is located on the C or D rings (Fig. 1). Their photochromic properties are also described.

EXPERIMENTAL

All the reactions were performed under nitrogen, with degassed solvents, in order to avoid decomposition of the chromium complexes, which are known to be very sensitive to oxygen, especially in solution. Infrared spectra were recorded on a Perkin-Elmer 297 spectrometer in Nujol suspension. ^1H and ^{13}C NMR spectra were recorded on a Bruker Ac 250 spectrometer. All the complexes

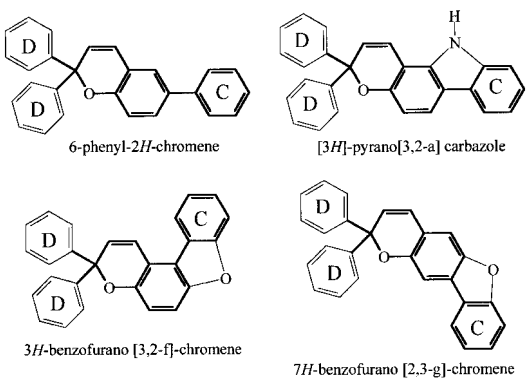


Figure 1 General structures of the chromenes used in this work.

* Correspondence to: Pierre Brun, Laboratoire de Synthèse Organique Sélective, GCOPL, ESA 6114, Université de la Méditerranée, 163 Av. de Luminy, 13288 Marseille Cedex 9, France.
E-mail: brun@chimlum.univ-mrs.fr

Table 1 Yields of the different complexes synthesized

Entry	Substrate	R	*R′*	*R″*	BF_3 (equiv.)	Yield (%)	Product
1	**1**	[5,6-*b*]Indolo	Me	Me	3	17	**1C**
2	**2**	[5,6-*b*]Indolo	Ph	Me	3	22	**2C**
3	**2**	[5,6-*b*]Indolo	Ph	Me	5	19	**2D**
4	**3**	[5,6-*b*]Indolo	Ph	Ph	3	21	**3C**
5	**3**	[5,6-*b*]Indolo	Ph	Ph	5	20	**3D**
6	**4**	[3,2-*f*]Benzofurano	Ph	Ph	3	0	
7	**5**	[2,3-*g*]Benzofurano	Ph	Ph	3	0	
8	**4**	[3,2-*f*]Benzofurano	Ph	Ph	5	15	**4D**
9	**5**	[2,3-*g*]Benzofurano	Ph	Ph	5	14	**5D**
10	**6**	6-Phenyl	Ph	Me	3	23	**6C**
11	**7**	H	Ph	Ph	3	22	**7D**

were characterized by oxidative decomplexation (I_2) and by comparison with the known parent chromenes. The position of the chromium carbonyl moiety was determined by ^1H and ^{13}C NMR

Spectrokinetic studies have been realized using the method described previously.[2] Depending on the substrate, one or two bleaching kinetic constants could be determined. This reflects the fact that the open forms can exist under different relative configurations (*cis*,*cis*,*cis*; *cis*,*trans*,*cis*; *cis*,*trans*,*trans*,etc.), whose back-closure kinetics are different. It must noted that the *cis*,*cis*,*cis* form might be trapped by complexation with iron tricarbonyl but we did not tried to do it as it is known that this form is a very minor one.

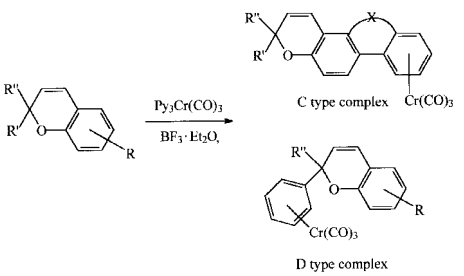
All the starting chromenes were prepared using classical methods.[4,5]

Preparation of the different complexes

Tricarbonyl(η^6-methoxybenzene)chromium and tricarbonyl(trispyridine)chromium were prepared according to the literature.[6]

