Anal. Calcd for $C_{11}H_{15}N_3O_4$: C, 52.17; H, 5.97; N, 16.59. Found: C, 52.24; H, 5.93; N, 16.56.

2,3′-(Phenylimino)-1-(3′-deoxy-β-D-lyxopyranosyl)uracil (4d) and 1-(3′-Anilino-3′-deoxy-β-D-lyxofuranosyl)uracil (5a). A mixture of **3f** (300 mg, 1.0 mmol), 6 N NaOH (3.8 mL), and EtOH (3.8 mL) was heated at 75–80 °C strictly as for the above cases. TLC-monitoring showed that an extremely mobile substance was forming together with the anticipated, slightly less polar product. After 21 h, the reaction was quenched with acetic acid and the mixture thoroughly evaporated. The residual solid was pulverized, heated to reflux in hot acetone/MeOH (9:1) (60 mL), and filtered after being cooled to room temperature. The filter-cake was again extracted with hot acetone (30 mL). The combined solutions were evaporated and the residue chromatographed on a silica gel plate (20 × 20 cm; $CHCl_3$/MeOH, 85:15, developed 3 times). The slower moving band was eluted with MeOH and the obtained solid recrystallized from MeOH to afford 102 mg (34.0%) of **4d** as a methanolate after drying under high vacuum at 80 °C for 4 h, mp above 300 °C.

Anal. Calcd for $C_{15}H_{15}N_3O_4 \cdot CH_3OH$: C, 57.65; H, 5.75; N, 12.61. Found: C, 57.58; H, 5.67; N, 12.75.

On the other hand, elution of the faster moving fraction with acetone gave a solid, which was recrystallized from acetone to afford 98 mg (30.7%) of **5a** as a monohydrate, mp 225–226 °C.

Anal. Calcd for $C_{15}H_{15}N_3O_4 \cdot H_2O$: C, 56.42; H, 5.37; N, 13.16. Found: C, 56.54; H, 5.37; N, 13.05.

2,3′-[(p-Methoxyphenyl)imino]-1-(3′-deoxy-β-D-lyxopyranosyl)uracil (4e) and 1-(3′-Anisidino-3′-deoxy-β-D-lyxofuranosyl)uracil (5b). A mixture of **3g** (110 mg, 0.33 mmol), 5 N NaOH (1 mL) and MeOH (1 mL) in an argon-filled pressure tube was stirred at 75–80 °C for 45 h. After neutralization with 0.8 N HCl, MeOH (10 mL) was added and the inorganic salt filtered off. The filtrate was concentrated and chromatographed on a silica gel plate (20 × 20 cm, $CHCl_3$/MeOH, 8:2). The slower moving band gave 23 mg (20.9%) of **4e**, mp 253–255 °C, after recrystallization from MeOH.

Anal. Calcd for $C_{16}H_{17}N_3O_5$: C, 58.00; H, 5.17; N, 12.68. Found: C, 57.87; H, 5.35; N, 12.63.

Similar processing with the faster running fraction afforded 27 mg (23.3%) of **5b** as crystals of mp 194–195 °C (MeOH).

Anal. Calcd for $C_{16}H_{19}N_3O_6$: C, 55.01; H, 5.48; N, 12.03. Found: C, 55.27; H, 5.52; N, 11.83.

2,3′-Imino-1-(3′-deoxy-β-D-lyxopyranosyl)uracil (4f). A solution of **4a** (25 mg, 0.098 mmol) and MCPBA (26 mg, 0.15 mmol) in acetic acid (0.5 mL) was stirred at room temperature for 1 h and 10 min. After the solvent was evaporated off, the residue was repeatedly coevaporated with methanol and then thoroughly digested with dry ether. The sparingly soluble solid was collected and repeatedly recrystallized from methanol to give 12 mg (54.4%) of **4f** as powdery crystals, mp above 300 °C.

Anal. Calcd for $C_9H_{11}N_3O_4$: C, 48.00; H, 4.92; N, 18.66. Found: C, 48.21; H, 5.08; N, 18.40.

Acknowledgment. We thank Prof. Y. Sawaki at this Faculty for an instructive discussion on the reaction mechanism.

Registry No. **1**, 56687-59-3; **2a**, 90597-04-9; **2b**, 90597-05-0; **2d**, 103251-64-5; **2e**, 103251-65-6; **2f**, 103251-66-7; **2g**, 104531-58-0; **2h**, 103251-67-8; **3a**·HCl, 104597-34-4; **3b**, 90597-07-2; **3c**, 56615-08-8; **3d**, 103251-68-9; **3e**, 103251-69-0; **3f**, 103251-70-3; **3g**, 104531-59-1; **3h**, 104531-60-4; **4a**, 103251-72-5; **4b**, 103251-73-6; **4c**, 103251-74-7; **4d**, 103251-75-8; **4e**, 104531-61-5; **4f**, 104548-71-2; **5a**, 104531-62-6; **5b**, 104531-63-7; methylhydrazine, 60-34-4; methylamine hydrochloride, 593-51-1; ethylamine hydrochloride, 557-66-4; aniline, 62-53-3; *p*-anisidine, 104-94-9; ethyl glycinate hydrochloride, 623-33-6.

Photochemical Cyclization of 2-Alkyl-3-aryl-2-cyclohexenones and 2-Alkoxy-3-aryl-2-cyclohexenones

Alexandre Feigenbaum, Yves Fort, Jean-Pierre Pete,* and Denise Scholler

Laboratoire de Photochimie, Unité Associée au CNRS No. 459, Université de Reims Champagne-Ardenne, 51062 Reims Cédex, France

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Irradiation at 254 nm of 2-alkyl-3-aryl-2-cyclohexenones and 2-alkoxy-3-aryl-2-cyclohexenones leads to oxidative cyclization involving the aryl group and the 2-alkyl or the 2-alkoxy substituent. This cyclization cannot be sensitized by triplet sensitizers nor trapped by triplet quenchers. A solvent effect and a concentration dependence have been detected for 2-ethyl-3-phenyl-2-cyclohexenone and for 2-methoxy-3-phenyl-2-cyclohexenone, which are indicative of a complex reaction mechanism.

The photochemistry of conjugated enones and especially cyclohexenones has attracted the efforts of many photochemists, due to their numerous synthetic applications. Among the reactions available to excited cyclohexenones, photocycloadditions[1] and rearrangements to lumiproducts[2] have received particular attention. Hydrogen abstraction by conjugated cyclohexenones is far less important than for aromatic ketones, although it can sometimes become the major process in hydrogen-atom-donating solvents.[3] By contrast, intramolecular γ-hydrogen abstraction is a general process for α-substituted conjugated enones; depending on the nature of the substituent X, cyclobutyl,[4]

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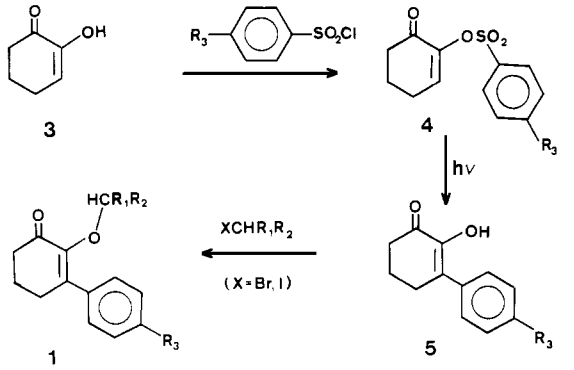
0022-3263/86/1951-4424$01.50/0

Table I. Photocyclization of 2-Alkoxy- and 2-Alkyl-3-aryl-2-cyclohexenones

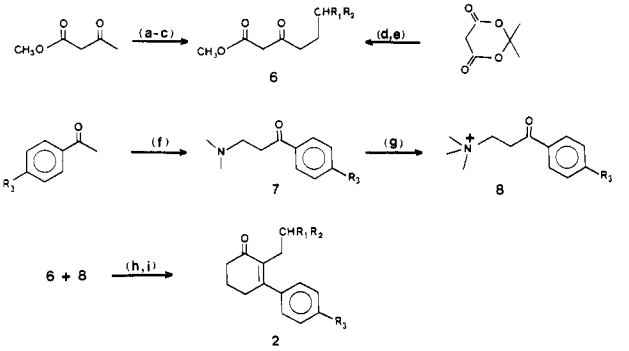
starting[a] enone	R_1	R_2	R_3	irradtn time, h	product formed	starting material consumed, %	yield,[b] %
1a	H	H	H	0.75	**9a**	80	50
1b	CH_3	H	H	1	**9b**	90	35
1c	$CO_2C_2H_5$	H	H	1.5	**9c**	70	20
1d	H	H	CH_3O	0.75	**9d**	70	30
1e	CH_3	H	CH_3O	1	**9e**	70	20
2a	H	H	H	20	**10a**	43	40
2b	CH_3	H	H	14	**10b**	37	40
2c	C_2H_5	H	H	7	**10c**	60	25
2d	CH_3	CH_3	H	4	**10d**	75	15
2e	H	H	CH_3O	14	**10e**	47	15

[a] Concentration 10^{-2}M; irradiation at 254 nm. [b] The chemical yield is based upon the amount of reacted starting material.

