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Formation of 2,2-dimethylchroman-4-ones during the photoinduced rearrangement of some aryl 3-methyl-2-butenoate esters. A mechanistic insight

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ABSTRACT

Several aryl 3-methyl-2-butenoate esters upon irradiation lead to the formation of [1,3]-migrated photoproducts, phenol and, surprisingly 2,2-dimethylchroman-4-one derivatives. The starting photochemical reaction takes place from the singlet excited state of the ester and as a total mechanism two consecutive reaction pathways are proposed. The former involves the photo-Fries rearrangement of the esters in all the solvents studied and, depending on the proticity of the solvent, the latter involves an ESIPT process followed by thermal 6π-electrocyclic reaction and/or thermal (intramolecular *oxa*-Michael addition) cyclization of the *ortho* regioisomers photoformed. This second pathway is responsible of the formation of the 2,2-dimethylchroman-4-one derivatives.

1. Introduction

The photo Fries-rearrangement has received considerable attention since its discovery in 1960.[1] Upon irradiation aryl esters, amides, thioesters and sulfonates undergo the photo Fries-rearrangement and these compounds have been used mainly to elucidate the underlying reaction mechanism.[2] However, this photochemical reaction has been successfully used in the synthesis of natural products such as griseofulvin,[3] daunomycine[4] and flavonoids.[5] The photo-Fries rearrangement is a mild and clean reaction where no hazardous solvents and Lewis acid catalysts are needed to accomplish the photoreaction. The photoproducts are formed in good chemical yield with a predictable regioselectivity. The radical mechanism of the photo-Fries rearrangement is well established and it is known that this rearrangement occurs mainly through the excited singlet state.[6]

Irradiation of aryl esters provides *o*-acylphenols which are useful organic compounds and versatile intermediates in the synthesis of biologically active naphthoquinones, pesticides, photographic agents and UV absorbents.[7] Indeed, substituted *o*-hydroxyphenones are also valuable intermediates in the preparation of substituted 2,2-dimethylchroman-4-one moieties that show biological activity.[8–12] The synthesis, chemistry, occurrence in nature and biological activity of chromanones has been the subject of several comprehensive reviews.[13] On the other hand, *ortho*-hydroxyphenones undergo intramolecular proton transfer in the excited state, which provides an efficient energy wasting channel, responsible for their ability to act as UV-stabilizers.[14a] However, *ortho*-hydroxyaryl alkenyl ketones, e.g., 2′-hydroxychalcones, show a different behavior and a 6-*exo*-*trig* intramolecular cyclization of the *cis*-isomer takes place efficiently to give 4-flavanones. In fact, a well-studied example was the photocyclization of 2′-hydroxychalcones to 4-flavanones, which is enzymatically catalyzed in plants and appear to be involved in the biosynthesis of flavonoids.[14b–d] Matsushima et al. have studied the photocyclization of substituted 2′-hydroxychalcones to 4-flavanones and concluded that the cyclization proceeded via a thermal 6π-electrocyclic process.[15a,b] In this regard, Miranda et al. have also studied the cyclization of different *cis*- and *trans*-*o*-hydroxyaryl alkenyl ketones from a mechanistic point of view under basic conditions, e.g., sodium acetate in DMSO (other bases likewise used are sodium hydroxide, tetraethyl ammonium hydroxide and potassium carbonate) and, under preparative conditions, a biphasic system was used, *viz.* hexane and aqueous sodium hydroxide (10%). In both cases, 2-methyl chroman-4-one derivatives were obtained quantitatively.[15c]

Previous studies on the product distribution of the photo-Fries rearrangement reaction of (hetero)aryl esters in isotropic media

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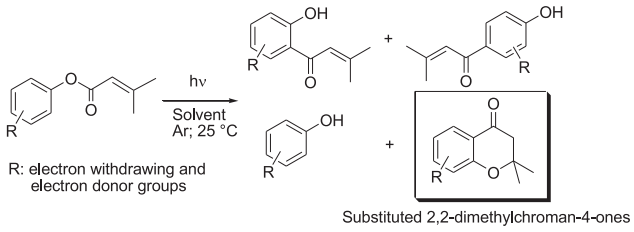
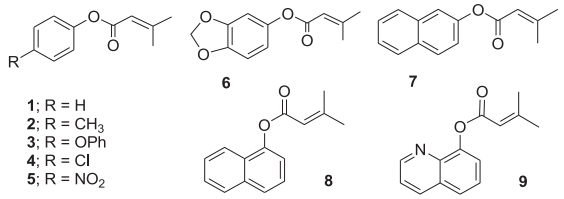
afforded *ortho* and *para* rearranged photoproducts as well as the corresponding phenol.[16] However, irradiation of aryl 3-methyl-2-butenoate esters in different organic solvents (cyclohexane, methanol and acetonitrile) undergoes the photo-Fries rearrangement yielding the expected photoproducts such as the rearranged photoproducts, phenol, 3-methyl-2-butenoic acid and, surprisingly, the substituted 2,2-dimethylchroman-4-ones as well (Scheme 1). These interesting results encouraged us to study the mechanism of formation of the 2,2-dimethylchroman-4-one derivatives since these heterocyclic compounds are not an expectable primary photoproduct from a photo-Fries rearrangement reaction.



Scheme 1. Product distribution of the irradiation of substituted aryl 3-methyl-2-butenoate esters.

In view of this background and in our interest on photo-Fries reaction,[17] we have selected representative (hetero)aryl 3-methyl-2-butenoate esters **1**–**9** (Scheme 2) which have been synthesized previously in our laboratory.[18,19] Then, a systematic study of their photochemical behavior has been performed in solution under UV irradiation. Noteworthy, Miranda et al. studied the photochemistry of ester **6** in hexane and in hexane containing anhydrous potassium carbonate.[17b,20]



Scheme 2. Aryl 3-methyl-2-butenoate esters studied.

