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Photochromic Properties of η^6-2*H*-Chromene Chromium Tricarbonyl Complexes

Patrick Hannesschlager and Pierre Brun*
Laboratoire de Synthèse Organique Sélective, GCOPL (Associé au CNRS), Université de la Méditerranée, 163 Av. de Luminy, 13288 Marseille, Cedex 9, France

In the 2*H*-chromene series, complexation of the aromatic ring with chromium tricarbonyl, under thermal conditions, is totally regioselective even when aromatic substituents are introduced on the pyran ring. The complexation stabilizes the open form of these photochromic compounds and reduces the thermal bleaching kinetic constant.

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

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INTRODUCTION

Photochromic compounds are very interesting substances owing to their ability to undergo a photo-induced reversible change of colour. Usually they are faintly coloured but, under UV irradiation or direct sunlight, assume an intense colour and return to the initial state when irradiation is stopped.

Many studies have been devoted to this class of compounds since photochromism was discovered in 1952[1]. Many applications were found,[2,3] the principal one being in the field of light-sensitive sunglasses. This application was the first to be used on an industrial scale. Two families of photochromic compounds are actually used, spiro-oxazines and 2*H*-chromenes.

In order to improve the photochromic properties and particularly the absorption wavelength of the open form and the thermal bleaching rate constant, structural modifications of the basic molecule and/or different substituents (electron-withdrawing or electron-donating groups) in different positions were introduced.[4] Recently, the introduction of an organometallic group as a substituent was reported and the synthesis and the photochromic properties of chromium tricarbonyl complexes of spiropyrans were described. The introduction of a chromium tricarbonyl group into the organic molecule induces modifications of the electronic distribution, and so modifies the reactivity and the substrate's properties. In the case of spiropyran, complexation[5,6] stabilizes the open form, and so reduces the thermal bleaching kinetic constant. When applied to fulgides,[7] complexation inhibits the photochromic properties.

We report here the results we have obtained with 2*H*-chromene-chromium tricarbonyl complexes.

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 when they are in solution.[8] Infrared spectra were recorded for Nujol suspensions on a Perkin-Elmer 297 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer.

The spectrokinetic studies were realized with a Beckman DU 7005 UV spectrometer, modified as described and used by Luccioni-Houzé *et al.*[9], with the solvents generally used for such experiments: toluene, acetonitrile and ethanol. In these solvents the maximum absorption wavelength of the open form under UV irradiation was first determined. Then, at that wavelength, the variation of the absorbance under UV irradiation was measured until the photostationary state was obtained. The irradiation was then stopped (Fig. 1) and the kinetic thermal bleaching was calculated from the experimental curve obtained.

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

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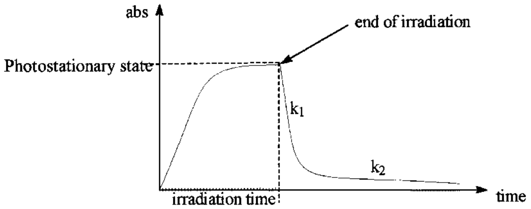


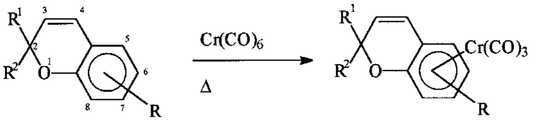
Figure 1 Typical absorbance evolution during and after UV irradiation of a photochromic compound.

Preparation of starting chromenes

The 2,2-dimethyl 2*H*-chromene **1** was prepared from coumarin according to a literature procedure.[10] The other 2*H*-chromenes were prepared by the condensation of the appropriate phenol with propargylic alcohol[11] in the presence of *p*-toluenesulphonic acid in methylene chloride at room temperature. Another method consists in reacting the phenol with titanium tetraethyloxide in refluxing toluene.[12] 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 eluent.

Preparation of complexes

A typical procedure was as follows: in a Stroheimer apparatus, under an inert atmosphere, 15 mmol of chromene was added to 10 mmol of chromium hexacarbonyl in 100 ml of butyl oxide and tetrahydrofuran mixture (10.2, v/v). The mixture was refluxed for 48 h, filtered onto Celite, washed with diethyl oxide (diethyl ether) and the solvent was removed under reduced pressure, the temperature not exceeding 50 °C. The crude product so obtained was quickly purified by column chromatography (pentane–diethyl oxide mixture). The crystalline products obtained were washed with pentane and dried under vacuum. All the complexes synthesized gave satisfactory elemental analysis or were characterized by oxidative decomplexation (I_2) and comparison with the parent 2*H*-chromenes (Eqn [1]). Our results are reported in Table 1.



[1]

The different complexes described in Table 1 were obtained by reaction with chromium hexacarbonyl under thermal conditions. The location of the chromium tricarbonyl moiety has been established by ^{1}H and/or ^{13}C NMR.

