

Chemical and transient spectroscopic evidence for radical and ionic pathways in the photolysis of 3-halo-2,3-dihydrobenzopyran-4-ones

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Dedicated to Waldemar Adam's 70th birthday

Abstract

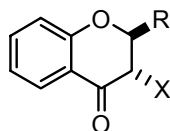
Photolysis of 3-halo-2,3-dihydrobenzopyran-4-ones **1a,b** and **2a,b** in acetonitrile and hexane led to dehalogenated dihydrobenzopyran-4-ones **3a,b** and benzopyran-4-ones **4a,b**. Their formation is accounted for in terms of primary cleavage of the carbon halogen bond to give α -carbonyl radicals (**I**) and/or cations (**II**). Intermediates **II**, precursors of **4**, can be generated either directly by heterolysis or by initial homolysis followed by electron transfer. The ionic routes are more favored in acetonitrile than in hexane. The involvement of radical and ionic pathways in the photochemistry of 3-halo-2,3-dihydrobenzopyran-4-ones is supported by detection of Br_2^- in the laser flash photolysis experiments performed on **2a**.

Keywords: α -Haloketones, laser flash photolysis, photocleavage, photoelimination photoreduction

Introduction

As an extension of our previous studies on the photochemistry of benzopyran-derived compounds,¹⁻⁴ we have been interested in the light induced fragmentation of 3-halo-2,3-dihydrobenzopyran-4-ones (3-halochromanones), which leads to the corresponding α -keto radicals and/or cations; these species are key intermediates in the electron transfer processes followed by 4-acetoxychromenes.⁴ Short lived intermediates of this type are also relevant because they are thought to play an important role in some processes of biosynthetic interest in the field of flavonoids, such as flavone-isoflavone isomerization or oxidation of the C3 bridge of flavanones affording flavones or flavonols.^{5,6} The photochemistry of some 3-bromochromanones has been described by us in the past.^{7,8} Here, we wish to report on the photochemical behavior of four 3-bromo- and 3-chloro-2,3-dihydrobenzopyran-4-ones under different conditions. Thus, in

1a and **2a** the only substituent of the dihydrobenzopyran ring is chlorine or bromine respectively, while compounds **1b** and **2b** also possess a *trans*- phenyl group attached to the 2- position (Chart 1).



1a: R = H, X = Cl

1b: R = Ph, X = Cl

2a: R = H, X = Br

2b: R = Ph, X = Br

Chart 1

Results and Discussion

Compounds **1a,b** and **2a,b** were obtained following known procedures,^{9,10} as detailed in the experimental section. Photolysis of these substrates was carried out for 1 h in acetonitrile or hexane at 254 or 350 nm. The results are summarized in Table 1 and Figure 1.

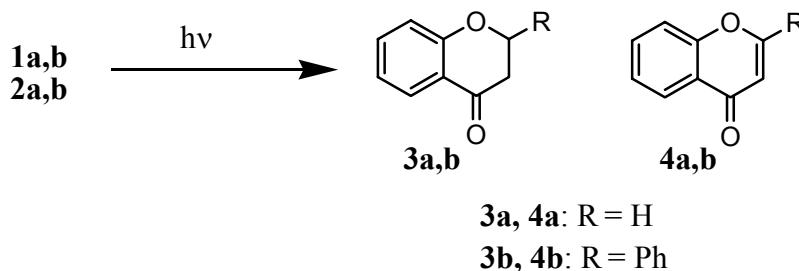


Figure 1. Photolysis of 3-halochromanones **1a,b** and/or **2a,b**.