Herein, the photo-Fries rearrangement of the esters will be conducted without any acid- or base-mediated catalysis with special attention to the preparative and mechanistic aspects. Also, we attempt to demonstrate that the formation of 2,2-dimethylchroman-4-one derivatives occurs through a thermal 6π-electrocyclization reaction when 2′-hydroxyphenyl 2-methylpropenyl ketone is irradiated in polar and non-polar aprotic solvents. However, when polar protic solvents are used, i.e., methanol, a competitive photochemical and thermal cyclization processes occur providing the 2,2-dimethylchroman-4-one derivative in fairly good yields.

2. Results and discussion

2.1. Spectrosocpic properties of esters 1–9

The absorption spectra of compounds **1**–**9** were recorded in methanol at 298 K and the λ_{max} of absorption of the band assigned to the lowest-lying excited electronic state ($^1L_b(S_1-S_0)$ electronic transition) are shown in Table 1. In general, on changing the solvent polarity from cyclohexane to acetonitrile, no shift of the λ_{max} was observed.

Table 1
Spectroscopic data for esters **1**–**9** in methanol solution

Esters	Absorption	Fluorescence	
	λ_{max}/nm	λ_{max}/nm	ϕ_f[a]
1	265	281	0.01
2	254	281	0.02
3	255	280	0.02
4	254	281	0.02
5	260	ND[b]	ND[b]
6	287	343	0.02
7	285	346	0.03
8	285	346	0.07
9	280	342	0.01

[a] Fluorescence reference: naphthalene (λ_{exc}: 285 nm; λ_{max}(fluo): 318 nm; ϕ_f: 0.04)[21]; Error of ±10%.
[b] ND: not detected.

Excitation at 265 nm of phenyl ester (**1**) induced a very weak fluorescence emission at 281 nm. Excitation at 255–285 nm for compounds **2**–**9** induced a weak fluorescence emission located in the 270–346 nm regions. The high-energy edge of the broad emission spectrum overlaps with the 0–0 band. The nearly negligible Stoke's shift reflects a high structural similarity between the ground and excited states. Table 1 includes the λ_{max} of fluorescence obtained for compounds **1**–**9** and Fig. 1 shows the UV-visible absorption spectrum and the fluorescence emission spectrum of compound **7** recorded in cyclohexane at 298 K. Also, the fluorescence quantum yields have been measured at 298 K using naphthalene as a fluorescence reference (ϕ_f=0.04[21]) and the values are collected in Table 1. Compound **5** did not show fluorescence emission due to the presence of a nitro group attached to the phenyl moiety which promotes the intersystem crossing process populating efficiently the triplet excited state.[22,23]

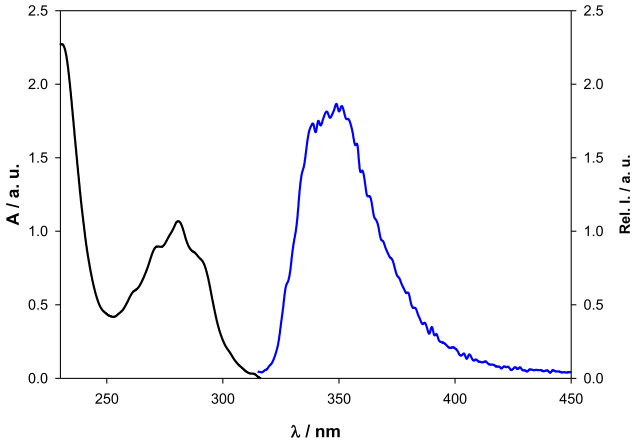


Fig. 1. UV-visible absorption spectrum (black line) and fluorescence emission spectrum (blue line) of ester 7 (1.04×10^{-5} mol dm^{-3}) recorded in cyclohexane at 298 K.

2.2. Preparative photochemistry of aryl 3-methyl-2-butenoate esters 1–9 in solution

We have irradiated systematically solutions of esters **1**–**9** (see Scheme 2) in preparative scale in order to isolate and characterize the photoproducts. The experiments were performed in different organic media (cyclohexane, acetonitrile and methanol) with excitation wavelengths of 254 and 313 nm under inert atmosphere (Ar) and at room temperature. After irradiation in preparative scale, the photolyzed solutions were evaporated under vacuum and the photoproducts were separated by column chromatography over

silica gel from the solid residue and were identified and characterized by means of physical and spectroscopical methods (mp, ^{1}H NMR and ^{13}C NMR). The photoreactions were followed spectrophotometrically and by GLC and HPLC as cross-checking. Similar photoproducts and yields were obtained by both chromatographic methods. This means that the phenols and the 2,2-dimethylchroman-4-ones, compounds that can sublimate, were not lost during chromatographic analysis.

Phenyl 3-methyl-2-butenoate ester (**1**) was irradiated in three different solvents at 254 nm affording the migrated products 1-(2-hydroxyphenyl)-3-methyl-2-buten-1-one (**1b**) and 1-(4-hydroxyphenyl)-3-methyl-2-buten-1-one (**1d**), together with 2,2-dimethyl chroman-4-one (**1a**), phenol (**1c**) and 3-methyl-2-butenoic acid (see Scheme 3 and Table 2). No secondary photoproducts were detected in the photolyzed solutions under our experimental conditions, *viz.* aryl aryl radical coupling, aryl alkyl radical coupling and extrusion of carbon monoxide. The molar ratio of **1a** and **1b** is ca. 1:1 in apolar (cyclohexane) and polar aprotic (MeCN) solvents while in MeOH compound **1b** is formed in amounts higher than compound **1a**. It is interesting to point out that thermal Fries rearrangement studies on compound **1** were carried out to produce the *ortho* regioisomer and the expected 2,2-dimethylchroman-4-one **1a** and they were obtained in low chemical yield from complicated reaction mixtures.[24] However, the photochemical reaction allows the formation of **1b** as well as **1a** under mild conditions and at room temperature. This photoreaction is advantageous over the thermal Fries rearrangement where higher temperature (80–120 °C) and Lewis acid catalysts ($AlCl_3$ or $FeCl_3$) are needed to accomplish the reaction.[25]

