APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **14**, 371–375 (2000)

Synthesis and photochromic properties of tricarbonylchromium complexes of 2*H*-η^6-benzochromenes

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

Although in the 2*H*-chromene (benzopyran) series complexation with tricarbonylchromium, under thermal conditions, is totally regioselective, in the naphthopyran series the same reaction cannot be observed. We show here that with tricarbonyl(trispyridine)chromium as complexing agent, in the presence of Lewis acid, complexation of naphthopyrans can be achieved and is totally regioselective. The complexes formed are photochromic compounds, and their thermal bleaching kinetic constants are reduced as compared with the non-complexed homologous compound. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: benzo-2*H*-chromene; naphthopyran; photochromism; tricarbonylchromium complexes; tricarbonyl(trispyridine)chromium.

Received 30 June 1999; accepted 25 November 1999

INTRODUCTION

2*H*-Chromenes and their derivatives are photochromic compounds[1] owing to their ability to undergo a photo-induced reversible change of color. Previously, we have shown that complexation of the ring of the basic framework with tricarbonylchromium is totally regioselective under thermal conditions.[2] Complexation reduces the thermal bleaching kinetic constant. For naphthopyrans the complexes were not isolated even when different complexing agents (Table 1) were used with thermal activation. These complexes are formed, but they are highly unstable. Indeed, with the dimethyl compound, we have observed some traces of complexed benzochromene, but during the purification phase the complex was totally degraded.

In fact, because of the thermal conditions, a thermochromic process occurs, leading to the open forms of these complexes, whose stabilities are very low because the π orbitals implicated in the coordination with chromium are modified during the ring-opening process.[3]

However, the electron-withdrawing properties of the tricarbonylchromium entity, and the photochromic properties of naphthopyrans, made it interesting to study the photochromism of the η^6-naphthopyran–tricarbonylchromium complex.

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.

The spectrokinetic studies were realized using

Table 1 Reaction of 2-R′-2-R″-2*H*-benzo[5,6] chromenes (R′, R″ = Me and/or Ph) with different complexing agents

Complexing agent	*T*(°C)	Yield (%)
$Cr(CO)_6$	131	0
$(NH_3)_3Cr(CO)_3$	100	0
η_6-NaphthaleneCr$(CO)_3$	70	0

---

* 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.

the continuous irradiation technique described in a previous paper.[2]

Preparation of starting chromenes

The 2*H*-benzochromenes were prepared by condensation of the appropriate naphthol with propargylic alcohol in presence of *p*-toluenesulfonic acid[4] in methylene chloride at room temperature. Another method involved reaction of the naphthol with titanium ethoxide [$Ti(OEt)_4$] in refluxing toluene.[5] The titanium complex formed is then reacted with acrolein derivatives in refluxing toluene. All the compounds were purified by column chromatography using pentane–ether gradients as eluents.

Preparation of the complexes[6]

Tricarbonyl(η^6-methoxybenzene)chromium

In a Stroheimer apparatus, under an inert atmosphere, 6.16 g of hexacarbonyl chromium was added to 40 g of methoxybenzene diluted into 120 ml of dibutyl ether/tetrahydrofuran mixture (10:2, v/v). The reaction medium was refluxed for 48 h, filtered on Celite, washed with diethyl ether and the solvents were removed under reduced pressure, the temperature not exceeding 50 °C. The yellow crystals obtained were washed quickly with cold pentane and dried under vacuum. The crystalline product was pure enough to be used without further purification: m.p. 84 °C. ^{1}H NMR (acetone-d_6): $\delta = 3.53$ (s, 3H), 4.89 (s, 1H), 5.19 (s, 2H), 5.59 ppm (s, 2H). ^{13}C NMR (acetone-d_6): $\delta = 55.9$ (q), 79.9 (d), 79.9 (d), 87.1 (d), 97.1 (d), 97.1 (d), 144.7 (s), 234 (s), 234 (s), 234 ppm (s).