Scheme I. Synthesis of 2-Alkoxy-3-aryl-2-cyclohexenones 1

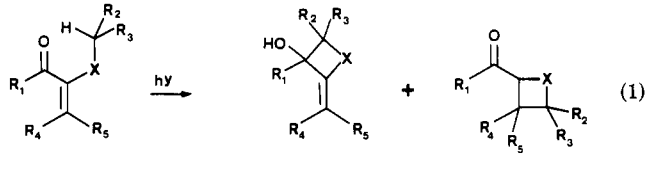


Scheme II. Synthesis of 2-Alkyl-3-aryl-2-cyclohexenones 2[a]



[a] (a) NaH, THF, 0 °C; (b) *n*-BuLi, hexane, 0 °C; (c) $R_1R_2CHCH_2X$, THF; (d) $R_1R_2CH(CH_2)_2COCl$, C_5H_5N, CH_2Cl_2; (e) CH_3OH, reflux; (f) $CH_2{=}{}^+N(CH_3)_2$, $CF_3CO_2^-$, CF_3CO_2H; (g) CH_3I, ether; (h) $C_2H_5O^-Na^+$, C_2H_5OH; (i) KOH, reflux.

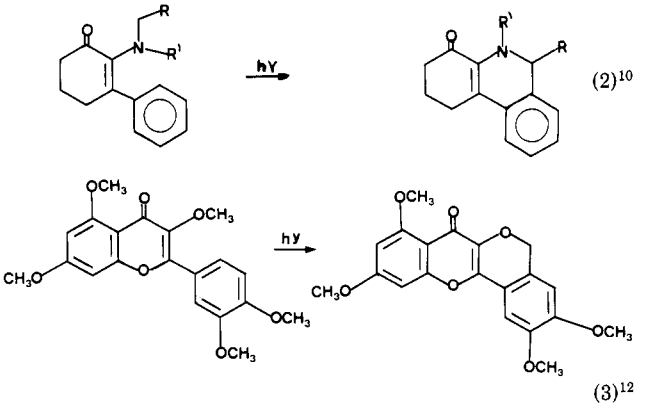
oxetanyl,[5] and azetidinyl[6] derivatives can be produced in quite good yields (eq 1).



(1)

X = CH_2, O, NR'

However, the course of the reaction is very sensitive to the nature of the substituents, and α-ketoaziridines[7] or rearranged products[8,9] can also be obtained. Furthermore, arylated enones (R_5 = aryl) can lead to cyclization of the side chain onto the aromatic ring with formation of a new six-membered ring (eq 2 and 3). Thus oxidative photo-



(2)[10]

(3)[12]

cyclization is observed with 2-(alkylamino)-3-arylcyclohexenones,[10] α-(dialkylamino)chalcones,[11] and flavone derivatives.[12] Surprisingly, α-methoxychalcone gives mainly an oxetanyl derivative and no product resulting from cyclization on the arene ring was detected (eq 4). It

(4)[13]

was proposed that the difference of reactivity between flavones and chalcone derivatives was caused by conformational and steric effects.[13]

The purpose of this work was (1) to try to generalize the oxidative photocyclization with α-substituted cyclohexenones whose conformational mobility is similar to that of flavones and (2) to obtain mechanistic information on the reaction and hopefully on the oxidation step. Hence, we studied the photochemical reactivity of 2-alkoxy- and 2-alkyl-3-arylcyclohexenones 1 and 2.

Results

Since it is well-known[14] that hydrogen abstraction reactions are very sensitive to the substituents on the γ

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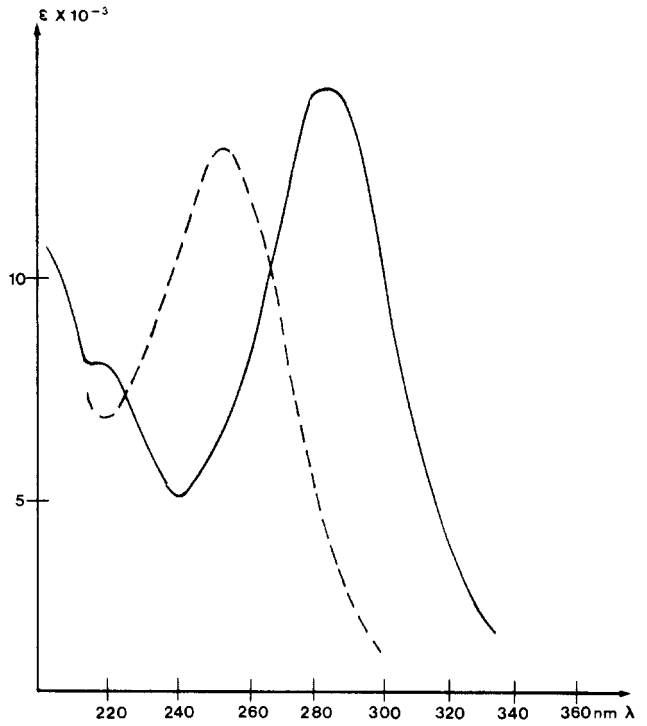

Figure 1. UV absorption spectra of **1a** (—) and **2a** (- - -) in methanol.

carbon, we prepared enones having primary or secondary γ hydrogens on the side chain (see Table I). We also prepared **1c** which might lead to a biradical having on the side chain a captodative radical site and perhaps to a better cyclization efficiency. In order to see the influence of the nature of the aryl group, we also prepared enones where the aryl is a phenyl or an anisyl group.

1. Preparation of the Starting Enones. Compounds **1** were obtained by the sequence in Scheme I.[15]

The preparation of the enones **2** was best realized according to Scheme II. Depending on the substitution, the keto ester **6** was prepared from methyl acetylacetate[16] or from Meldrum's acid.[17] In basic medium, **6** was condensed with the ammonium salt **8**[18] to give directly enone **2**.

Enones **1** and **2** have several absorption bands in the UV region and the spectra are very sensitive to the nature of the substituent on C-2; as shown in Figure 1 there is a very important shift of the (π,π^*) transition when the alkyl is replaced by an alkoxy group. Comparison of the (π,π^*) absorption maximum for **2a** with the position of the absorption for cinnamyl derivatives and with the calculated value[19a] indicates an hypsochromic shift of this absorption and a resonance inhibition in **2a**. We can conclude that

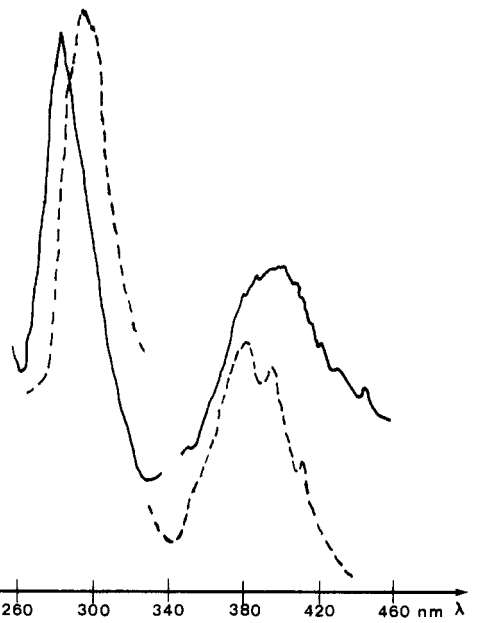

Figure 2. Emission spectrum of **2a** (—) (10^{-4} M) in methanol and of benzene (- - -) (excitation wavelength, 243 nm).

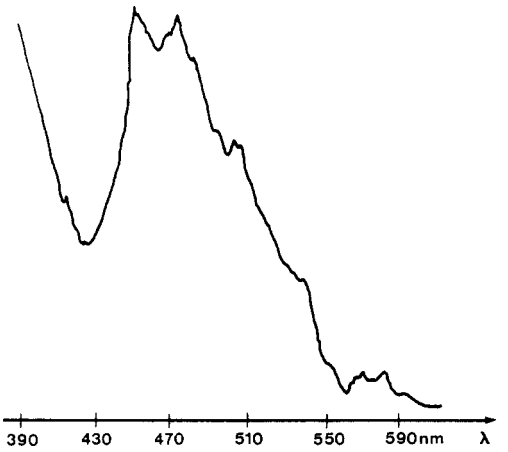

Figure 3. Emission spectrum of **2a** (10^{-4} M) at 77 K (excitation wavelength, 321 nm).

steric hindrance between the 3-aryl group and the 2-alkyl substituent leads to a considerable deformation of the conjugated chromophore and to a significant angle between the planes of the enone and aryl chromophores.[20] With 2-alkoxy substituents, steric hindrance to conjugation is much less important, since the maximum for **1a** at 283 nm is quite near the predicted value for a cinnamyl system.[20b]

The emission spectrum of **2a** at low temperature is compared with the emission spectra obtained for benzene under the same conditions (Figures 2 and 3). The emission at long wavelength (λ >430 nm) by excitation at 320 nm of the (n,π^*) transition of the carbonyl group was attributed to phosphorescence of the enone chromophore by analogy with the emission observed under the same conditions with testosterone derivatives.[21] No emission could be detected for **1a** at room temperature or even at 77 K. Neither the absorption spectra of **1a** and **2a** nor the emission spectrum of **2a** were affected by changes in concentration over a range from 10^{-2} to 10^{-4} mol L^{-1}.