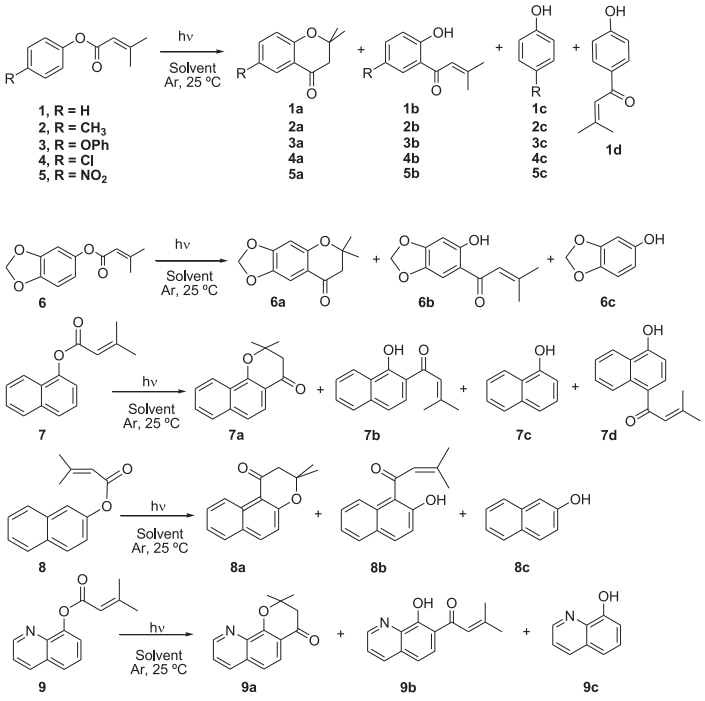
Examination of the photochemical reaction of several 4-substituted esters **2**–**5** bearing electron–withdrawing and electron–donating groups was conducted. Upon irradiation with wavelength of 254 nm these esters gave the *ortho* regioisomers (**2b**–**4b**), phenols (**2c**–**4c**), and the 2,2-dimethylchroman-4-one derivatives (**2a**–**4a**), with the exception of compound **5** (see Table 2). Similar solvent effect on the chemical yield of esters **2**–**4** was observed which is comparable to the yields obtained for ester **1** in the same solvents.

Table 2
Yields of photoproducts obtained and quantum yields (ϕ) of irradiation of esters **1**–**5** in different organic media at λ_{exc}=254 nm[a]

Compound	Solvent	Yields of photoproducts (%)[b]				ϕ[c]
		1a	**1b**	**1c**	**1d**	
1	Cyclohexane	14	11	21	22	0.13
	MeCN	17	15	22	20	0.09
	MeOH	14	25	19	20	0.08
2		**2a**	**2b**	**2c**		
	Cyclohexane	23	23	12		0.10
	MeCN	20	27	15		0.11
	MeOH	5	40	31		0.07
3		**3a**	**3b**	**3c**		
	Cyclohexane	20	21	23		0.12
	MeCN	23	27	25		0.11
	MeOH	11	36	21		0.06
4		**4a**	**4b**	**4c**		
	Cyclohexane	27	25	22		0.14
	MeCN	25	21	26		0.17
	MeOH	16	28	25		0.07
5		**5a**	**5b**	**5c**		
	Cyclohexane	—	5	23		0.04
	MeCN	—	—	38		0.02
	MeOH	—	—	54		0.01

[a] Concentration: 1.06×10^{-3} mol dm^{-3}; *T*: 298 K; Atmosphere: Ar.
[b] Calculated by GC.
[c] Quantum yields of disappearance of esters **1**–**5** measured at low conversions (ca. 10%) under argon atmosphere; actinometer: potassium ferrioxalate; λ_{exc}=254 nm; Error: ±0.02.

A different photochemical behavior was observed for ester **5**. No photoproducts **5a** and **5b** were formed during the irradiation of ester **5** with the exception in cyclohexane where a very low amount (ca. 5%) of **5b** was observed. Instead, the phenol **5c** was obtained independently of the medium. These results suggested that a different reactive excited state is involved in the photoreaction of ester **5**. We attributed this behavior to the nitro group attached to the



Scheme 3. The photo-Fries rearrangement of esters **1**–**9**. Product distribution.

phenyl moiety that populates efficiently the triplet excited state (T_1) of ester **5** rendering **5c** as the sole photoproduct. It is known that the photochemical reactivity of nitro arenes takes place from T_1 since they show ϕ_{isc} in the order or higher than 0.50.[22,23]

The photochemical behavior of esters **6**–**9**, which are examples of polycyclic and heterocyclic systems, was also studied (Scheme 3). Irradiation at two different excitation wavelength (254 and 313 nm) of esters **6**–**9** in cyclohexane and under Argon atmosphere, gave the *ortho* regioisomers (**6b**–**9b**), the corresponding phenols (**6c**–**9c**) and the 2,2-dimethylchroman-4-one derivatives (**6a**–**9a**) (Scheme 3 and Table 3). The *ortho* regioisomers (**6b**–**9b**) are always the main photoproducts. On the other hand, Miranda et al.[21] studied the photochemistry of ester **6** and after 20 h of irradiation at λ_{exc}=254 nm in hexane no photochemical reaction took place. Otherwise, when the photoreaction of **6** was carried out in the same experimental conditions but in the presence of anhydrous K_2CO_3 compound **6b** was formed in only 22% yield. However, in our experimental conditions, ester **6** gives the expected photo-Fries products as well as the 2,2-dimethylchroman-4-one **6a** at irradiation time lower than 120 min without any basic catalysis (see Scheme 3).