Irradiation of **1a** in acetonitrile led exclusively to chromone **4a** (Table 1, entries 1 and 2). However, when hexane was used as solvent (Table 1, entries 3 and 4), appreciable amounts of the corresponding dihydro derivative (4-chromanone, **3a**) were also found in the photolysate. In the case of the bromo derivative **2a**, photolysis led to mixtures of **3a** and **4a** under the different conditions employed (Table 1, entries 5-8), but the ratios **4a/3a** were considerably higher in acetonitrile than in hexane (*ca.* 25:1 in acetonitrile to 6:1 in hexane). The presence of a phenyl substituent at the 2-position of the dihydrobenzopyran ring of **1a** or **2a** (as in compounds **1b** or **2b** respectively) did not change the trend; again the benzopyran derivative (flavone, **4b**) was the major photoproduct although flavanone **3b** (resulting from reductive dehalogenation) was also formed; the latter was found in higher amounts when hexane was used as solvent (Table 1, entries 9-16). Conversion was always higher for the bromochromanones than for their chloro analogues. This is in good agreement with the lower energy of the C-Br bond *vs.* the of C-Cl bond.¹¹ On the other hand, the presence of the phenyl group at the 2-position resulted in higher

conversions; this can be attributed in part to the additional light absorption by the aromatic substituent.

Table 1. Photolysis of 3-halochromanones **1a,b** and **2a,b** under different conditions

Entry	Compound	Conditions*	Conversion	3	4
1	1a	A	37	-	100
2	1a	B	16	-	100
3	1a	C	55	13	87
4	1a	D	47	15	85
5	2a	A	63	4	92
6	2a	B	54	4	95
7	2a	C	90	15	85
8	2a	D	81	29	71
9	1b	A	64	-	100
10	1b	B	46	-	100
11	1b	C	70	36	64
12	1b	D	56	22	78
13	2b	A	95	2	98
14	2b	B	90	3	97
15	2b	C	100	13	87
16	2b	D	93	20	80

*A: acetonitrile, $\lambda = 254$ nm; B: acetonitrile, $\lambda = 350$ nm; C: hexane, $\lambda = 254$ nm; D: hexane, $\lambda = 350$ nm.

In general, formation of **3a,b** and **4a,b** can be rationalized as follows: primary photochemical cleavage of the carbon-halogen bond affords radicals (**I**) and/or ions (**II**).¹²⁻¹⁸ The latter intermediates can be generated either directly by heterolysis (route ii) or by initial homolysis (i) followed by electron transfer (iii), as shown in Figure 2. Clearly, routes (ii) and (iii) should be favored in more polar solvents. Therefore, **4a,b** are obtained in higher yields in acetonitrile than in hexane.

The involvement of both radical and ionic pathways in the photochemistry of α -halo ketones has been previously suggested in the literature.¹²⁻¹⁸ Looking for a clear evidence supporting the involvement of these routes in the photolysis of 4-halochromanones **1a,b** and **2a,b**, laser flash photolysis (LFP) experiments were performed in acetonitrile and hexane at 266 nm. Detection of $X_2^{\cdot-}$ species (resulting from combination of X^{\cdot} and $X^{\cdot-}$) would provide a proof for the mixed radical/ionic mechanism. This was actually found to be the case. For instance, starting from **2a**, a transient with maximum at 360 nm in acetonitrile (350 nm in hexane) was observed (Figure 3) after 266 LFP under N_2 . It was attributed to $Br_2^{\cdot-}$, by comparison with the spectrum reported in the literature for this species, generated from 1,2-dibromoethane.^{19,20} Obviously, the observed

Br_2^- is formed by recombination of the bromine atom generated after homolytic cleavage (route i) with bromide ion produced in the heterolytic pathway (ii) or after electron transfer (route iii). The lifetime of this species ranged in the microsecond scale.