2. Photolysis. When irradiated at 254 nm in deoxygenated methanol, **1a** and **2a** reacted quite rapidly and

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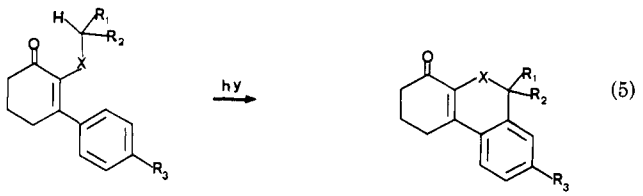
Table II. Quantum Yields for Appearance of 9a and 10a; Solvent and Wavelength Effects

reaction	solvent	λ irradn, nm	concn, M × L^{-1}	Φ^a	Φ_{rel}
1a → 9a	pentane	254	10^{-3}	0.30	1
	ether	254	10^{-3}	0.25	0.84
	ethanol	254	10^{-3}	0.24	0.8
	methanol	254	10^{-3}	0.21	0.71
	CH_3CN	254	10^{-3}	0.20	0.66
	pentane	313	10^{-3}	0.13	0.43
	pentane	366	10^{-3}	0.10	0.3
2a → 10a	methanol	254	1.25×10^{-3}	0.007	0.023
	isopropyl alcohol	254	1.25×10^{-3}	0.0025	0.0083
	CH_3CN	254	1.25×10^{-3}	0.0026	0.0087
	hexane	254	1.25×10^{-3}	0.0035	0.0012
	ether	254	1.25×10^{-3}	0.0021	0.007
	benzene	254	1.25×10^{-3}	0.001	0.0033
	methanol	254	1.5×10^{-2}	0.028	0.092
	methanol	313	2.5×10^{-2}	0.0063	0.021
2b → 10b	methanol	254	10^{-4}	0.0075	0.025

[a] The quantum yields have been determined by extrapolation to 0% conversion from experimental values obtained from 0 to 10% conversion of starting material.

yielded a new product which could be cleanly isolated from a complex mixture of polar compounds. The results are summarized in eq 5 and in Table I. The chemical yield



(5)

1 X = O
2 X = CH_2

9 X = O
10 X = CH_2
11 X = NR'

of each isolated product was very sensitive to the conversion. Yields reported in Table I for the preparative experiments did not exceed 50% for **1** or 40% for **2**. Structures of the isolated products **9** and **10**, determined unambiguously from spectroscopic data, especially NMR and mass spectra, indicated that they resulted from oxidative photocycloaddition of the chain on the aryl group. The IR and UV spectra confirm the presence of a conjugated carbonyl group. The same oxidative photocyclization occurred also in other solvents such as hexane, benzene, ether, acetonitrile, and alcohol (Table II).

Since the reaction involved loss of two hydrogen atoms, we checked whether the yields could be improved in the presence of oxygen. We carried out irradiations of **1a** and **2a** with solutions under an oxygen atmosphere or carefully deoxygenated by continuous bubbling of pure argon. Almost the same yields of photocyclized products were obtained. Furthermore, irradiation of **2a** at 254 nm in the presence of small amounts of iodine did not increase the chemical yield in **10a**.

When the irradiations of **1a** and **2a** were run at 313 nm or at 366 nm on a preparative scale, the photoproducts could not be isolated. This was rather intriguing since irradiation at these wavelengths essentially populates the $^1(n,\pi^*)$ states of enones, which are known to be the reactive excited states in γ-H abstractions.[4-6] Reactions mixtures were analyzed by HPLC in order to verify whether the photoproducts were formed for low conversion ratios. We found that **9a** was formed from **1a** at 313 nm and 365 nm when the conversion yield was less than 5%; at 366 nm the

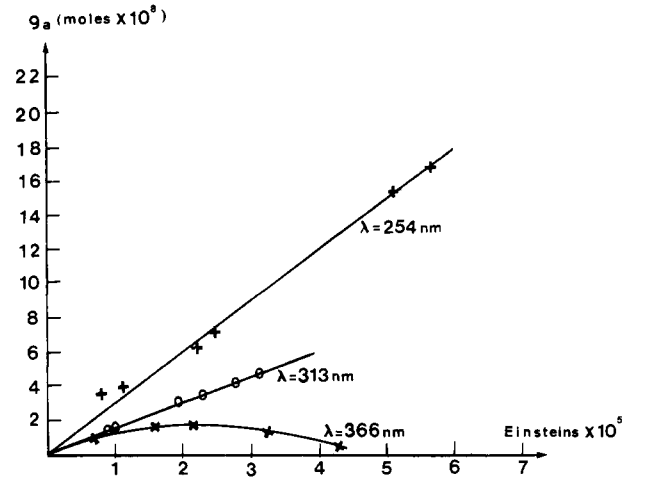


Figure 4. Dependence of the amount of **9a** to the light absorbed for less than 5% starting material consumed (4×10^{-6} mol **1a** irradiated).

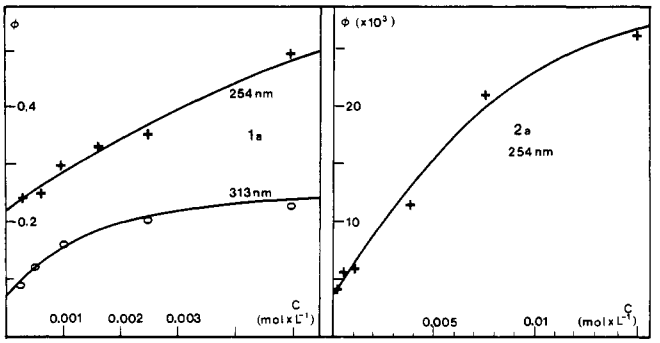


Figure 5. Dependance of Φ on *c* for **1a** (in pentane) and **2a** (in methanol).

amount of **9a** was maximum for 0.5% conversion (Figure 4). On the other hand, **10a** was present in the reaction mixture at 313 nm when conversion was lower than 5%, but **10a** could not be detected at 366 nm. **9a** and **10a** have much larger extinction coefficients at 313 and 366 nm than **1a** and **2a**, respectively. Even for a low conversion of the starting material an important part of the light is absorbed by the photoproducts. We verified that **9a** and **10a** were rapidly photodegradated when irradiated at these wavelengths, giving complex reaction mixtures.

To get more information, we irradiated **1a** and **2a** and determined the quantum yield of appearance of photoproducts **9a** and **10a** for low conversions (see Figure 4 and Table II). Our results indicate that there is a wavelength effect, since the initial quantum yields were different depending on the wavelength (see Table II): for **9a**, the quantum yield of the reaction measured at 254 nm (Φ = 0.30) was much higher than at 313 nm (Φ = 0.13) (see Table II). The quantum yield measured at 366 nm (Φ = 0.10) was quite similar to the value obtained at 313 nm.

The efficiency of the reaction was also sensitive to the solvent, but this solvent effect was much more pronounced for **2a**. The highest quantum yield values were obtained in pentane for **1a** and in methanol for **2a**. The quantum yield of the reactions increased significantly with concentration of starting enones, at any wavelength (Figure 5). The dependence of $^1/_\Phi$ on $^1/_c$ is classically a linear relationship when a bimolecular step is involved; however, for **1a** and **2a**, the relation between Φ and *c* seems to be more complex and we could not determine it (Figure 6).

We also monitored the reaction by recording the UV spectra of **1a** (6×10^{-4} M in methanol) at different irradiation times. The absorption bands of **9a** rapidly ap-

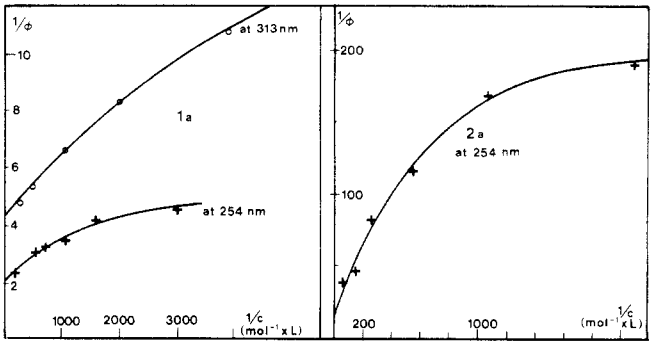


Figure 6. Dependance of $1/\Phi$ on $1/c$ for **1a** (in pentane) and **2a** (in methanol).