Table 3
Yields of photoproducts obtained and quantum yields (ϕ) of irradiation of esters **6**–**9** in cyclohexane at different excitation wavelength[a]

Compounds	λ_{exc} (nm)	Yield of photoproducts (%)[b]				ϕ^c
		6a	**6b**	**6c**		
6	254	24	30	20		0.10
	313	25	27	21		0.11
		7a	**7b**	**7c**	**7d**	
7	254	15	48	10	9	0.12
	313	17	47	11	10	0.12
		8a	**8b**	**8c**		
8	254	17	41	19		0.14
	313	19	39	21		0.13
		9a	**9b**	**9c**		
9	254	18	40	19		0.14
	313	19	41	20		0.14

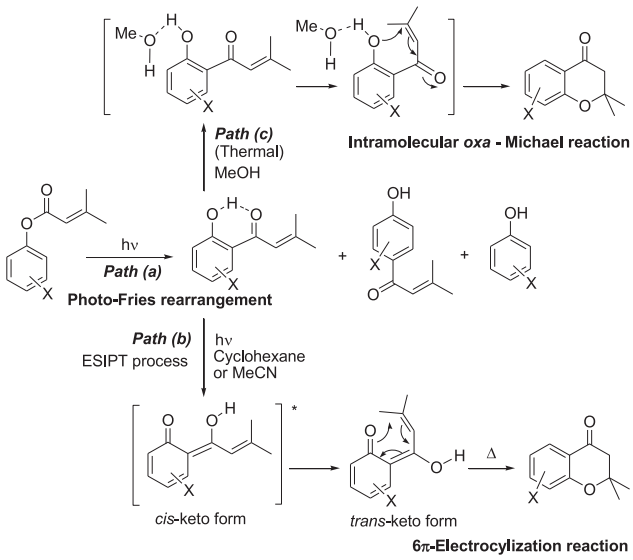
[a] Concentration: 1.06×10^{-3} mol dm^{-3}; T: 298 K; Atmosphere: Ar.
[b] Calculated by GC.
[c] Quantum yields of disappearance of esters **6**–**9** measured at low conversions (ca. 10%) under argon atmosphere; actinometer: potassium ferrioxalate; λ_{exc}=254 nm; Error: ±0.02.

Noteworthy, the data collected in Table 3 also show the same photoproduct distribution and no significant differences in the chemical yield are observed as a function of excitation wavelength. This behavior implies that the lowest excited state of the esters is the photo reactive state responsible of the formation of the photoproducts.

The quantum yields (ϕ) of disappearance of esters **1**–**9** were determined in different organic media using potassium ferrioxalate as actinometer and are collected in Tables 2 and 3.[26–28] The conversion of the esters was monitored by GC and HPLC analysis and was not higher than 10%. The ϕ values for esters **1**–**5** in all the solvents studied are almost the same within the experimental error (±0.02) which accounts for a similar degree of stabilization of the reaction intermediates in polar and non-polar solvents. In the case of esters **6**–**9** the ϕ values do not depend on the excitation wavelength which accounts for the same photo reactive excited state involved in the photoreaction.

2.3. Formation of chroman-4-ones during the photochemical reaction

During the photochemical rearrangement of esters **1**–**9**, it was observed that the 2,2-dimethylchroman-4-one derivatives were formed. Thus, we believe that the whole photochemical reaction takes place really in two consecutive steps: i) the photochemical Fries rearrangement of the esters that provides the rearranged *ortho*- and *para*-regioisomers and the phenols (***path a***; Scheme 4); ii) the intramolecular photoinduced cyclization of the *ortho* regioisomer to the corresponding 2,2-dimethylchroman-4-ones through a thermal 6π-electrocyclization reaction (***path b***; Scheme 4) in apolar and polar aprotic solvents. However, when the solvent is a polar protic one, e.g., methanol, an intramolecular *oxa*-Michael addition reaction takes place (***path c***; Scheme 4) even though a low photochemical contribution to the cyclization process can not be rule out.

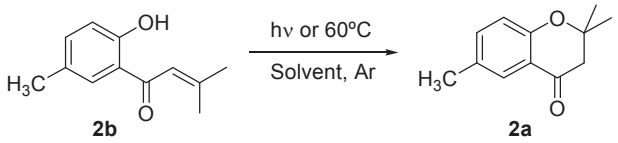


Scheme 4. Proposed reaction mechanism for the photochemical reaction of esters **1**–**9**.

The success of the electrocyclization reaction can be ascribed to the formation of *trans*-keto tautomer in the ground state which is the precursor for the production of the cyclization product. This tautomer was formed by the intramolecular proton transfer process (ESIPT)[29] of the *ortho* regioisomer to produce *cis*-keto form in the excited state followed by deactivation with twisting of the newly produced C=C double bond of the tautomer before undergoing intersystem crossing to triplet excited state. The rapid radiationless deactivation of the *cis*-keto form in the singlet excited state gives the *trans* tautomer in its ground state which has the required geometry to proceed effectively via a thermal 6π-electrocyclic process recovering the aromaticity and furnishing the 2,2-dimethylchroman-4-one derivatives. This behavior is usually observed with β-hydroxy carbonyl compounds such as 2′-hydroxychalcones where, in π,π* excited states, phenolic groups usually become more acidic and carbonyl groups more basic, enhancing the proton transfer and, therefore, favoring the one way *cis*–*trans* isomerization of 2′-hydroxychalcones.[30] Curiously, this behavior depends on the nature of the solvent used.

Table 4 depicts the results obtained under photoinduced and thermal conditions for compound **2b**. When the solvents are polar aprotic (MeCN) or non polar (cyclohexane), the 6π-electrocyclization reaction takes place efficiently due to a favored intramolecular hydrogen bonding providing 2,2-dimethylchroman-4-one **2a** in good yields. Noteworthy, irradiation of **2b** at different wavelength (254 nm and 366 nm) provides compound **2a** with similar chemical and quantum yields. This behavior accounts for the same photo reactive excited state involved in the cyclization photoreaction.