Complexation of 2H-chromenes

To a 150 ml Schlenck tube containing freshly prepared tricarbonyl(trispyridine)chromium, a nitrogen-saturated solution of chromene (1.75 mmol) in diethyl ether (10 ml) was transferred via a cannula. Boron trifluoride etherate ($BF_3{\cdot}Et_2O$) was then added to the reaction mixture, which turned immediately orange–yellow. After 2 h, nitrogen-saturated water (15 ml) was added to the reaction medium, which was extracted with diethyl ether. The organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to afford a solid which was purified by column chromatography (pentane–diethyl ether mixture). All the complexes synthesized gave satisfactory elemental analysis or were characterized by oxidative decomplexation (I_2) and comparison with the parent 2*H*-chromenes. The results of the syntheses are reported in Table 1, and Eqn [2] depicts the reactions and types of complexes obtained.



[2]

Tricarbonyl(3,3-dimethyl-3H-pyrano[3,2-a]-η^6-carbazole)chromium (1C)

M.p. 135 °C (dec.). IR ($CHCl_3$, cm^{-1}); 1970, 1905 (ν CO). ^1H NMR ($CDCl_3$, ppm); δ = 1.38 (s, 6H); 5.42 (s, 1H); 5.63 (m, 2H); 5.92 (s, 1H); 6.02 (s, 1H); 6.51 (d, J = 8.0 Hz, 1H); 7.08 (m, 2H); 7.32 (d, J = 8.0 Hz, 1H); 7.65 (d, J = 8.4 Hz, 1H); 7.83 (d, J = 7.8 Hz, 1H); 10.30 (s, 1H). ^{13}C NMR ($CDCl_3$, ppm); δ = 27.34 (q); 27.35 (q); 73.2 (d); 76.6 (s); 84.8 (d); 86.2 (s); 86.4 (d); 88.8 (d).

Tricarbonyl(3-methyl-3-phenyl-3H-pyrano[3,2-a]-η^6-carbazole)chromium (2C)

M.p. 147 °C (dec.). IR ($CHCl_3$, cm^{-1}); 1955, 1880

(ν CO). ^{1}H NMR ($CDCl_3$, ppm); δ = 1.65 (s, 3H); 5.41 (s, 1H); 5.60 (s, 1H); 5.87 (s, 2H); 6.02 (s, 1H); 6.67 (m, 2H); 7.17 (m, 3H); 7.71 (m, 3H); 10.10 (s, 1H).

Tricarbonyl(3,3-diphenyl-3H-pyrano[3,2-a]-η^6-carbazole)chromium (3C)
M.p. 205 °C (dec.). IR. ($CHCl_3$, cm^{-1}); 1955, 1880 (ν CO). ^{1}H NMR ($CDCl_3$, ppm); δ = 5.43 (s, 1H); 5.64 (s, 1H); 5.85 (s, 1H); 6.00 (s, 1H); 6.38 (d, J = 9 Hz, 1H); 6.60 (d, J = 9 Hz, 1H); 7.01 (m, 2H); 7.46 (m, 6H); 7.63 (s, 2H); 7.97 (m, 1H); 10.05 (s, 1H). ^{13}C NMR ($CDCl_3$, ppm); δ = 61.3 (d); 74.5 (d); 78.7 (s); 85.0 (d); 86.8 (s); 86.9 (d); 89.3 (d); 106.8 (d); 113.9 (s); 115.3 (d); 116.9 (d); 122.7 (d); 122.7 (d); 122.8 (d); 122.8 (d); 122.8 (d); 123.4 (d); 123.6 (d); 123.9 (d); 123.9 (d); 124.2 (d); 124.2 (d); 124.5 (d); 134.0 (s); 136.2 (s); 141.1 (s); 141.4 (s); 148.5 (s); 231 (s); 231 (s); 231 (s).