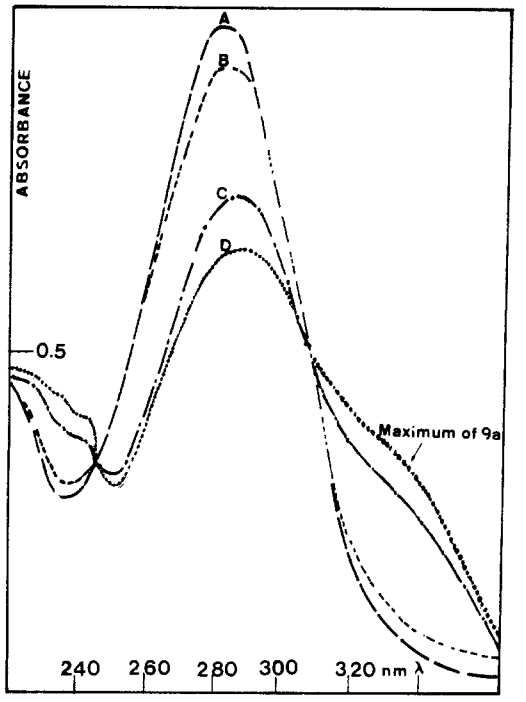


Figure 7. Evolution of the UV spectrum of **1a** in methanol at 0 °C for different irradiation times (irradiation wavelength, 254 nm): (A) before irradiation; (B) irradition time 1 min; (C) 2 min; (D) 3 min.

peared and the changes in the spectrum involved isobestic points (Figure 7), thus indicating the formation of a single new product.

In order to get additional information we tried to determine if the product of the photocyclization might result from a biphotonic process. However, the quantum yields for the transformations of **1a** and **2a** were not affected by light intensity.

When irradiation of **1a** was conducted on preparative scale, the deoxygenated solution was deep yellow after irradiation, but the yellow color disappeared gradually when the tube was left on the bench. When the solution was slightly heated, or exposed to air, the decoloration was very fast. This suggested that the color was due to an intermediate. We thus irradiated a cooled (0 °C), well deoxygenated solution of **1a** (2×10^{-2} M in methanol) and monitored the changes in the visible absorption spectra (Figure 8). After irradiation for a 3-min period, an intense band appeared at 390 nm, which disappeared on allowing the solution to warm up to room temperature or on opening the cell to air (Figure 8). This absorption band in the visible spectrum might suggest an intermediate unstable toward heat and oxygen. For longer irradiation times the band at 390 nm does not grow in intensity

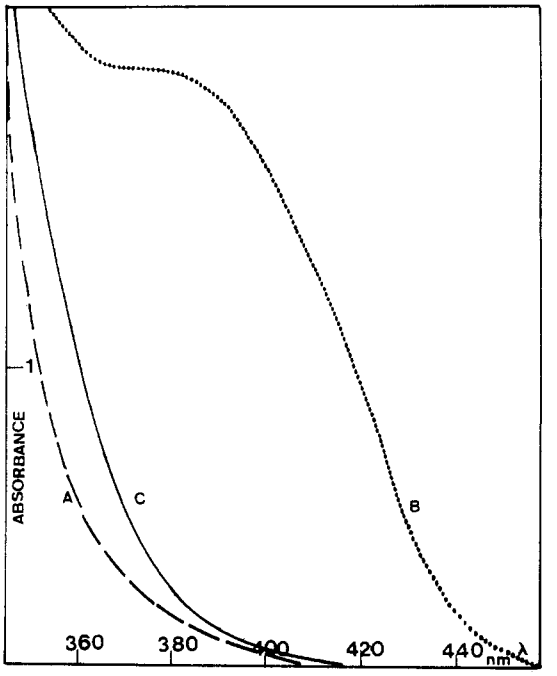


Figure 8. Evolution of the visible spectrum of **1a** in methanol at 0 °C for different irradiation times (irradiation wavelength, 254 nm): (A) before irradiation; (B) irradiation time 3 min; (C) 3 min and opening the cell to air.

probably because the intermediate also absorbs light. Despite our efforts, we could not find conditions allowing the characterization of an intermediate prior to formation of the cyclized product. The intermediate thus appears to be also light-sensitive. We also tried to trap the intermediate by adding immediately after irradiation to the cold solution trimethylsilyl chloride and triethylamine. However, no silylated enol ether could be detected in the reaction mixture.

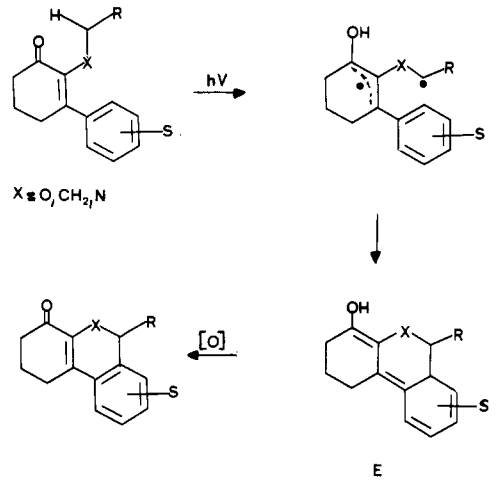
In order to determine the multiplicity of the reactive excited state, we tried to quench the reaction in the presence of triplet inhibitors. The presence of naphthalene (E_T = 245 kJ/mol) did not cause any modification of the quantum yield of the reactions of **1a** and of **2a**. At low temperature, we detected a phosphorescence for **2a** whose starting point allowed evaluation of the energy of the triplet excited state at about 290 kJ/mol in methanol. The energy transfer from **2a** excited in its triplet excited state to naphthalene should be controlled by the diffusion of molecules. The lack of inhibition for **2a** suggests that the observed cyclization occurs either in a singlet excited state or in a triplet state of very short lifetime.

To check if triplet states might be involved in the photocyclizations of **1a** and **2a**, we tried the use of sensitizers. However, benzophenone (E_T = 287 kJ/mol), *p*-methoxyacetophenone (E_T = 305 kJ/mol), and acetone (E_T = 330 kJ/mol) were not able to sensitize either of the two cyclizations. This suggests that the reaction is initiated in an excited singlet state.

Discussion

It has been observed previously that α-substituted cyclohexenones bearing no β-aryl substituent also show a similar photoreactivity.[4,5] Their photocyclizations could neither be sensitized nor quenched by triplet–triplet energy transfer although the cyclization products were shown to arise from γ-hydrogen abstraction on the side chain. For **1** and **2** the first step of the photocyclizations could also be a γ-hydrogen abstraction (Scheme III). This is in agreement with the observation of isosbestic points, which

Scheme III. Mechanism



indicate that a single product is formed at low conversion rates. But the strong dependence of the quantum yields on the concentration clearly shows that polymolecular steps should be involved.

We could get no evidence for association of starting compounds in the ground state nor of excimer formation, since neither the absorption spectra of **1a** and **2a** nor the emission spectrum of **2a** were affected by the enone concentration, and so, we do not know the nature of this polymolecular process.

The UV spectra of the enones **1a** and **2a** at high wavelengths exhibit the characteristic behavior of (n,π^*) absorptions: the (n,π^*) band appears as a shoulder, which is shifted to longer wavelengths when going from methanol to a hydrocarbon solvent. But the solvent effect on the quantum yield of cyclization is typical of γ-hydrogen abstraction reactions by ketones only for **2a**, since its highest value is obtained in methanol.[22] By contrast, the best quantum yield for **1a** is obtained in pentane. It should be noted, however, that in all cases, the solvent effect is small.

Varying the structures of the substrates by replacing hydrogen atoms of **1a** and **2a** by the substituents R_1, R_2, and R_3 listed in Table I had only little effect on the chemical yields of the cyclizations.

Furthermore, the photocyclization of **1** and **2** was sensitive to the wavelength, and **9a** was produced at low conversion rates at 313 nm and 254 nm as well. The selective excitation of the (n,π^*) transition of **1a** at 366 nm, the absence of sensitization and quenching in the presence of triplet sensitizers and quenchers, respectively, led us to conclude that the ^{1}(n,π^*) excited state should be able to abstract the γ-hydrogen on the side chain (Scheme III) and lead to a biradical. However, the wavelength effect on the quantum yield indicates that the same reaction can also be induced via a higher energy singlet state. Irradiation at 254 nm allows population of this state which leads to reaction and may also convert to S_1 by vibrational deactivation (eq 6). This is consistent with the fact that the

$$S_0 \xrightarrow{254\ nm} S_x \longrightarrow S_1 \xrightarrow{313\ nm} S_0 \qquad (6)$$

biradical

quantum yield at 254 nm is always higher than at 313 nm: at 254 nm, the compound has more chance to react.