Tricarbonyl(trispyridine)chromium

In a 150-ml Schlenck tube charged with 0.48 g of tricarbonyl(η^6-methoxybenzene)chromium, under a nitrogen atmosphere, 8 ml of nitrogen-saturated pyridine was added via a cannula. The resulting yellow solution was heated at 110 °C for 3 h, whereupon it turned dark red. The solution was allowed to cool in an ice bath and cold nitrogen saturated diethyl ether was added until red crystals appeared. These were filtered off under nitrogen, washed with cold saturated diethyl ether (3 × 5 ml) and dried under vacuum. Since this complex was unstable it was kept under a nitrogen atmosphere and used directly without purification in the same flask.

Complexation of 2*H*-benzochromenes

To a 150-ml Schlenck tube containing freshly prepared tricarbonyl(trispyridine)chromium, a nitrogen-saturated solution of the chromene (1.75 mmol) in diethyl ether (10 ml) was transferred via a cannula. Boron trifluoride–diethyl ether (0.7 ml, 5.6 mmol) was then added to the reaction mixture, which immediately turned orange–yellow. The reaction was stirred for 2 h and then nitrogen-saturated water (15 ml) was added. The aqueous layer was extract with diethyl ether, dried on magnesium sulfate 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 analyses or were characterized by oxidative decomplexation (I_2) and comparison with the parent 2*H*-benzochromenes.

RESULTS AND DISCUSSION

Complexation reactions

Results are reported in Fig. 1 and Table 2, and the products are described below.

The position of the tricarbonyl chromium moiety has been established by ^{1}H and ^{13}C NMR. For compounds **1b**, **2b** and **3b** position of the tricarbonylchromium moiety was verified by X-ray crystallography.[7–9]

The low yields can be explained by the fact that

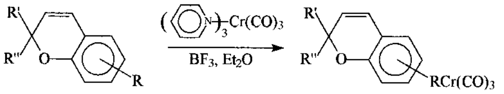

Figure 1 Chromium tricarbonyl complexation of 2*H*-benzochromenes. R, R′ and R″ are specified for substrates **1**–**6** and products **1b**–**6b** in Table 2.

Table 2 Complexation of various 2*H*-benzochromenes with tricarbonyl(trispyridine)chromium

Substrate	Annelation, R	R′	R″	Yield (%)	Product
1	[5,6]Benzo	Me	Me	25	**1b**
2	[5,6]Benzo	Ph	Me	23	**2b**
3	[5,6]Benzo	Ph	Ph	26	**3b**
4	[7,8]Benzo	Me	Me	24	**4b**
5	[7,8]Benzo	Ph	Me	23	**5b**
6	[7,8]Benzo	Ph	Ph	26	**6b**

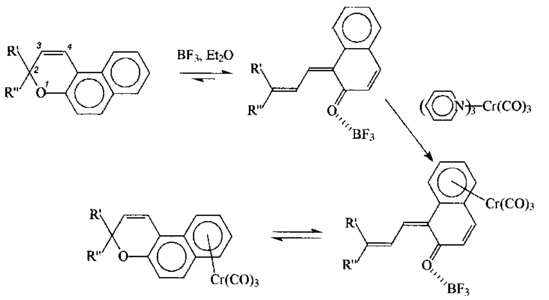

Figure 2 Mechanism proposed for the complexation of benzochromenes with tricarbonyl(trispyridine)chromium.

the complexing agent had to be synthesized and used without isolation and thus its purity could not be checked. In fact the yields indicated in Table 2 correspond to the conversion ratio, as all of the uncomplexed chromene can be totally recovered.

We observed that the reaction was totally regioselective, and contrary to results observed under thermal activation, complexation occurred exclusively on the aromatic ring adjacent to the chromene moiety. This fact can be explained by the mechanism proposed in fig. 2.