Tricarbonyl(2-methyl-2-phenyl-6-η^6-phenyl-2H-chromene)chromium (6C)
M.p. 99.5 °C. IR ($CHCl_3$, cm^{-1}): 1975, 1900 (ν CO). ^{1}H NMR ($CDCl_3$, ppm): δ = 1.77 (s, 3H); 5.29 (s, 2H); 5.40 (s, 1H); 5.59 (s, 2H); 5.96 (s, 1H); 6.48 (s, 1H); 7.25 (m, 8H).

Tricarbonyl(3-methyl-3-η^6-phenyl-3H-pyrano[3,2-a]-carbazole)chromium (2D)
M.p. 166 °C (dec.). IR ($CHCl_3$, cm^{-1}); 1970, 1900 (ν CO). ^{1}H NMR ($CDCl_3$, ppm): δ = 1.58 (s, 3H); 5.34 (m, 2H); 5.52 (d, J = 6.34 Hz, 1H); 5.72 (m, 2H); 6.60 (d, J = 9.8 Hz, 1H); 6.75 (d, J = 8.4 Hz, 1H); 7.15 (m, 4H); 7.40 (s, 1H); 7.72 (d, J = 7.4 Hz, 1H).

Tricarbonyl(3-phenyl-3-η^6-phenyl-3H-pyrano[3,2-a]carbazole)chromium (3D)
M.p. 213 °C (dec.). IR ($CHCl_3$, cm^{-1}): 1970, 1900 (ν CO). ^{1}H NMR ($CDCl_3$, ppm): δ = 5.34 (m, 2H); 5.57 (d, J = 6.2 Hz, 1H); 5.72 (t, J = 6.05 Hz, 2H); 6.37 (d, J = 9.87 Hz, 1H); 6.82 (d, J = 8.35 Hz, 1H); 7.00 (d, J = 7.18 Hz, 1H); 7.11 (m, 7H); 7.60 (d, J = 7.28 Hz, 2H); 7.80 (s, 1H); 7.83 (d, J = 7.70 Hz, 1H). ^{13}C NMR ($CDCl_3$, ppm): δ = 81.7 (s); 83.7 (s); 91.5 (d); 91.6 (d); 94.8 (d); 95.1 (d); 95.9 (d); 109.7 (d); 111.4 (d); 117.2 (s); 120.0 (d); 120.3 (d); 121.5 (s); 121.8 (d); 124.2 (s); 125.4 (d); 126.3 (d); 127.5 (d); 127.5 (d); 128.1 (d); 128.8 (d); 128.8 (d); 140.5 (s); 144.5 (s); 146.5 (s); 151.5 (s); 230.1 (s); 230.1 (s); 230.1 (s).

Tricarbonyl(3-phenyl-3-η^6-phenyl-3H-benzofurano[3,2-f]chromene)chromium (4D)
M.p. 137 °C (dec.). IR ($CHCl_3$, cm^{-1}): 1965, 1880 (ν CO). ^{1}H NMR ($CDCl_3$, ppm): δ = 5.40 (m, 2H); 5.61 (m, 1H); 5.75 (m, 2H); 6.38 (d, J = 9.8 Hz, 1H); 7.05 (d, J = 8.5 Hz, 1H); 7.23 (m, 6H); 7.34 (m, 4H); 7.88 (d, J = 7.3 Hz, 1H).

Tricarbonyl(7-phenyl-7-η^6-phenyl-7H-benzofurano[2,3-g]chromene)chromium (5D)
M.p. 178 °C (dec.). IR ($CHCl_3$, cm^{-1}): 1965, 1890 (ν CO). ^{1}H NMR ($CDCl_3$, ppm): δ = 5.32 (m, 2H); 5.53 (m, 1H); 5.68 (m, 2H); 6.31 (d, J = 9.8 Hz, 1H); 6.71 (d, J = 9.7 Hz, 1H); 7.29 (s, 1H); 7.19 (s, 1H); 7.26 (m, 6H); 7.46 (m, 2H); 7.82 (d, J = 7.5 Hz, 1H).