The biradical thus produced would be able to cyclize onto the arene ring thus leading to the enol E (Scheme III). It is tempting to consider the enol E is the transient observed at low temperature and short irradiation periods. It is known that the lifetime of conjugated enols can be very long and that enols can even be isolable molecules.[23] However, such enols would be very sensitive intermediates easily oxidized and probably polymerized. The observation that similar polycyclic nonaromatic molecules can be oxidized in the reaction mixture even in the absence of oxygen has already been recognized by several groups.[12a,24,25] The fact that we could neither realize selectively the conversion of **1a** to the intermediate nor trap this species with Me_3SiCl is certainly due to the fact that E strongly absorbs light and is thus rapidly photodegradated. Its concentration in the reaction mixture would thus be kept low because it is photolabile.

The complexity of the effect of the concentration on the product formation, the numerous byproducts, and oligomers do not allow us to describe with more precision the observed oxidative photocyclization. However, the absence of significant amounts of oxetanyl or cyclobutyl compounds indicates that the cyclohexenones **1** and **2** behave similarly to flavone derivatives and allow preferential cyclization of the side chain radical on the very close aryl group.

Experimental Section

^{1}H NMR spectra were recorded on a Brucker WP80CW instrument and ^{13}C NMR spectra on a Brucker WP60 instrument, if not otherwise stated. The 300-MHz ^{1}H NMR and 75.5-MHz ^{13}C NMR spectra were recorded on a Brucker AC-300 spectrometer. ^{1}H and ^{13}C NMR spectral data are reported in ppm. Chemical shifts (δ) are relative to tetramethylsilane as internal standard. IR spectra were obtained with a Pye Unicam SP2000 spectrophotometer and UV spectra with a Beckman-Acta III spectrophotometer. Mass spectra were obtained from UER Pharmacie, Reims. Melting points were determined on a Kofler Bank and are not corrected. Compounds were characterized by elemental analyses or high resolution mass spectra. Fluorescence and phosphorescence spectra were obtained from the Laboratoire de Photochimie Solaire du CNRS, Thiais.

All the HPLC determinations were achieved with a Waters UV detector (Model 440) connected to a Hewlett-Packard 3390A integrator. Irradiation devices and conditions: (1) Philips HPW 125 lamp (λ = 365 nm); (2) 12 Philips TUV 15 lamps, quartz vessel (λ = 254 nm); (3) Hanau TNN15 lamp, quartz vessel (λ 254 nm); (4) Hanau TQ 150 lamp, wood glass filter (λ 366 nm); (5) Hanau TQ 150 lamp, potassium chromate (0.2 g L^{-1}), potassium carbonate (50 g L^{-1}), (λ 313 nm); (6) as in (5) but an additional filter, ($CoSO_4 \cdot 7H_2O$ (240 g L^{-1}); (7) Philips HOQ 400 W potassium chromate (0.2 g L^{-1}); potassium carbonate (50 g L^{-1}) (λ 313 nm).

Unless otherwise stated, the solutions were deoxygenated prior to irradiation by bubbling argon through them for 30 min.

The quantum yields have been determined by extrapolation to 0% conversion, from experimental values obtained from 0 to 10% conversion of starting material.

Preparation of 2-Alkoxy-3-arylcyclohexenones 1. Procedure for 1a,b,d,e. To a solution of 3-phenylcyclohexane-1,2-dione (**5a**)[15] (200 mg) in acetone (1.5 m L) were added potassium carbonate (140 mg), and the appropriate alkyl halide (1.5 equiv). The solution was stirred and refluxed for 6 h. After filtration the solvent was evaporated and the enone was isolated by preparative thin layer chromatography (70/30 cyclohexane/ethyl acetate).

1a: 70% yield; mp 55 °C; ^{1}H NMR ($CDCl_3$) δ 7.4 (5 H), 3.5 (s, 3 H), 3–1.8 (6 H); ^{13}C NMR ($CDCl_3$) δ 22.523, 30.902, 38.794, 59.800, 126.218, 127.979, 128.222, 128.586, 128.890, 137.511,

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143.825, 149.107, 195.794; IR ($CHCl_3$) 3030, 1670, 1610, 1500, 1230, 1140, 995, 940 cm^{-1}; UV (Et_2O) λ_{max} 280 (ϵ 16700), 220 nm (7200); MS, *m/e* (relative intensity) 202 (100), 201 (55), 187 (15), 171 (11), 156 (10), 145 (15), 117 (27), 115 (18), 105 (19), 103 (21), 91 (15), 77 (20), 57 (41), 50 (12); HRMS 202.0971, calcd for $C_{13}H_{14}O_2$, 202.0993. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.2; H, 6.98. Found: C, 76.81; H, 6.91.

1b: 40% yield; ^1H NMR ($CDCl_3$) δ 7.4 (5 H), 3.7 (q, 7 Hz, 2 H), 2–3 (6 H), 1.15 (t, 7 Hz, 3 H); IR ($CHCl_3$) 3030, 1670, 1610, 1500, 1140, 925 cm^{-1}; UV (Et_2O) λ_{max} 280 (ϵ 12800), 215 nm (7600); MS, *m/e* (relative intensity) 216 (100), 199 (42), 198 (43), 187 (35), 184 (21), 172 (37), 171 (48), 156 (21), 159 (22), 144 (33), 129 (22), 117 (45), 115 (33), 103 (22), 94 (19), 91 (28), 77 (26); HRMS 216.1124, calcd for $C_{14}H_{16}O_2$ 216.1149.

1d: 60% yield; mp 50 °C; ^1H NMR ($CDCl_3$) δ 7.13 (m, 4 H), 3.75 (s, 3 H), 3.4 (s, 3 H), 2.3 (6 H); IR ($CHCl_3$) 2930, 1660, 1600, 1585, 1505, 1250, 1170, 1130, 985, 885, 820 cm^{-1}; UV (Et_2O) λ_{max} 302 (ϵ 16000), 222 nm (7800); MS, *m/e* (relative intensity) 232 (100), 217 (74), 201 (39), 147 (28). Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.3; H, 6.94. Found: C, 72.07; H, 6.89.

1e: 30% yield; ^1H NMR ($CDCl_3$) δ 7.16 (q, 9 Hz, 4 H), 3.8 (s, 3 H), 3.67 (q, 8 Hz, 2 H), 3–2 (6 H), 1.13 (t, 8 Hz, 3 H); IR ($CHCl_3$) 3020, 1665, 1600, 1565, 1510, 1460, 1450, 1410, 1375, 1360, 1340, 1325, 1300, 1285, 1250, 1175, 1100, 1090, 1030, 925, 825 cm^{-1}; UV (ether) λ_{max} 302 nm (ϵ 12300), 225 (6150); MS, *m/e* (relative intensity) 246 (100), 218 (14), 217 (13), 215 (29), 202 (18), 201 (17), 190 (15), 189 (14), 187 (12), 147 (47), 134 (12), 108 (19); HRMS 246.1236, calcd for $C_{15}H_{18}O_3$ 246.1255.

Procedure for 1c. Under an argon atmosphere, to a solution of potassium *tert*-butoxide (271 mg, 2.4 mmol) in THF (30 mL) was added at 0 °C 3-phenyl-cyclohexane-1,2-dione (**5a**) (451 mg, 2.4 mmol) dissolved in THF (50 mL). The solution was stirred for 20 min and became yellow. Then ethyl bromoacetate (400 mg, 24 mmol) was added, and the reaction mixture was maintained at 0 °C for 2 h. After the THF was evaporated **1c** was extracted with methylene chloride and purified by preparative thin layer chromatography (70/30 cyclohexane/ethyl acetate).

1c: 70% yield; ^1H NMR ($CDCl_3$) δ 7.5 (5 H), 4.4 (s, 2 H), 4.15 (q, 8 Hz, 2 H), 3–2 (6 H), 1.2 (t, 8 Hz, 3 H); IR ($CHCl_3$) 1765, 1688, 1615, 1230, 1150; UV (Et_2O) λ_{max} 285 (ϵ 15400), 220 (6600); MS, *m/e* (relative intensity) 274 (10), 201 (100), 117 (40), 115 (20), 103 (15), 91 (15), 77 (10), 55 (12); HRMS 274.1172, calcd for $C_{16}H_{18}O_4$ 274.1204.

Preparation of 2-Alkyl-3-arylcyclohexenones 2. β-Keto esters **6** were prepared according to Weiler[16] or Yonemitsu.[17] The Mannich bases **7** were obtained following the procedure of Jasor[18] and the corresponding ammonium iodides **8** according to Henin and Pete.[26]

General Procedure. A solution of the gummy Mannich base methiodide (8.5 mmol) in absolute ethanol (20 mL) was added to a warm solution of sodio β-keto ester previously prepared by adding a solution of the β-keto ester (10 mmol) in ethanol (10 mL) to sodium ethoxide (10 mmol) in absolute ethanol (10 mL). The reaction mixture was refluxed for 4 h; then a solution of potassium hydroxide (0.6 g, 11 mmol) in water (2 mL) was added and the heating was continued for a further 8 h. Most of the ethanol was evaporated under vacuum, and water (5 mL) was added to the residue. An oil separated, which was taken up in ether and washed with water, and finally purified by flash chromatography on silica gel[27] (90/10 pentane/ethyl acetate). Further purification of the enones was best achieved by sublimation or microdistillation.