Table 4
Yields of 6-methylchroman-4-one (**2a**) in different experimental conditions



Solvent	T/°C	λ_{exc}/nm	Yields of **2a** (%)[a]	ϕ[c]
MeOH	25	254	23	0.02
	25	366	16	0.01
	60[b]	—	32	—
Cyclohexane	25	254	79	0.05
	25	366	48	0.04
	60[b]	—	0	—
MeCN	25	254	74	0.05
	25	366	44	0.06
	60[b]	—	0	—

[a] Isolated yields; Δt=120 min.
[b] Under thermal conditions (bath temperature: 60 °C); Δt=300 min; Atmosphere: Ar.
[c] Quantum yields of disappearance of **2b** measured at low conversions (ca. 10%); actinometer: potassium ferrioxalate.

Fig. 2 shows that irradiation of compound **2b** undergoes a cyclization reaction to compound **2a** as suggests from the spectral profile of the UV-visible absorption spectra run in cyclohexane during 120 min.

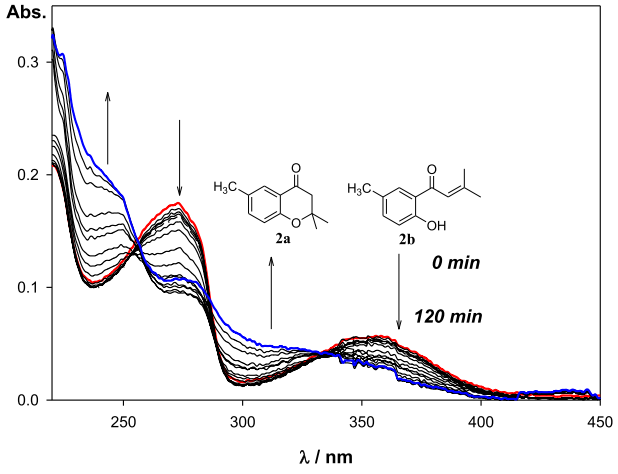


Fig. 2. Change of the UV-visible absorption spectrum of compound **2b** (1.10×10^{-5} mol dm^{-3}) upon irradiation at 254 nm in cyclohexane. Total irradiation time 120 min.

On the other hand, in polar protic solvents (methanol), the 6π-electrocyclization also undergoes to produce the desired 2,2-dimethylchroman-4-one **2a** but in lower chemical and quantum yields (Scheme 4). In this case, methanol breaks the intramolecular hydrogen bond by forming an intermolecular hydrogen bonds with compound **2b** (see ***Path (c)***, Scheme 4), as it was observed for different 2′-hydroxychalcones.[30c] Additionally, we have measured the UV-visible spectra of compound **2b** in different solvents and a hypsochromic shift of the lower energy band was observed (compare these data: λ_{max}=357 nm in cyclohexane, λ_{max}=356 nm in acetonitrile and λ_{max}=349 nm in methanol). These facts indicate that the hypsochromic shift of the absorption band of **2b** in methanol should be related to an intermolecular hydrogen bonding interactions.[31] However, the thermal cyclization reaction of **2b** to **2a** undergoes in fairly good yield when the reaction is conducted in methanol and at 60 °C (Table 4). Likewise, the cyclization process of **2b** also takes place at room temperature (25 °C) but requiring long period of reaction time. Noteworthy, the thermal cyclization reaction of **2b** does not take place in acetonitrile and in cyclohexane at 60 °C (Table 4). These results demonstrate that under polar aprotic and non-polar solvents the intramolecular hydrogen bond is so strong that no thermal reaction occurs while upon irradiation 2,2-dimethylchroman-4-one **2a** is produced efficiently.

On the other hand, both photochemical and thermal cyclization reactions of **2b** in methanol occur, being more efficient at 60 °C. Therefore, we suggest that there must be a compromise of the intramolecular and intermolecular hydrogen bonding in methanol solution. Thus, those molecules of **2b** bearing intramolecular hydrogen bonds may undergo photoinduced hydrogen atom transfer in the excited state, as depicted in ***Path (b)*** (Scheme 4), giving the cyclization product **2a**. Instead, those molecules showing intermolecular hydrogen bonds with methanol may undergo through an intramolecular cyclization *oxa*-Michael addition reaction in the ground state of compound **2b** (thermal condition; ***Path (c)*** in Scheme 4), since 2,2-dimethylchroman-4-one **2a** is formed in fairly good yields when the reaction is carried out at 60 °C (Table 4). The success of the *oxa*-Michael addition reaction in the ground state can be ascribed to the polarization of the double bond, due to conjugation with the ketone group that determines the occurrence of the nucleophilic attack of the hydroxyl group exclusively at C(3) of the 3-methyl acrylic moiety (reactivity of α,β-ethylenic carbonyl compounds).[14] Therefore, our results show that the nucleophilicity of the hydroxy group in synthon **2b** is enough for promoting the nucleophilic attack exclusively at C(3) to achieve the intramolecular cyclization process under thermal condition.

In this regard, we selected and irradiated esters **3** and **4** in cyclohexane, acetonitrile and methanol with the aim to show that the cyclization reaction of the *ortho*-regioisomers to the corresponding 2,2-dimethylchroman-4-ones takes place during the irradiation of the esters. Since the *ortho*-regioisomers **3b** and **4b** show a characteristic absorption band around 350 nm, the irradiation of the esters were followed by UV-visible absorption spectroscopy. Fig. 3 shows nicely the rapid formation of the *ortho*-regioisomers and their consumption to the formation of the corresponding 2,2-dimethylchroman-4-one derivatives (**3a** and **4a**) during the irradiation of the esters when the solvent is cyclohexane and acetonitrile. In the same figure the formation of the 2,2-dimethylchroman-4-one derivatives are also shown. Instead, when the solvent is methanol, the formation of the *ortho*-regioisomers are also fast but their consumption are noticeable slower and consequently, a slow formation of the 2,2-dimethylchroman-4-one derivatives are observed.