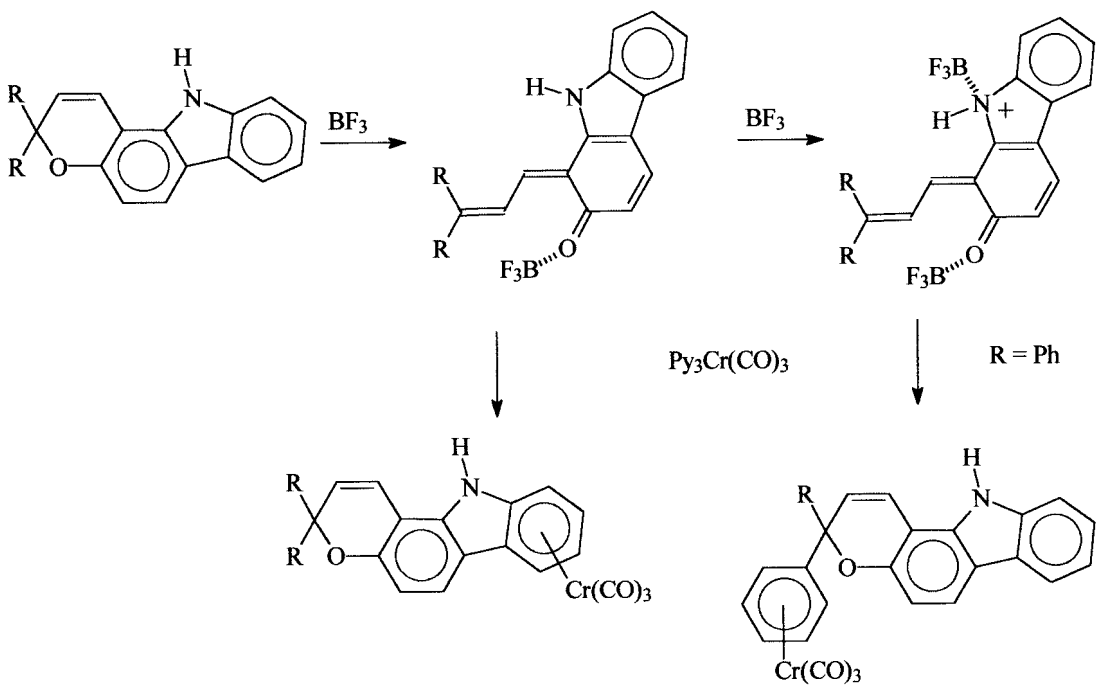
Tricarbonyl(2-phenyl-2-η^6-phenyl-2H-chromene)chromium (7D)
M.p. 123 °C (dec.). IR (Nujol, cm^{-1}): 1975, 1890 (ν CO). ^{1}H NMR (acetone-d_6, ppm): δ = 5.24 (m, 2H); 5.49 (m, 1H); 5.60 (m, 2H); 6.04 (d, J = 9.8 Hz, 1H); 6.24 (d, J = 9.8 Hz, 1H); 6.66 (m, 1H); 7.32 (m, 6H). ^{13}C NMR (acetone-d_6, ppm): δ = 81.2 (s); 91.47 (d); 91.59 (d); 94.9 (d); 95.2 (d); 96.2 (d); 116.9 (s); 117.3 (d); 122.6 (d); 124.8 (d); 127.32 (d); 127.6 (d); 128.2 (d); 128.9 (d); 129.0 (d); 129.0 (d); 129.2 (d); 130.6 (d); 144.2 (s); 152.8 (s); 233 (s); 233(s); 233 (s).

RESULTS AND DISCUSSION

We observe that complexation is totally regioselective. The yields are low but were not optimized as we were mainly interested in the photochromic behaviour of these compounds. However, the yields indicated in Table 1 correspond to the conversion ratio, as all of the chromenes not complexed can be totally recovered.

The regioselectivity for the heteroatomic chromenes (entries 1 to 7) depends on the concentration of the Lewis acid. This selectivity can be explained by the mechanism shown in Scheme 1.