2a: yield 1.31 g (77%); F = 46 °C; ^1H NMR ($CDCl_3$) δ 0.9 (t, 7 Hz, 3 H), 1.75–2.5 (m, 8 H), 6.9–7.6 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.388, 20.034, 22.888, 33.512, 38.248, 126.643, 127.736, 128.525, 138.057, 141.700, 156.696, 199.315; IR ($CHCl_3$) 3020, 2950, 1655, 1615, 1570, 1455, 1380, 1330, 1320, 1290, 1190, 1130, 1100, 900 cm^{-1}; UV (MeOH) λ_{max} 325 (ϵ 61), 249 nm (ϵ 13150); MS, *m/e* (relative intensity) 200 (60), 199 (88), 172 (28), 159 (4), 158 (24), 130 (20), 129 (100), 115 (40), 77 (16), 65 (8), 53 (20). Anal. Calcd for $C_{14}H_{16}O$: C, 83.95; H, 8.05. Found: C, 83.79; H, 8.10.

2b: yield 0.921 g (51%); ^1H NMR ($CDCl_3$) δ 0.9 (t, 7 Hz, 3 H), 1.3 (m, 2 H), 1.85–2.33 (m, 4 H), 2.33–2.70 (m, 4 H), 7–7.5 (m, 5 H); IR ($CHCl_3$) 1660, 1615, 1595, 1520, 1490, 1455, 1440, 1430, 1360, 1325, 1220, 1120, 1030 cm^{-1}; UV (MeOH) λ_{max} 255 nm (ϵ 10500); MS, *m/e* (relative intensity) 214 (100), 213 (82), 186 (38), 185 (37), 172 (64), 157 (15), 144 (77), 143 (54), 129 (52), 128 (50), 115 (49), 91 (23), 77 (14), 55 (48). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.48. Found: C, 84.14; H, 8.50.

2c: yield 0.820 g (42%); ^1H NMR ($CDCl_3$) δ 0.8 (t, 7 Hz, 3 H), 1.0–1.5 (m, 4 H), 1.75–2.3 (m, 4 H), 2.3–2.75 (m, 4 H), 6.9–7.5 (m, 5 H); IR ($CHCl_3$) 1660, 1615, 1595, 1490, 1450, 1355, 1325, 1230, 1190, 1115, 905 cm^{-1}; UV (MeOH) λ_{max} 255 nm (ϵ 9000); MS, *m/e* (relative intensity) 228 (100), 227 (90), 200 (22), 199 (20), 186 (15), 185 (71), 182 (16), 181 (84), 171 (22), 158 (9), 157 (13), 144 (9), 143 (18), 142 (10), 141 (15), 130 (19), 129 (45), 128 (28), 115 (20), 91 (18), 77 (6), 55 (54). Anal. Calcd for $C_{16}H_{20}O$: C, 84,20; H, 8.77. Found: C, 84.19; H, 8.70.

2d: yield 0.870 g (45%); 300-MHz ^1H NMR ($CDCl_3$) δ 0.65 (d, 6 H, 7 Hz), 1.63 (nonet, 1 H, 7 Hz), 2.09 (m, 4 H), 2.51 (t, 2 H, 7 Hz), 2.60 (t, 2 H, 6 Hz), 7.25–7.40 (m, 5 H); 75.5-MHz ^{13}C NMR δ 22.4 (q), 22.7 (t), 27.7 (d), 33.9 (t), 126.9 (d), 127.4 (d), 128.2 (d), 135.6 (s), 141.7 (s), 157.7 (s), 199.8 (s); IR ($CHCl_3$) 1660, 1615, 1595, 1485, 1450, 1355, 1320, 1230, 1190, 1110, 900 cm^{-1}; UV (MeOH) λ_{max} 255 nm (ϵ 8000); MS, *m/e* (relative intensity) 228 (80), 213 (10), 200 (20), 195 (35), 185 (100), 167 (8), 157 (30), 141 (25), 129 (35), 128 (28), 115 (20), 81 (28), 77 (15), 55 (90); HRMS 228.1523, calcd for $C_{16}H_{20}O$ 228.1513.

2e: yield 1.02 g (52%); ^1H NMR ($CDCl_3$) δ 0.9 (t, 7 Hz, 3 H), 1.75–2.75 (m, 8 H), 3.8 (s, 3 H), 6.75–7.30 (m, 4 H); IR ($CHCl_3$) 1660, 1600, 1570, 1510, 1460, 1430, 1370, 1350, 1320, 1300, 1280, 1245, 1190, 1170, 1110, 1030 cm^{-1}; UV (MeOH) λ_{max} 282 (ϵ 12500), 226 (13000), 200 nm (12000); MS, *m/e* (relative intensity) 230 (62), 229 (56), 215 (9), 202 (19), 200 (17), 199 (100), 189 (14), 174 (18), 173 (14), 159 (27), 145 (10), 77 (5), 55 (16); HRMS 230.1306, calcd for $C_{15}H_{18}O_2$ 230.1287. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.22; H, 7.89. Found: C, 77.98; H, 7.75.

Preparative Irradiations of 1 and 2. In a typical experiment a degassed methanolic solution (10^{-2} M) was irradiated at 254 nm (condition 2). The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography[27] or by preparative thin layer chromatography.

9a: irradiation time 0.75 h; conversion 80%; yield 50%; mp 116 °C; ^{13}C NMR δ 21.673, 24.284, 38.126, 68.057, 122.515, 124.336, 128.525, 129.315, 129.922, 136.650, 131.015, 145.889, 193.426; ^1H NMR ($CDCl_3$) δ 7.3 (4 H), 5.1 (s, 2 H), 3–1.8 (m, 6 H); IR ($CHCl_3$) 3030, 1675, 1610, 1570, 1390, 1335, 1195, 1125, 1025, 1010, 910, 895 cm^{-1}; UV (Et_2O) λ_{max} 320 (ϵ 14000), 242 (12000), 235 nm (12500); MS, *m/e* (relative intensity) 200 (100), 172 (15), 171 (22), 155 (18), 145 (25), 144 (18), 139 (20), 128 (15), 117 (17), 116 (37), 115 (50); HRMS 200.0874, calcd for $C_{13}H_{12}O_2$ 200.0837. Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.97; H, 6.04. Found: C, 77.33; H, 5.93.

9b: irradiation time 1 h; conversion 90%; yield 35%; ^1H NMR ($CDCl_3$) δ 7.4 (4 H), 5.25 (q, J = 8 Hz, 1 H), 3–2 (6 H), 1.6 (3 H); IR ($CHCl_3$) 3015, 1670, 1610, 1565, 1450, 1120; UV (Et_2O) λ_{max} 320 (ϵ 8500), 242 (7200), 235 (7700); MS, *m/e* (relative intensity) 214 (25), 199 (100), 171 (8), 143 (8), 141 (8), 128 (15), 115 (18), 84 (10); HRMS 214.0970, calcd for $C_{14}H_{14}O_2$ 214.0993.

9c: irradiation time 1.5 h; conversion 70%; yield 20%; mp 145 °C; ^1H NMR ($CDCl_3$) δ 7.4 (4 H), 6.75 (s, 1 H), 4.12 (q, J = 10 Hz, 2 H), 3–2 (6 H), 1.2 (t, J = 10 Hz, 3 H); IR ($CHCl_3$) 1760, 1685, 1630, 1382, 1150, 1125 cm^{-1}; UV (Et_2O) λ_{max} 320 (ϵ 7000), 250 (7500), 243 nm (7000); MS, *m/e* (relative intensity) 272 (5), 200 (15), 199 (100), 115 (8), 91 (3), 71 (8), 57 (15); HRMS 272.1049, calcd for $C_{16}H_{16}O_4$ 272.1048.

9d: irradiation time 0.75 h; conversion 70%; yield 30%; mp 124 °C; ^1H NMR ($CDCl_3$) δ 6.5–7.5 (3 H), 5.12 (s, 2 H), 3.88 (s, 3 H), 3–2 (m, 6 H); IR ($CHCl_3$) 3000, 1660, 1600, 1565, 1500, 1450, 1430, 1380, 1280, 1230, 1140, 1080, 1040, 1020, 925 cm^{-1}; UV (Et_2O) λ_{max} 330 (ϵ 18400), 235 nm (13000); MS, *m/e* (relative intensity) 230 (100), 229 (13), 187 (11), 175 (11), 174 (50), 159 (14), 147 (10), 146 (39), 131 (17), 115 (10); HRMS 230.0922, calcd for $C_{14}H_{14}O_3$ 230.0920.