2,2-Dimethyl-2*H*-η^6-chromene tricarbonyl chromium (1a)

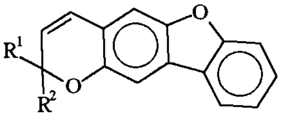
M.p.: decomposition at 118 °C. IR: (Nujol, cm^{-1}) 1955, 1860 (ν(CO)). ^{1}H NMR (acetone-d$_6$, ppm): δ = 0.96 (s, 3H), 1.30 (s, 3H), 4.02 (S, 1H), 4.60 (m,

Table 1. Complexation of various chromenes by $Cr(CO)_6$

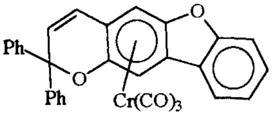
Expt	Substrate	R	R^1	R^2	CR(%)[a]	Yield(%)	Product
1	**1**	H	Me	Me	45	63	**1a**
2	**2**	H	Me	Ph	49	69	**2a**
3	**3**	H	Ph	Ph	47	72	**3a**
4	**4**	6-Phenyl	Me	Me	43	82	**4a**
5	**5**	[5,6]Benzo	Me	Me	47	0	Degradation
6	**6**	[5,6]Benzo	Me	Ph	36	0	Degradation
7	**7**	[5,6]Benzo	Ph	Ph	29	0	Degradation
8	**8**	[2,3]Benzofurano[b]	Ph	Ph	43	33	**8a**[c]

[a] The conversion ratio (CR) has been calculated relative to chromium hexacarbonyl consumption.

[b] The starting material was the [2, 3]benzofuranochromene



[c] Structure **8a**



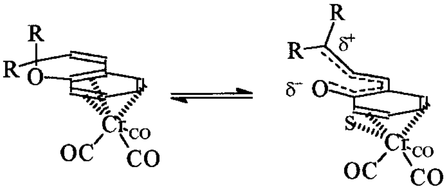


Figure 2 Structure of the complexed chromenes in their closed and open forms.

3H), 4.93 (d, $J = 9.9$ Hz, 1H), 5.42 (d, $J = 9.9$ Hz, 1H). ^{13}C NMR (acetone-d$_6$, ppm): $\delta = 27.7$ (q), 28.9 (q), 79.4 (s), 80.8 (d), 86.9 (d), 90.5 (s), 94.4 (d), 96.1 (d), 119.9 (d), 131.5 (d), 138.8 (s), 234.6 (s), 234.6 (s), 234.6 (s).

2-Methyl-2-phenyl-η^6-2*H*-chromene tricarbonyl chromium (2a)

M.p.: decomposition at 114 °C. IR (Nujol, cm^{-1}) 1965, 1870 (ν (CO)). ^{1}H NMR (CDCl$_3$, ppm): $\delta = 1.53$ (S, 3H), 5.16 (S, 1H), 5.69 (m, 3H), 5.92 (d, $J = 9.6$ Hz, 1H), 6.41 (d, $J = 9.8$ Hz, 1H), 7.10 (S, 3H), 7.33 (S, 2H). ^{13}C NMR (CDCl$_3$, ppm): $\delta = 30.1$ (q), 79.8 (s), 81.2 (d), 86.8 (d), 90.7 (s), 94.7 (d), 96.1 (d), 117.0 (d), 123.2 (d), 126.0 (d), 126.0 (d), 129.2 (d), 129.2 (d), 131.5 (d), 138.8 (s), 145.3 (s), 230.5 (s), 230.5 (s), 230.5 (s).

2,2-Diphenyl-2*H*-η^6-chromene tricarbonyl chromium (3a)

M.p.: decomposition at 133 °C. IR (Nujol, cm^{-1}): 1970, 1890 (ν (CO)). ^{1}H NMR (CDCl$_3$, ppm): $\delta = 5.49$ (S, 1H), 5.88 (m, 3H), 6.57 (d, $J = 9.5$ Hz, 1H), 7.05 (d, $J = 9.3$ Hz, 1H), 7.39 (m, 4H), 7.72 (S, 4H), 7.96 (2H). ^{13}C NMR (CDCl$_3$, ppm): $\delta = 81.1$ (s), 88.8 (s), 89.2 (d), 94.8 (d), 94.9 (d), 95.2 (d), 115.2 (s), 117.1 (d), 122.1 (d), 122.4 (d), 125.2 (d), 127.0 (d), 127.3 (d), 127.5 (d), 128.9 (d), 128.9 (d), 130.6 (d), 130.6 (d), 142.8 (s), 146.8 (s), 233 (s), 233 (s), 233 (s).

2,2-Dimethyl-6-phenyl-2*H*-η^6-chromene tricarbonyl chromium (4a)

M.p.: decomposition at 111.2 °C. IR (CHCl$_3$, cm^{-1}) 1965, 1900 (ν (CO)). ^{1}H NMR (CDCl$_3$, ppm): $\delta = 1.45$ (S, 6H), 5.28 (S, 1H), 5.49 (m, 1H), 5.62 (m, 1H), 6.34 (m, 1H), 6.79 (m, 1H), 7.26 (m, 5H).

2-Methyl-2,6-diphenyl-2*H*-η^6-chromene tricarbonyl chromium (5a)

IR (CHCl$_3$, cm^{-1}): 1980, 1910 (ν (CO)). ^{1}H NMR (CDCl$_3$, ppm): $\delta = 1.80$ (S, 3H), 5.23 (S, 1H), 5.43 (S, 1H), 5.69 (S, 1H), 6.49 (S, 1H), 7.37 (m, 10H).