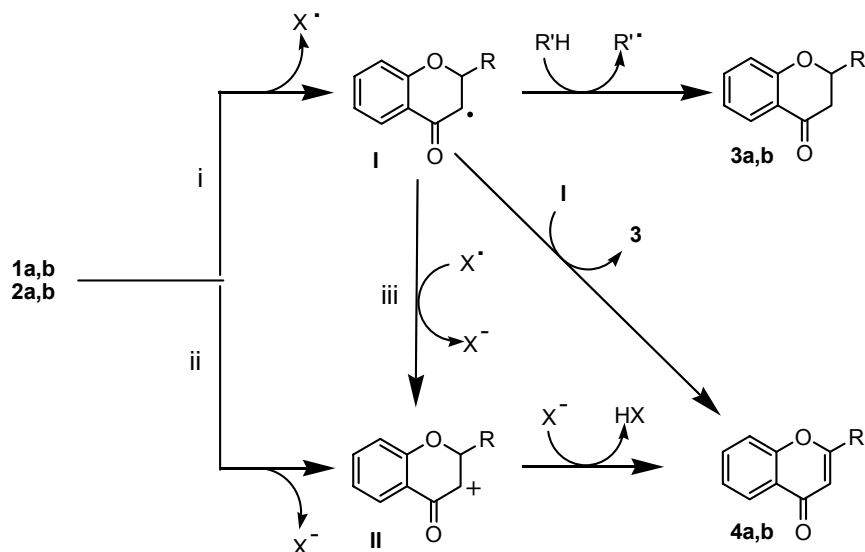


Figure 2. Main routes leading to **3a,b** and **4a,b**.

In order to generate Br_2^- in higher yield, a solution of **2a** in acetonitrile in the presence of a bromide salt (Et_4NBr) was submitted to LFP. As expected, the shape and position of the band was the same as that recorded in the absence of bromide, but much more intense. On the other hand, when hexane was used as solvent, the optical density (OD) at 360 was higher than in acetonitrile; this points to an enhancement of the radical pathway, which leads to higher amounts of **3a** (Table 1, entries 7,8). In Figure 4, a comparison between the top ΔOD values (LFP, signal monitored at 360 nm) for **2a** in acetonitrile (A), hexane (B) and acetonitrile in the presence of Et_4NBr (C) is shown.

In summary, both radical and ionic pathways are involved in the photolysis of 3-halochromanones. This is supported by chemical evidence (formation of chromanones and chromones), as well as by detection of Br_2^- ($\lambda_{\text{max}} = 360 \text{ nm}$) in the laser flash photolysis experiments.

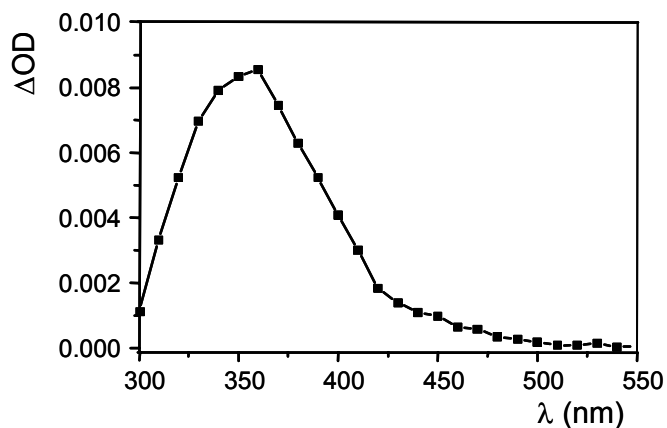


Figure 3. Laser flash photolysis of **2a** in MeCN/N₂. Transient spectra obtained 1.3 μs after the laser pulse.