In the presence of $BF_3{\cdot}Et_2O$, depending on the stoichiometry of the Lewis acid, two pathways can be observed. With 3 equiv. of $BF_3{\cdot}Et_2O$, the oxygen of the pyran ring is complexed. This complexation induces pyran ring opening. Complexation with chromium tricarbonyl then occurs on the C ring (entries 1, 2, 4 and 10). In the case of compounds **4** and **5** (entries 6 and 7), no complex was formed. When the amount of $BF_3{\cdot}Et_2O$ is increased to



Scheme 1 Mechanism proposed to explain the regioselectivity of the complexation.

5 equiv., the oxygen of the pyran ring is still complexed but this is also the case for the oxygen or nitrogen of the benzofurano or indolo moiety of the system. That complexation results in the presence of a positive charge α- to the C ring and thus induces a deactivation of that ring towards complexation with the $Cr(CO)_3$ moiety. Complexation occurs in this case on the D ring (entries 3, 5, 8 and 9).

That explanation is supported by the behaviour of compound **6** in which there is no heteroatom α to the C aromatic ring. In the presence of 3 or 5 equiv. of $BF_3{\cdot}Et_2O$ complexation occurs exclusively on the C ring.

Table 2 Spectrokinetic properties of the complexed chromenes.

Entry	Compound	Absorption range (nm)	Kinetic constants (s^{-1})
1	**1**	360–440	1.7×10^{-3}; 2×10^{-5}
2	**1C**	360–500	10^{-4}
3	**2**	360–480	0.27; 5×10^{-4}
4	**2C**	430–500	3×10^{-4}
5	**2D**	380–650	1.3×10^{-2}; 2×10^{-4}
6	**3**	360–490	0.12; 3×10^{-4}
7	**3C**	360–500	1.7×10^{-2}; 10^{-4}
8	**3D**	380–650	1.7×10^{-2}; 1.7×10^{-3}
9	**4**	370–620	0.7; 7×10^{-4}
10	**4D**	380–600	9×10^{-2}; 2×10^{-4}
11	**5**	370–640	1.5; 7×10^{-4}
12	**5D**	380–580	0.2; 1.3×10^{-3}
13	**6**	No photochromic properties in our experimental conditions	
14	**6C**	360–520	3×10^{-4}
15	**7**	360–560	0.5; 3×10^{-4}
16	**7D**	360–510	5×10^{-4}

Spectrokinetic studies of complexes

In Table 2, we summarize our results obtained in acetonitrile. In this solvent fewer degradation reactions are observed than in ethanol or toluene.

Complexation on the C ring does not result in a significant shift of the open-form absorption wavelength compared with that of the parent compound. However, the upper limit of the absorption band is slightly shifted to longer wavelengths (entries 1–2, 3–4 and 6–7). For D type complexes the situation is not as clear cut as for **2D** and **3D**, where the shifts are important (150 nm), while for **4D**, **5D** and **7D** (entries 9–10, 11–12 and 15–16) the bandwidth is smaller and the upper limit is displaced towards lower wavelengths.

As for chromenes complexed on the A or B rings, it can be seen that the first kinetic constant has disappeared or is very small as compared with the first kinetic constant, of the parent compounds. This results in an overall decrease of the thermal bleaching of the complexed chromenes. This enables the observation of photochromic properties for compound **6C** which were not detectable on the parent chromene **6**.

When the second kinetic constants are compared, those of the complexed forms are slightly higher than those of the parent compounds. It must be noted that the observed changes are of the same order of magnitude for either C or D complexes. However the C type complexes are very sensitive compounds and degradation occurs very rapidly under UV irradiation

CONCLUSION

In this and previous papers, we have shown that regioselective complexation of 2*H*-chromene derivatives with a chromium tricarbonyl moiety can be achieved on A, B, C or D rings. The effect of this complexation is a stabilization of the open forms resulting from UV irradiation and thus a decrease of the thermal bleaching kinetic constants. This influence changes with the distance between the chromium and the pyran ring.

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