9e: irradiation time 1 h; conversion 70%; yield 20%; oil; ^1H NMR δ 6.5–7.4 (3 H), 5.2 (q, J = 9 Hz, 1 H), 3.82 (s, 3 H), 2–3 (6 H), 1.6 (d, J = 9 Hz, 3 H); IR ($CHCl_3$) 3010, 1660, 1605, 1560, 1505, 1495, 1460, 1450, 1425, 1370, 1330, 1315, 1280, 1265, 1230, 1190, 1165, 1155, 1135, 1080, 1035, 940, 900 cm^{-1}; UV (Et_2O) λ_{max} 330 nm (ϵ 11000), 244 (5500), 236 (6600); MS, *m/e* (relative

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(27) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

intensity) 244 (42), 230 (18), 229 (100), 99 (20), 97 (17), 85 (12), 83 (20), 81 (13), 71 (18), 69 (19); HRMS 244.1100, calcd for $C_{15}H_{16}O_3$ 244.1099.

10a: irradiation time 20 h; conversion 43%; yield 40%; ^1H NMR ($CDCl_3$) δ 1.75–3.0 (m, 10 H), 6.8–7.5 (4 H); ^{13}C NMR ($CDCl_3$) δ 19.852, 22.402, 26.227, 27.745, 37.580, 124.640, 126.765, 127.918, 129.679, 132.836, 134.500, 138.482, 149.714, 198.829; IR ($CHCl_3$) 3000, 2920, 1665, 1610, 1510, 1460, 1430, 1390, 1280, 1190 cm^{-1}; UV (MeOH) λ_{max} 229 (ϵ 14 550), 235 (14 480), 297 (17 330), 394 nm (15 100); MS, m/e (relative intensity) 198 (100), 197 (70), 170, 155, 142, 141, 129, 128, 115, 77, 71, 55; HRMS 198.1041, calcd for $C_{14}H_{14}O$ 198.1044.

10b: irradiation time 14 h; conversion 37%; yield 40%; ^1H NMR ($CDCl_3$) δ 0.9 (t, J = 7 Hz, 3 H), 1.9–3.05 (m, 9 H), 7.0–7.5 (4 H); IR ($CHCl_3$) 1655, 1610, 1570, 1520, 1470, 1460, 1380, 1330, 1280, 1210 cm^{-1}; UV (MeOH) λ_{max} 228 nm (ϵ 12 400), 235 (11 800), 294 (12 500), 306 nm (10 400); MS, m/e (relative intensity) 212, 211, 197, 184, 179, 172, 155, 142, 141, 129, 128, 115, 91, 77, 55; HRMS 212.1215, calcd for $C_{15}H_{16}O$ 212.1201.

10c: irradiation time 7 h; conversion 60%; yield 25%; ^1H NMR ($CDCl_3$) δ 0.9 (t, J = 7 Hz, 3 H), 1.2–1.8 (m, 2 H), 1.9–3.0 (m, 9 H), 7.0–7.7 (m, 4 H); IR ($CHCl_3$) 1655, 1610, 1570, 1510, 1455, 1380, 1330, 1290, 1240, 1180, 1130, 1010, 900 cm^{-1}; MS, m/e (relative intensity) 226, 225, 197, 159, 141, 129, 128, 115, 91, 77, 55; HRMS 226.1348, calcd for $C_{16}H_{18}O$ 226.1356.

10d: irradiation time 4 h; conversion 60%; yield 25%; 300-MHz ^1H NMR ($CDCl_3$) δ 1.25 (s, 6 H), 2.15 (quint, 2 H, 7 Hz), 2.48 (s, 2 H), 2.50 (t, 2 H, 7 Hz), 2.80 (t, 2 H, 7 Hz), 7.20–7.50 (m, 4 H); 75.5 MHz ^{13}C NMR ($CDCl_3$) δ 22.5 (t), 26.1 (t), 28.2 (q), 33.2 (s), 34.5 (t), 37.5 (t), 124.1 (d), 125.0 (d), 126.2 (d), 130.2 (d), 131.2 (s), 133.1 (s), 147 (s), 149.0 (s), 199.3 (s); IR ($CHCl_3$) 3005, 2960, 2890, 2830, 1655, 1615, 1570, 1450, 1390, 1380, 1300, 1185, 1135 cm^{-1}; MS, m/e (relative intensity) 226 (30), 211 (100), 193 (13), 155 (25), 85 (25), 83 (40); HRMS 226.1375, calcd for $C_{16}H_{18}O$ 226.1358.

10e: irradiation time 14 h; conversion 47%; yield 15%; 300-MHz ^1H NMR δ 2.12 (quint, 2 H, 7 Hz), 2.50 (m, 4 H), 2.75 (m, 4 H), 6.78 (m, 2 H), 7.38 (d, 1 H, 8 Hz); 75.5-MHz ^{13}C NMR ($CDCl_3$) δ 19.8 (t), 22.4 (t), 26.2 (t), 28.2 (t), 37.5 (t), 55.3 (q), 111.7 (d), 113.5 (d), 126.2 (d), 127.3 (s), 130.6 (s), 140.6 (s), 149.9 (s), 160.7 (s), 198.7 (s); IR ($CHCl_3$) 3010, 2970, 1640, 1600, 1560, 1500, 1430, 1380, 1310, 1280, 1240, 1180, 1140, 1040 cm^{-1}; MS, m/e (relative intensity) 228, 227, 200, 197, 185, 172, 171, 157, 141, 129, 128, 115, 77, 57, 55; HRMS 228.1207, calcd for $C_{15}H_{16}O_2$ 228.1151.

Preparative Scale Experiments: Optimization of Conversion Rates. For **2a** we determined the conversion giving the best chemical yield. For this purpose, 10^{-2} M solutions of enones in methanol (100 mL) were irradiated for different times (condition 2) and the photocyclized product was isolated as described in the preceding section. Thus after 20-h irradiation, 43% of **2a** was converted and **10a** was isolated in 40% yield. When irradiation times were longer the yields in isolated **2a** dropped markedly.

In the case of **1c**, we observed that the conversion and the chemical yield could be improved slightly if **9c** was isolated intermediately:

irradtn time, h	overall convn, %	yield in isolated **9c**, %
2	70	20
1 + 1[a]	85	25

[a] After an hour, **1c** and **9c** were separated and **1c** was irradiated again for 1 h.

Quantum Yield of 1a at 254 nm. A deoxygenated solution of the enone (10^{-3} M) in pentane (3 mL) was irradiated in calibrated quartz tubes (0.8 cm i.d.) on a merry-go-round apparatus (condition 3). Simultaneously identical tubes containing a potassium ferrioxalate solution as actinometer[19b] were irradiated so that all tubes received statistically the same amount of light. The irradiation time varied from 1 to 15 min. A solution of xanthone (10^{-3} M in pentane) was added as internal standard and the amount of **9a** was determined by HPLC on a 25-cm column filled with Chrompack 10-μm spherical silica gel, using as mobile phase a hexane (90 vol)–ethyl acetate (10 vol) mixture (flow rate 1.5 mL × min^{-1}). Detection was achieved at 313 nm.

The results are reported in Table II and in Figure 4.

Quantum Yield of 1a at 366 nm. A solution of **1a** (10^{-3} M) in pentane (2 mL) was irradiated (condition 4) on a merry-go-round apparatus and analyzed as above. The results are summarized in Table II and Figure 4.

Quantum Yield of 1a at 313 nm. A solution of **1a** (10^{-3} M) in pentane (2 mL) was irradiated on a merry-go-round apparatus (condition 6) together with tubes containing a 5×10^{-3} M solution of Aberchrome in toluene as actinometer.[28] Determination of **9a** was achieved as before. The results are summarized in Table II and Figure 4.

Quantum Yield of 2a at 254 nm. A deoxygenated 1.25×10^{-3} M solution of **2a** in methanol (3 mL) was irradiated as in preceeding section. After irradiation, a solution of xanthone as internal standard was added and the solvent was then removed under vacuum. The residue was dissolved in the same solvent mixture as the one used as mobile phase (93/7 hexane/ethyl acetate). HPLC determination was achieved with a 30-cm column and Waters Microporasil 10-μm silica gel as stationary phase. Each determination was the average of three experiments.

10a formed (mol × 10^9)	4	5.65	7.9	11.90
absorbed light (einsteins × 10^7)	9.25	13.4	20.0	23.1

Quantum Yield of 2a at 313 nm. 2a was irradiated (condition 7) and analyzed as above. Each value was the average of two independent determinations.

10a formed (mol × 10^8)	4.6	7.2	7.5	8	8.5	11	11.9	9.9
absorbed light (einsteins × 10^5)	1.3	2.6	4.1	5.6	7.1	8.5	16.0	22.0

Quantum Yield of 2a at 366 nm. 2a was irradiated (condition 4) and analyzed as above. No trace of **10a** could be detected.