The profiles shown in Fig. 3 are in agreement with the proposed reaction mechanism described in Scheme 4. The formation of the 2,2-dimethylchroman-4-ones from the *ortho*-regioisomers in cyclohexane and acetonitrile takes place through an ESIPT process followed by a thermal 6π-electrocyclization reaction (***Path (b)***; Scheme 4) while the *ortho*-regioisomers are formed by the photo-Fries rearrangement of the corresponding esters (***Path (a)***; Scheme 4). On the other hand, the slow consumption profile of the *ortho*-regioisomers (**3b** and **4b**) during the irradiation in methanol of esteres **3** and **4**, respectively, implies how significative is the disruption of the intramolecular hydrogen bonding in the *ortho*-regioisomers disfavoring the 6π-electrocyclization reaction (***Path (b)***; Scheme 4) and favoring the intramolecular *oxa*-Michael addition reaction (***Path (c)***; Scheme 4).

3. Conclusions

Esters **1**–**4** undergo the photo-Fries rearrangement reaction upon irradiation with 254 nm wavelength providing the *ortho* and

para regioisomers, the corresponding phenols and the 2,2-dimethylchroman-4-one when the photoreaction is carried out in different solvents at room temperature. Polycyclic aryl and heteroaryl esters (**6**–**9**) show a similar photochemical behavior when are irradiated with 254 nm and 313 nm wavelength rendering similar photoproduct distribution. These photoreactions take place from the lowest singlet excited state with quantum yields ranging from 0.01 to 0.15. In the case of ester **5** the lowest triplet excited state is efficiently populated and the photochemical behavior turned out quite different providing the *p*-nitrophenol as the solely photoproduct in all the solvents used.

Also, we were able to demonstrate that the *ortho* regioisomers are converted to the corresponding 2,2-dimethylchroman-4-one derivatives under photochemical or thermal conditions depending on the nature of the reaction medium. Thus, a 6π-electrocyclization process from the *trans*-keto form of the *ortho* regioisomer after an excited state intramolecular proton transfer (ESIPT) process is involved in the formation of the 2,2-dimethylchroman-4-one derivatives when the solvents are cyclohexane and acetonitrile (***Path (b)***; Scheme 4). On the other hand, when the solvent is methanol, production of 2,2-dimethylchroman-4-one derivatives can be achieved mainly through an intramolecular *oxa*-Michael addition reaction, a thermal process, that takes place during the photoreaction (***Path (c)***; Scheme 4). However, a photoinduced *trans*-keto form formation followed by a thermal 6π-electrocyclization process can participate with sluggish quantum efficiency. Further experiments related to the photochemical behavior of a series of substituted (hetero)aryl 3-methyl-2-butenoate esters in homogeneous and heterogeneous media are in course in our laboratory.

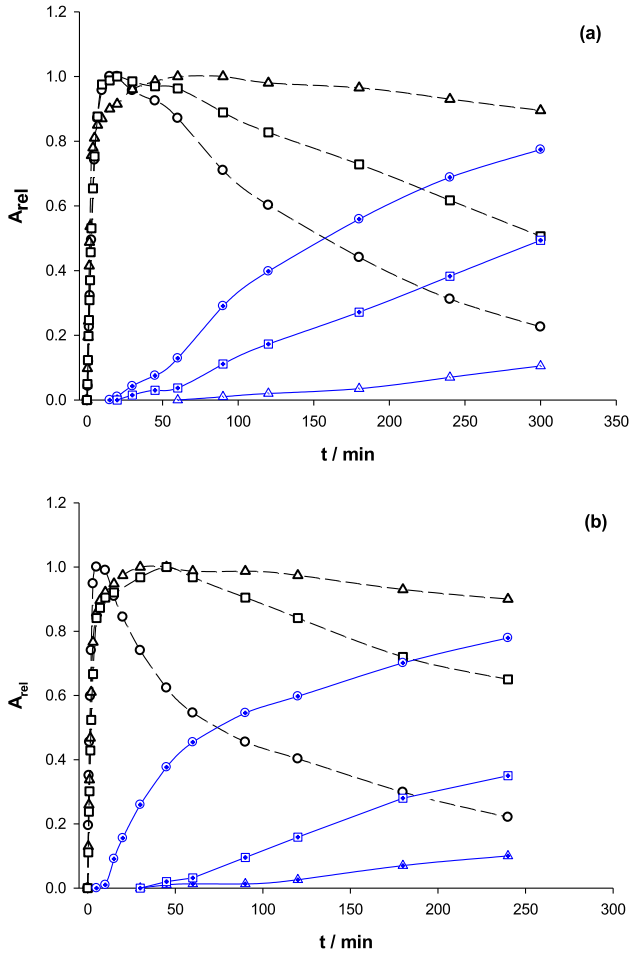


Fig. 3. Relative absorbance (A_{rel}) profiles against time of compounds (a) **3a** and **3b** and (b) **4a** and **4b** upon irradiation of esters **3** and **4** in different solvents. Solvents: ○ cyclohexane; Δ methanol; □ acetonitrile. Unfilled black symbols belong to the *ortho*-regioisomers and dotted blue symbols belong to 2,2-methylchroman-4-one derivatives.