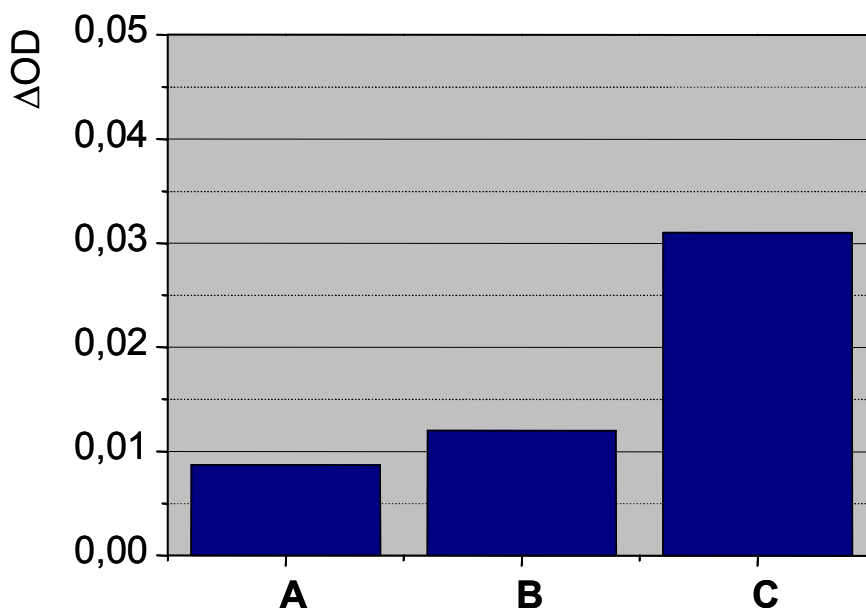


Figure 4. Top Δ OD values (signal at 360 nm) of the transient species formed after 266 LFP of **2a** in acetonitrile (A), hexane (B) and acetonitrile/Et₄NBr (C).

Experimental Section

General Procedures. Solutions of **1a,b** and **2a,b** (5 mM) in hexane or acetonitrile were irradiated for 1 h through quartz, inside a Luzchem multilamp photoreactor, with the light from 4 8W-lamps emitting mainly at 254 nm (monochromatic) or 350 nm (Gaussian distribution). The course of the reaction was followed by GC, GC-MS and ¹H-NMR; the conversion, product

distribution and mass balance were determined using adequate standards. The structures of the photoproducts were confirmed by comparison with retention times and fragmentation patterns of authentic samples.

Laser flash photolysis experiments were performed by using a Q-switched Nd:YAG laser (Quantel Brilliant, 266 nm, 14 mJ per pulse, 5 ns fwhm) coupled to a mLFP-111 Luzchem miniaturized equipment. All transient spectra were recorded employing 10×10 mm² quartz cells with 4 mL capacity. The absorbance of the halochromanones was found to be *ca.* 0.2 at the laser wavelength. The experiments were carried out in hexane or acetonitrile at room temperature (22 °C) and under inert atmosphere.

3-Chloro-2,3-dihydrobenzopyran-4-one (1a).²¹ To 1.48 g (10 mmol) of 4-chromanone in 20 mL of acetic acid, maintained under stirring, 1.03 g of manganese dioxide and 3.3 mL (42 mmol) of acetyl chloride were added. The mixture was maintained for 12 h at 20 °C. Then, 50 mL of a NaHCO₃ aqueous solution were added, and the resulting suspension was extracted three times with methylene chloride. The crude mixture was submitted to column chromatography to afford 0.73 g of **1a** (40%).

3-Bromo-2,3-dihydrobenzopyran-4-one (2a).²² A solution of Br₂ (1.0 g, 6.25 mmol) in 30 mL of CCl₄ was added to a well stirred solution of 4-chromanone (6.25 mmol) in CCl₄ (30 mL). After 2 h, the reaction mixture was evaporated *in vacuo*, and **2a** (1.37 g, 60%) was isolated by column chromatography using methylene chloride as eluent.

3-Chloro-2-phenyl-2,3-dihydrobenzopyran-4-one (1b).²³ To 2.24 g (10 mmol) of 4-flavanone in 20 mL of acetic acid, maintained under stirring, 1.03 g of manganese dioxide and 3.3 mL (42 mmol) of acetyl chloride were added. The mixture was maintained for 12 h at 20 °C. Then, 50 mL of a NaHCO₃ aqueous solution were added, and the resulting suspension was extracted three times with methylene chloride. The crude mixture was submitted to column chromatography to give 0.91 g of pure **1b** (35%).

3-Bromo-2-phenyl-2,3-dihydrobenzopyran-4-one (2b).²⁴ A solution of Br₂ (1.0 g, 6.25 mmol) in 30 mL of CCl₄ was added to a well stirred solution of 4-flavanone (6.25 mmol) in CCl₄ (30 mL). After 2 h, the reaction mixture was evaporated *in vacuo*, and **2b** (1.61 g, 72%) was isolated by column chromatography using methylene chloride as eluent.

Acknowledgements

Financial support from the MEC (CTQ2004-03811) is gratefully acknowledged.

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