The Lewis acid stabilizes the open form and displaces the equilibrium in favor of the open forms. This phenomenon has been verified by comparison of the ^{13}C NMR spectra of compound **1** with and without boron trifluoride. In the presence of the Lewis acid, a peak appears at 134 ppm corresponding to an *sp*^{2}-hybridized C-2 in the open form. Thus, the complexation reaction is automatically directed onto the benzo condensed ring.

Tricarbonyl(2,2-dimethyl-2*H*-η^6-benzo[5,6]chromene)chromium (1b)

M.p.: decomposition at 137 °C. IR (Nujol): 1940, 1880 cm^{-1} (ν_{CO}). ^{1}H NMR: (acetone-d$_6$) $\delta = 1.40$ (s, 3H), 1.41 (s, 3H), 5.28 (dd, $J = 6.39$, 6.32 Hz, 1H), 5.55 (dd, $J = 6.61$, 6.33 Hz, 1H), 5.65 (d, $J = 9.99$ Hz, 1H), 6.06 (dd, $J = 6.61$, 6.29 Hz, 2H), 6.65 (d, $J = 9.97$ Hz, 1H), 6.90 (d, $J = 9.08$ Hz, 1H), 7.31 ppm (d, $J = 9.08$ Hz, 1H). ^{13}C NMR (acetone-d$_6$): $\delta = 27.4$ (q), 28.0 (q), 77.2 (s), 84.0 (d), 90.2 (d), 93.0 (d), 93.4 (d), 99.3 (s), 106.5 (s), 112.6 (s), 116.9 (d), 122.5 (d), 130.3 (d), 131.0 (d), 153.3 (d), 236 (s), 236 (s), 236 ppm (s).

Tricarbonyl(2-methyl-2-phenyl-2*H*-η^6-benzo[5,6]chromene)chromium (2b)

M.p.: decomposition at 139.5 °C. IR ($CHCl_3$) 1970, 1905 cm^{-1} (ν_{CO}). ^{1}H NMR: ($CDCl_3$): $\delta = 1.76$ (s, 3H), 5.28 (m, 1H), 5.50 (m, 1H), 6.02 (m, 2H), 6.81 (d, $J = 9.95$ Hz, 1H), 7.01 (d, $J = 9.08$ Hz, 1H), 7.21 (m, 5H), 7.43 ppm (d, $J = 7.1$ Hz, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 29.0$ (q), 79.8 (s), 84.2 (d), 90.4 (d), 92.9 (d), 93.2 (d), 99.7 (s), 105.8 (s), 113.1 (s), 117.5 (d), 122.2 (d), 125.3 (d), 125.3 (d), 127.8 (d), 128.5 (d), 128.5 (d), 129.3 (d), 137.3 (d), 145.3 (s), 153.1 (s), 231 (s), 231 (s), 231 ppm (s).

Tricarbonyl(2,2-diphenyl-2*H*-η^6-benzo[5,6]chromene)chromium (3b)

M.p.: degradation at 141 °C. IR (Nujol) 1960, 1870 cm^{-1} (ν_{CO}). ^{1}H NMR: ($CDCl_3$): $\delta = 5.26$ (dd, $J = 6.15$, 6.23 Hz, 1H), 5.48 (dd, $J = 6.10$, 5.98 Hz, 1H), 5.97 (d, $J = 6.63$ Hz, 1H), 6.07 (d, $J = 6.87$ Hz, 1H), 6.17 (t, $J = 10.0$ Hz, 2H), 6.96 (d, $J = 10.0$ Hz, 1H), 7.02 (d, $J = 9.1$ Hz, 1H), 7.24 (m, 7H), 7.60 (m, 2H), 7.87 ppm (d, $J = 8.34$ Hz, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 83.4$ (s), 83.8 (d), 90.2 (d), 92.3 (d), 92.8 (d), 99.6 (s), 105.4 (s), 113.1 (s), 117.7 (d), 118.3 (???.?), 119.5 (d), 121.3 (d), 122.0 (d), 123.6 (d), 126.8 (d), 127.0 (d), 127.1 (d), 127.7 (d), 128.2 (d), 128.3 (d), 129.8 (d), 131.3 (d), 143.9 (s), 144.8 (s), 153.2 (s), 216 (s), 216 (s), 216 ppm (s).