4. Experimental

4.1. General information

3,3-Dimethylacryloyl chloride, phenol, 4-methyl-, 4-phenoxy-, 4-chloro-, 4-nitrophenol, oxine and 3,4-methylenedioxyphenol were purchased from *Aldrich* and were used without further purification. α-Naphthol and β-naphthol were purchased from *Aldrich* and were purified by column chromatography. Spectrograde solvents were obtained from *J. T. Baker* and were used as received. The esters **1**–**9** were synthesized in our laboratory according to the procedure described in the literature.[18,19] Melting Points were determined on a Fisher Jones apparatus and are not corrected. ^{1}H and ^{13}C NMR spectra were registered on a Bruker AC-200 spectrometer; chemical shifts) (δ) are reported in part per million (ppm), relative to internal tetramethylsilane. Coupling constant (J) values are given in Hz. The measurements were carried out using the standard pulse sequences. GC analysis was carried out on a Hewlett Packard 5890 gas chromatograph using an Ultra 2 capillary chromatographic column. For esters **1**–**6**, the chromatograms were recorded with the following program: *initial temperature*: 100 °C, 2 min; *rate*: 10 °C.min^{-1}; *final temperature*: 250 °C, 10 min. For esteres **7**–**9**, the chromatograms were recorded as follows: *initial temperature*: 150 °C, 2 min; *rate*: 10 °C.min^{-1}; *final temperature*: 250 °C, 15 min. Reverse phase HPLC analysis was carried out on a JASCO PU 1580 with a UV detector PU 1575 using a RP-18 reverse chromatographic column (Supelco; eluent: MeCN–H_2O mixtures; flow: 1 mL min^{-1}; detector: UV, λ 230 and 260 nm). The chromatographic runs were conducted in the presence of biphenyl as internal standard. UV absorption spectra were obtained using a Shimadzu UV-1203 UV-visible spectrophotometer. All the measurements were made with 1 cm stopped quartz cells at 298 K. Fluorescence measurements were performed using a Hitachi F500 spectrofluorimeter. Corrected fluorescence spectra, measured at room temperature, were recorded in a 1 cm path length (in both the excitation and emission directions) quartz cell. The fluorescence quantum yields (ϕ_f) at room temperature were determined from the corrected fluorescence spectra, integrated over the entire emission profile, using naphthalene as reference (λ_{exc}: 285 nm; λ_{max}(fluo): 318 nm; ϕ_f: 0.040).[21] The error of the measurements was ±10%. To avoid inner filter effects the absorbance of the solutions, at the excitation wavelength, was kept below 0.10.

4.2. Quantum yields

Quantum yields were determined using potassium ferrioxalate as an actinometer.[26] A 6.0×10^{-3} M solution of $K_3Fe(C_2O_4)_3\cdot3H_2O$ was prepared for measurements at 254 and 313 nm. The aryl 3-methyl-2-butenoate esters (1.0×10^{-4} M) was dissolved in the selected organic solvent and irradiated simultaneously with the actinometer using a medium pressure Hg lamp (Hereaus TQ150-Z_3) and an interference filter (Schott, band path 5 nm) which gives a nearly parallel beam at 313 nm for compounds **6**–**9** or using four 18 W lamps (Philips) which gives a nearly parallel beam at 254 nm for compounds **1**–**5**. The conversions of the esters were monitored by GC and were lower than 10%.

4.3. Photoirradiations

General procedure for aryl 3-methyl-2-butenoate esters. Solutions of esters (**1**–**9**; 0.106 mmol) were prepared in different organic media (100 mL). Photoirradiations of the esters were performed as follow: i) *analytical scale*: a 2 mL aliquot of solution was placed in a stoppered 3 mL quartz cell and degassed with argon for 20 min; ii) *preparative scale*: a 65 mL aliquot was placed in a stoppered 100 mL Erlenmeyer quartz flask and degassed with argon for 30 min. The quartz cell as well as the Erlenmeyer quartz flask were placed in a home made optical bench provided with the possibility to use two or four lamps. The solutions of the esters were stirred during the irradiation process. Irradiations with λ_{exc}=313 nm were carried out with four phosphorous–coated lamps (HelioQuartz, each of 18 Watts) that give a nearly parallel beam at 313 nm. Irradiations with λ_{exc}=254 nm were carried with four germicide lamps (Philips, each of 20 Watts).

The progress of the reaction was monitored by four different methods: (i) UV spectroscopy; (ii) TLC [eluent: hexane–ethyl acetate (8: 2 v/v); spots were visualized with UV light (254 and 366 nm) and with I_2]; (iii) GC analysis (Ultra 2 capillary column); (iv) HPLC analysis (RP-18 column).

In order to isolate, purify and characterize the photoproducts formed, preparative photolysis (*preparative scale*) was conducted according to the following procedure. A solution of ester (0.106 mol) in cyclohexane (65 mL) was placed in a stoppered Erlenmeyer quartz flask and was irradiated with stirring under an Ar atmosphere employing the optical bench above described. The irradiation time varied depending on the ester studied and the progress of the reaction was monitored by TLC and GC as well as HPLC. When the conversion of the starting material reached the appropriate level, the photolyzed solution was evaporated carefully to dryness under reduced pressure. The yellowish solid residue obtained was worked up by silica gel column chromatography (eluent: hexane 100% followed by hexane–ethyl acetate mixtures). From the eluted fractions, the photoproducts were isolated and characterized by mean of physical and spectroscopic methods.

Photoproducts **1a**–**1d**,[18] **2a**,[14b] **2b**,[14b] **3a**,[19] **4a**,[19] **6a**,[18] **6b**,[20] **7a**,[18] **7b**,[18] **7d**,[32] **8a**[18] and **9a**[18] as well as the esters **1**,[18] **2**,[24b] **3**,[19] **4**[24b] and **5**[19] show similar physical and spectroscopic properties as those reported in the literature.

1-(2-Hydroxy-5-phenoxyphenyl) isobutenyl ketone (**3b**): colorless oil; δ_H(200 MHz; $CDCl_3$; Me_4Si) 12.63 (s, 1H, ArOH), 7.50 (d, $J_{3,5}$=2.8 Hz, 1H, H-3), 7.37–7.26 (m, 1H, H-4′), 7.19 (dd, $J_{3,5}$=2.6 and $J_{5,6}$=8.8 Hz, 1H, H-5), 7.09 (d, $J_{5,6}$=8.8 Hz, 1H, H-6), 7.02–6.92 (m, 2H, H-2′ and H-3′), 6.68 (s, 1H, *H*–C=C), 2.27 (s, 3H, CH_3), 2.02 (s, 3H, CH_3). δ_C(50 MHz, $CDCl_3$, Me_4Si) 195.5 (C=O), 159.8 (C-1′), 159.0 (C-1), 158.5 (C-4), 147.4 (*C*=C–H), 129.8 (C-3′), 128.6 (C-5), 122.5 (C-4′), 120.5 (C-2), 120.7 (C-3), 119.7 (C-2′), 119.6 (C-6), 117.9 (C=*C*–H), 28.3 (CH_3), 21.5 (CH_3). *Anal.* Found: C, 76.03; H, 5.97. $C_{17}H_{16}O_3$ requires C, 76.10; H, 6.01%.