Influence of the Solvent on the Quantum Yield of 1a and 2a. Solutions of **1a** (10^{-3} M) in different solvents (3 mL) were irradiated on the merry-go-round apparatus (condition 3) for 8 min. The xanthone solution was then added and the solvents were evaporated under vacuum. The residues were dissolved in pentane and **9a** was analyzed by HPLC as previously described. The same procedure was applied with **2a** (1.25×10^{-3} M) which was irradiated for a 1-h period.

All the results are summarized in Table II.

Influence of the Concentration on the Quantum Yield. Solutions of **1a** (3 mL) at different concentrations in pentane were irradiated together in identical quartz test tubes (0.8 cm i.d.) on the merry-go-round apparatus. After addition of xanthone as internal standard the reaction mixtures were analyzed by HPLC as previously indicated.

At 254 nm: irradiation using condition 3. The actinometer was potassium ferrioxalate.

concn of **1a** (M × 10^3)	0.33	0.66	1	1.66	2	5
convn (%)	12.4	6.8	5.4	3.6	3.2	1.8
ϕ^{254}(corr)[29]	0.24	0.25	0.30	0.33	0.35	0.48

At 313 nm: irradiation using condition 6. The actinometer was Aberchrome.

concn of **1a** (M × 10^3)	0.25	0.5	1	2.5	5
convn (%)	6	4	2.7	1.5	0.8
ϕ^{313}(corr)[29]	0.095	0.12	0.16	0.2	0.22

Solutions of **2a** (12 mL) at different concentrations in methanol were irradiated together at 254 nm on a merry-go-round apparatus (condition 3). **10a** was determined as described previously. Potassium ferrioxalate was used as chemical actinometer.

concn of **2a** (M × 10^4)	1	4.7	9.4	18.7	37.5	75	150
$\phi^{254} \times 10^3$ (corr)[29]	4.1	5.5	6	8.4	12.5	22.5	26

Influence of the Light Intensity on the Quantum Yield of 1a and 2a. Three tubes containing 10^{-3} M solutions of **1a** in pentane (3 mL) were irradiated successively on a merry-go-round apparatus (condition 3). Each tube was irradiated together with an identical tube containing ferrioxalate as chemical actinometer,

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which received the same amount of light.

The light intensity was modified by surrounding the source with wire netting, and the irradiation time was adjusted in order that all the tubes receive approximately the same amount of photons. The amount of **9a** formed was then determined as previously described. Φ remained equal to 0.33 ± 0.01 for 8.10 and 15 × 10^{-7} einstein/h light intensities.

Identical results were obtained when **2a** (10^{-3} M) was irradiated similarly in methanol.

UV-Visible Spectra at Low Temperature. Thoroughly deoxygenated solutions of **1a** (see text for the concentrations) in pentane were placed in a UV cell which was immersed in a quartz Dewar containing ice-water and irradiated at 254 nm (condition 3).

After 3-min irradiation, absorption spectra were recorded immediately (see Figures 7 and 8).

Attempted Trapping of the Intermediate. A solution of **1a** (240 mg, 1.2 mmol) in acetonitrile (50 mL) was irradiated at −30 °C for 45 min at 254 nm (conditions 3). The solution turned deep yellow. Immediately, triethylamine (240 mg, 2.4 mmol) and trimethylchlorosilane (190 mg, 1.8 mmol) were added to the solution which was then allowed to warm to room temperature. After evaporation under vacuum, no silylated product was determined by ^{1}H NMR.

Quenching Experiments. A 10^{-3} M solution of **1a** in pentane (3 mL) was irradiated in the presence of various concentrations of naphthalene ranging from 0 to 8 × 10^{-5} M. Determination of **9a** by HPLC showed that naphthalene had no effect on the quantum yield.

Similar results were obtained for **2a**, 10^{-3} M in methanol, with concentrations of naphthalene ranging from 0 to 3.33 × 10^{-4} mol L^{-1}.

Sensitization Experiments. **1a** (2 × 10^{-4} M) was irradiated in acetone (3 mL) as solvent and sensitizer at 254 nm (condition 3). Irradiation times ranged from 1 to 20 min. No trace of **9a** was detected by HPLC.

When a solution of **1a** (10^{-4} M) and *p*-methoxyacetophenone (2 × 10^{-3} M) in pentane (3 mL) was irradiated under the same conditions, no trace of **9a** was detected by HPLC.

2a (10^{-4} M) was irradiated in acetone (3 mL) as sensitizer at 254 nm (condition 3). No trace of **10a** was detected by HPLC.

When solutions of **2a** (10^{-4} M) and *p*-methoxyacetophenone or benzophenone (10^{-2} M) in methanol (3 mL) were irradiated in the same conditions, no trace of **10a** was detected by HPLC.

In all these experiments, the sensitizers absorbed more than 98% of the incident light.

Influence of Oxygen and Iodine. Calibrated quartz tubes containing the three solutions a, b, and c were irradiated for 90 min at 254 nm (condition 3) on a merry-go-round apparatus. The determinations of **2a** and **10a** were achieved by HPLC: **10a** by detection at 313 nm using xanthone as internal standard and **2a** by detection at 254 nm. Tube a: 10^{-3} M solution of **2a** in methanol (3 mL) previously deoxygenated. Tube b: 10^{-3} M solution of **2a** in methanol (3 mL) previously oxygenated by a 20-min oxygen stream. Tube c: 10^{-3} M solution of **2a** in methanol (3 mL) and 10^{-3} M in iodine, previously deoxygenated.

The UV spectra of the solutions a, b, and c were identical.

tube	convn, %	yield in **10a**, %
a (argon)	25	30
b (O_2)	42	23.5
c (I_2)	38	33

Similar results were obtained when **1a** (10^{-3} M) in pentane (3 mL) was irradiated at 254 nm (condition 3).

Registry No. **1a**, 89114-50-1; **1b**, 89114-51-2; **1c**, 104214-12-2; **1d**, 89114-53-4; **1e**, 89114-54-5; **2a**, 89228-94-4; **2b**, 89228-95-5; **2c**, 89228-96-6; **2d**, 89228-97-7; **2e**, 104214-13-3; **5a**, 70871-45-3; **6a**, 30414-54-1; **6b**, 39815-78-6; **6c**, 22348-95-4; **6d**, 104214-14-4; **8a**, 5724-15-2; **8e**, 24252-43-5; **9a**, 89114-55-6; **9b**, 89114-56-7; **9c**, 104214-15-5; **9d**, 89114-58-9; **9e**, 89114-59-0; **10a**, 62264-34-0; **10b**, 89228-98-8; **10c**, 89228-99-9; **10d**, 89229-00-5; **10e**, 14427-61-3.

6-Endo-Dig vs. 5-Exo-Dig Ring Closure in *o*-Hydroxyaryl Phenylethynyl Ketones. A New Approach to the Synthesis of Flavones and Aurones

Hermenegildo García, Sara Iborra, and Jaime Primo

Departamento de Química, ETSI Industriales, Universidad Politécnica, Apartado 22012, 46022-Valencia, Spain

Miguel A. Miranda*

Departamento de Química Orgánica, Facultad de Farmacia, 46010-Valencia, Spain

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The aryl phenylpropynoates **3a-c**, prepared by esterification of phenylpropynoic acid with the corresponding phenols, by means of *N,N'*-dicyclohexylcarbodiimide, give upon irradiation the *o*-hydroxyaryl phenylethynyl ketones **4a-c**. The cyclization of these compounds in basic media follows two alternative pathways: 6-endo-dig ring closure, to give the flavones **8a-c**, and/or 5-exo-dig ring closure, to give the aurones **9a-c**. The predominance of one or the other cyclization mode is strongly influenced by the reaction conditions. Thus, the use of potassium carbonate in acetone as cyclizing reagent favors the 6-endo-dig process, while the 5-exo-dig process becomes clearly enhanced when using sodium ethoxide or potassium carbonate in ethanol. The mechanistic implications of these facts are discussed within the framework of Baldwin's rules. From the preparative point of view, the above results disclose the synthetic possibilities of the key ketones **4** as precursors of flavones and aurones.

Less than 10 years ago, Baldwin described a set of simple rules to predict the relative facility of different ring forming reactions.[1] Since then, the general validity of these rules has been confirmed by an overwhelming number of publications, and the borderlines between favored and disfavored processes have been defined in a more precise way.[2]

Nonetheless, for cyclizations involving nucleophilic attacks at triple bonds, the situation remains less clear-cut than for the analogous ring closures in tetrahedral or trigonal systems. Thus, the original rules postulated an

(1) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.

(2) A systhematic search through the Science Citation Index reveals that ref 1 has been cited by several hundreds of papers since the data of publication.

0022-3263/86/1951-4432$01.50/0