Tricarbonyl(2,2-dimethyl-2*H*-η^6-benzo[7,8]chromene)chromium (4b)

M.p.: decomposition at 131 °C. IR (Nujol) 1940, 1880 cm^{-1} (ν_{CO}). ^{1}H NMR: ($CDCl_3$): $\delta = 1.50$ (s, 6H), 5.26 (s, 1H), 5.61 (m, 2H), 6.10 (s, 1H), 6.48 (d, $J = 9.8$ Hz, 1H), 6.62 (s, 1H), 7.3 ppm (m, 2H). 13C NMR ($CDCl_3$): $\delta = 27.8$ (q), 28.3 (q), 77.5 (s), 83.2 (d), 90.7 (d), 93.1 (d), 93.7 (d), 99.8 (s), 105.8 (s), 115.7 (s), 122.2 (d), 124.7 (d), 128.2 (d), 129.9 (d), 149.7 (s), 231 (s), 231 (s), 231 ppm (s).

Tricarbonyl(2-methyl-2-phenyl-2*H*-η^6-benzo[7,8]chromene)chromium (5b)

M.p.: decomposition at 134 °C. IR ($CHCl_3$) 1970, 1905 cm^{-1} (ν_{CO}). ^{1}H NMR ($CDCl_3$): $\delta = 1.93$ (s, 3H), 5.32 (s, 1H), 5.60 (s, 1H), 6.12 (m, 3H), 6.70 (d, $J = 9.7$ Hz, 1H), 7.31 (d, $J = 8$ Hz, 1H), 7.45 (m, 5H), 8.65 ppm (d, $J = 8.2$ Hz, 1H).

Tricarbonyl(2,2-diphenyl-2*H*-η^6-benzo[7,8]chromene)chromium (6b)

M.p.: decomposition at 141 °C. IR ($CHCl_3$) 1970, 1885 cm^{-1} (ν_{CO}). ^{1}H NMR: ($CDCl_3$): $\delta = 5.21$ (s, 1H), 5.52 (S, 1H), 6.03 (S, 2H), 6.15 (d, $J = 9.7$ Hz, 1H), 6.70 (d, $J = 9.8$ Hz, 1H), 7.12 (d, $J = 8.12$ Hz, 1H), 7.40 (m, 10H), 8.30 ppm (d, $J = 7.8$ Hz, 1H).

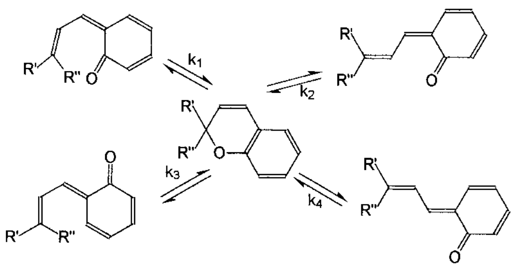

Figure 3 UV-induced ring-opening of 2*H*-chromenes into cisoid and transoid forms.

Spectrokinetic studies of complexes

The photochromism is explained by the formation under irradiation, of some ring-opened forms differing from each other in the unsaturated chain configuration (Fig. 3)

During the ring closure, each opened form has a particular closure kinetic rate constant, and with available technology, some of them are so fast that they are not detectable.

The results of our studies are reported in Table 3 and were obtained using acetonitrile as solvent. When toluene or ethanol was used, fast decomposition of the complexes was observed.

Depending on the structure of the substrate, either one or two rate constants could be determined. It must be noted that under the conditions we used, very fast thermal bleaching rate constants could not be calculated. Experimentally, we observed that the complexation did not induce a significant shift in the absorption wavelength of the ring-opened form in any of the three solvents used. The positive solvatochromism observed indicated that the open forms were in a quinonic stabilized form, as observed for the uncomplexed chromenes.