1-(2-Hydroxy-5-chlorophenyl) isobutenyl ketone (**4b**): colorless oil;[33] δ_H(200 MHz; $CDCl_3$; Me_4Si) 12.70 (1H, Ar–OH), 7.35 (1H, dd, $J_{5,6}$ 9.0 and $J_{3,5}$ 2.2, 5-H), 7.32 (1H, d, $J_{3,5}$ 2.2, 3-H), 7.05 (1H, d, $J_{5,6}$ 9.0, 6-H), 5.91 (1H, s, C=C–H), 2.24 (3H, s, Me), 2.00 (3H, s, Me). δ_C(50 MHz, $CDCl_3$, Me_4Si) 195.0 (C=O), 160.6 (1-C), 149.2 (9-C), 135.5 (4-C), 129.3 (3-C), 123.2 (5-C), 120.1 (2-C), 119.4 (8-C), 114.9 (6-C), 27.7 (Me), 20.5 (Me).

1-(2-hydroxy-5-nitrophenyl) isobutenyl ketone (**5b**) yellowish oil; δ_H(200 MHz; $CDCl_3$; Me_4Si) 13.10 (1H, Ar–OH), 8.27 (1H, d, $J_{5,6}$ 8.3, 6-H), 8.10 (1H, d, $J_{3,5}$ 2.1, 3-H), 6.91 (1H, dd, $J_{3,5}$ 8.3 and $J_{5,6}$ 2.1, 5-H), 5.97 (1H, s, C=C–H), 2.17 (3H, s, Me), 1.97 (3H, s, Me). δ_C(50 MHz, $CDCl_3$, Me_4Si) 195.0 (C=O), 166.1 (1-C), 149.6 (9-C), 140.1 (4-C), 132.4 (3-C), 124.8 (5-C), 118.0 (2-C), 117.3 (8-C), 117.4 (6-C), 27.9 (Me), 21.4 (Me). *Anal.* Found: C, 59.81; H, 5.05; N, 6.28. $C_{11}H_{11}NO_4$ requires C, 59.73; H, 5.01; N, 6.33%.

1-(2-Hydroxynaphthyl) isobutenyl ketone (**8b**): mp 110 °C; δ_H (200 MHz; $CDCl_3$; Me_4Si) 15.20 (1H, br s, OH), 8.43 (1H, m, 8-H), 7.80–7.12 (5H, m, Ar–H), 6.80 (1H, m, C=C–H), 2.20 (3H, s, Me), 2.00 (s, 3H, Me). δ_C(50 MHz, $CDCl_3$, Me_4Si) 182 (C=O), 166.9 (2-C), 149.7 (3′-C), 139.3 (4-C), 134.3 (8a-C), 131.9 (5-C), 129.7 (7-C), 127.8 (4a-C), 125.4 (8-C), 125.1 (6-C), 121.4 (3-C), 117.2 (2′-C), 113.5 (1-C), 27.9 (Me), 23.1 (Me). *Anal.* Found: C, 79.61; H, 6.21. $C_{15}H_{14}O_2$ requires C, 79.62; H, 6.24%.

1-(8-Hydroxyquinolyl) isobutenyl ketone (**9b**): mp 143 °C. δ_H(200 MHz; $CDCl_3$; Me_4Si) 11.8 (1H, br s, OH), 8.71 (1H, dd, $J_{2,3}$ 5 and $J_{2,4}$ 2, 2-H), 7.97 (1H, d, $J_{6,5}$ 8.5, 6-H), 7.89 (1H, dd, $J_{4,3}$ 5 and $J_{4,2}$ 2, 4-H), 7.54 (1H, d, $J_{5,6}$ 8.5, 5-H), 7.32 (1H, q, $J_{3,2}$ 5, 3-H), 6.37 (1H, s, C=C–H), 2.17 (3H, s, Me), 1.97 (3H, s, Me). δ_C(50 MHz; $CDCl_3$; Me_4Si) 178.1 (C=O), 162.6 (8-C), 150.9 (1-C), 150.0 (3′-C), 141.8 (4a-C), 139.4 (3-C), 138.3 (8a-C), 126.9 (6-C), 124.6 (5-C), 122.1 (2-C), 121.2 (7-C), 117.3 (2′-C), 28.0 (Me), 23.1 (Me). *Anal.* Found: C, 73.97; H, 5.79; N, 6.14. $C_{14}H_{13}NO_2$ requires C, 73.99; H, 5.77; N, 6.16.

*General procedure for the photochemical cyclization of 1-(2-hydroxy-5-methylphenyl) isobutenyl ketone (**2b**).* Solutions of ketone **2b** (0.10 mmol) were prepared in different organic media (100 mL). Photoirradiations were performed in *analytical scale*: a 2 mL aliquot of solution was placed in a stoppered 3 mL quartz cell and degassed with argon for 20 min. The quartz cell was placed in a home made optical bench provided with four germicide lamps (Philips, each of 20 Watts) that give a nearly parallel beam at 254 nm and the solutions were stirred during the irradiation process. The progress of the reaction was monitored by UV spectroscopy, TLC [eluent: hexane–ethyl acetate (8: 2 v/v); spots were visualized with UV light (254 and 366 nm) and with I_2] and GC analysis (Ultra 2 capillary column).

*General procedure for the thermal cyclization of 1-(2-hydroxy-5-methylphenyl) isobutenyl ketone (**2b**).* Solutions of ketone **2b** (0.10 mmol) were prepared in different organic media (100 mL) and a 2 mL aliquot of solution was placed in a stoppered 3 mL quartz cell and degassed with argon for 20 min. The quartz cell was placed in a thermal bath at 60 °C. The progress of the reaction was monitored by UV spectroscopy, TLC [eluent: hexane–ethyl acetate (8: 2 v/v); spots were visualized with UV light (254 and 366 nm) and with I_2] and GC analysis (Ultra 2 capillary column).

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