7,7-Diphenyl-7*H*-benzofurano [2,3-*g*]-η^6-chromene tricarbonyl chromium (9a)

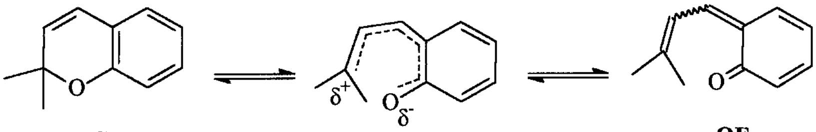
M.p.: decomposition at 164 °C. IR (CHCl$_3$, cm^{-1}): 1975, 1900 (ν (CO)). ^{1}H NMR (CDCl$_3$, ppm): $\delta = 5.12$ (S, 1H), 5.30 (S, 1H), 6.37 (d, $J = 9.8$ Hz, 1H), 6.75 (d, $J = 9.6$ Hz, 1H), 7.31 (m, 9H), 7.51 (m, 4H), 7.79 (S, 1H).

RESULTS AND DISCUSSION

Generally, the photochromic properties of 2*H*-chromenes are enhanced by the presence of additional aromatic rings on the basic structure. Thus 2,2-diphenylchromenes and benzochromenes are frequently used. In such cases complexation

Table 2. Absorption range and thermal bleaching kinetic constants

Expt	Compound	Absorption range (nm)	Kinetic constant (s^{-1})
1	**1**	No photochromic properties in our experimental conditions	
2	**1a**	340–460	10^{-4}
3	**2**	No photochromic properties in our experimental conditions	
4	**2a**	400–500	6×10^{-4}
5	**3**	360–560	0.5; 3×10^{-4}
6	**3a**	350–500	2×10^{-4}
7	**4**	No photochromic properties in our experimental conditions	
8	**4a**	350–500	8×10^{-4}
9	**5**	No photochromic properties in our experimental conditions	
10	**5a**	350–500	4×10^{-4}
11	**9**	370–640	1.5; 7×10^{-4}
12	**9a**	370–620	0.11; 9×10^{-4}



CF **OF**

Figure 3 Closed and open forms of 2*H*-chromenes.

with chromium hexacarbonyl can lead to different regioisomers.

We observed that the complexation reaction is totally regioselective and that the chromium carbonyl is exclusively located on the aromatic ring of the chromene framework. The yields are good except for Experiments 5–7. As it is known that naphthalene chromium tricarbonyl complexes are labil, it is not surprising that, under thermal conditions, the complexes corresponding to Experiments 5–7 are not stable.[8]

Spectrokinetic studies

Complexation does not induce a significant shift in the open-form absorption wavelength in any of the three different solvents used, as compared with the non-complexed forms.

However, in ethanol, a decomplexation reaction takes place as soon as the irradiation is started. In fact this solvent is a less stabilizing ligand than toluene or acetonitrile, and the intermediate η^4-complex resulting from the opening process is highly unstable (Fig. 2).

In toluene, the open-form absorption overlaps with the absorption spectra of the starting complex. This phenomenon associated with degradation reactions does not allow accurate kinetic-constant determination.

In acetonitrile these problems do not occur; our results are summarized in Table 2.

Photochromism is explained by the formation of open form(s) **OF**(s) on irradiation (Fig. 3).

One or several isomeric **OF**s can exist in equilibrium with the closed form **CF**. When the irradiation is stopped, the **OF**s are closed again, becomings **CF** by visible irradiation or by a thermal process. If several **OF**s exist in equilibrium in an appreciable concentration, several kinetic constants can be determined for the ring-closure process. If the closing kinetic constant is high, the concentration of the **OF** remains very small and photochromism cannot be detected.

It can be seen from Table 2 that the chromenes which are not disubstituted by phenyl groups are not photochromic on the normal detection scale used (Experiments 1, 3, 7 and 9). Complexation of these chromenes induces the appearance of detectable photochromic properties (Experiments 1–2, 3–4, 7–8, 9–10). It thus seems, as described previously for spiropyrans, that complexation with chromium tricarbonyl stabilizes the **OF** and so reduces the closure kinetic constant. This can be seen when Experiments 5 and 6 are compared. Compound **3**, which is normally photochromic, presents two kinetic constants which are higher than the kinetic constant of the complexed form, namely **3a**. The same observation can be made for chromene **9** and the complexed form **9a** (Experiments 11 and 12) although the second kinetic constant is slightly higher for the complexed form **9a**.

Experimentally, we can also observe that the absorption decreases when chromenes are complexed. This decrease induces a narrowing of the absorption range (Experiments 5–6, 11–12).

CONCLUSION

The complexation of different 2*H*-chromenes by chromium tricarbonyl induces the appearing or the modification of the photochromic properties of these compounds. The main effect is a stabilization of the open form(s) due to a decrease in the ring closure kinetic constant. In several cases it is thus possible to observe photochromic behavior for 2*H*-chromenes which, in their non-complexed forms, are not photochromic.

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