For complexes **2b**, **3b** and **4b** the first rate constants were identical to those determined for the uncomplexed forms. This may reflect the fact that some decomplexation occurred very rapidly under irradiation, and that the observed kinetic constants were in fact those for these uncomplexed chromenes. This was no longer the case, however, for the second rate constants, which indicated that thermal bleaching was very slow. It must be noted that a photostationary state could not be observed experimentally in our conditions for this type of compound.

For compound **6** and **6b** we observed that the thermal bleaching rate constant was very low. Complexation did not induce any modification to the absorption wavelength. However, we observed that, under irradiation, complex **6b** exhibited a much more intense coloration than the homologous compound **6**.

The differences observed for the non-complexed compounds between the [5,6]chromene series (**1**, **2** and **3**) and the [7,8]chromene series (**4**, **5** and **6**) were still present after complexation (**1b**, **2b**, **3b** and **4b**, **5b**, **6b**).

When the kinetic parameters of the complexed forms are compared with those described previously for tricarbonylchromium chromenes it can be noted that, in all cases, complexation induces the same type of effect, i.e. a decrease in the thermal bleaching rate constant.

Table 3 Spectrokinetic studies of complexes in acetonitrile

Compound	Absorption range (nm)	Rate constants (s^{-1})		
1	380–460	3.5		5×10^{-4}
1b	380–460		2×10^{-4}	
2	380–500	0.16		4×10^{-4}
2b	380–470		8×10^{-4}	
3	360–520	5.6×10^{-2}		1.1×10^{-3}
3b	370–470	7×10^{-2}		1×10^{-3}
4	470–535	1.6×10^{-2}		1×10^{-3}
4b	370–520	1.6×10^{-2}		7×10^{-4}
5	370–570	7.8×10^{-3}		1×10^{-3}
5b	370–540	1.1×10^{-2}		1×10^{-4}
6	370–600		5×10^{-4}	
6b	370–575		5×10^{-4}	

CONCLUSION

We have found a totally regioselective method for benzochromene complexation with the tricarbonylchromium moiety. The complexation of different 2*H*-benzochromenes by chromium tricarbonyl on the benzo ring does not induce the appearance of any important modifications of the photochromic properties of these compounds. The main effect is, as observed for complexed chromenes, a stabilization of the ring-opened form(s) due to a decrease in the ring-closure rate constant.

REFERENCES

1. Becker RS, Mich J. *J. Am. Chem. Soc.* 1966; **88**: 5931.
2. Hannesschlager P, Brun P. *Appl. Organomet. Chem.* 1999; **13**: 1.
3. Davies R, Kane Maguire LAP. ‘Chromium compounds with η^2–η^8 carbon ligands’. In *Comprehensive Organometallic Chemistry*, Wilkinson G, Stone FGA, Abel EW, (eds), Pergamon, New York, 1982; 1001–1051.
4. Van Gemert B, Bergoni M, Knowles D. *Mol. Cryst. Liq. Cryst.* 1994; **146**: 67.
5. Sartori G, Casiraghi G, Bolzoni L, Casnati G. *J. Org. Chem.* 1979; **44**: 803.
6. Perez-Encabo A, Perrio S, Slwin AMZ, Thomas SE, Wierzchleyski AT, Williams DJ. *J. Chem. Soc., Perkin Trans. 1* 1994; 629.
7. Hannesschlager P, Brun P, Pèpe G. *Acta Crystallogr. Sect. C* 1998; **54**: 221.
8. Hannesschlager P, Brun P, Pèpe G. *Acta Crystallogr., Sect. C* 1999; **55**: 200.
9. Hannesschlager P, Brun P, Pèpe G. *Acta Crystallogr., Sect. C* 2000; **56**, in press.