Photochemical Cyclization of 2'-Hydroxychalcones

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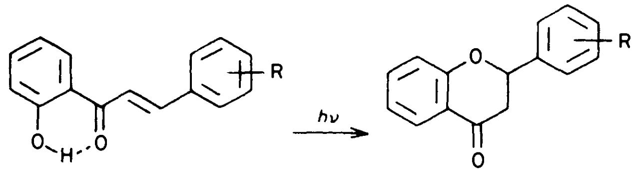
A series of 4-substituted 2'-hydroxychalcones underwent photocyclization to give the corresponding flavanones selectively, but in low quantum yields, on visible irradiation in polar aprotic solvents. Hydroxylic solvents, which disturbed the formation of a cyclic intramolecular hydrogen bond, strongly retarded the photoreaction, while neither triplet quenchers nor free radical inhibitors affected the reaction. The quantum yields were independent of the light intensity, implying a one-photon process, but strongly depended on the wavelength of irradiation. Mechanisms were proposed assuming π,π^* excited states and Weller's postulate of a dynamic equilibrium in a proton-transfer double-minimum potential.

Photochemical cyclizations of 2-allylphenols[1,2] and 2-allylanilines[3] have been shown to occur mainly in the Markovnikoff direction. Zwitterionic mechanisms involving intramolecular proton transfer[2] or electron transfer followed by proton transfer,[1,3] in the excited singlet states, have been proposed. In these systems intramolecular hydrogen bonding seems to play an important role. A similar mechanism has been suggested for the photocyclization of 2'-hydroxychalcone,[4] though the mechanistic details have been little studied as yet. The present study was undertaken to investigate in some detail the scope and mechanism of the photocyclization reaction of 2'-hydroxychalcones, in the light of the well studied photodynamics of the excited-state proton transfer of internally hydrogen-bonded *o*-hydroxycarbonyl compounds[5–8] which give no final isolable photoproducts.



(1) (2)

a; R = H
b; R = 4-Me
c; R = 4-MeO
d; R = 4-F
e; R = 4-Cl
f; R = 4-Br
g; R = 4-NO_2
h; R = 2,4-$(MeO)_2$

Results and Discussion

U.v. Absorption Spectra.—Figure 1 illustrates the u.v. absorption spectra of some 2'-hydroxychalcones (hereafter often denoted as chalcones) in cyclohexane, while the absorption maxima ($\lambda > 300$ nm) in ethanol and solvent shifts are included in Table 4 together with the m.p.s. The intense band of (**1a**) at *ca.* 316 nm is extensively red-shifted by the substitution of electron-donating groups at the 4-position in ring B, *e.g.*, 330 (**1b**), 366 (**1c**), and 380 nm (**1h**), while the shoulder at *ca.* 350 nm is essentially not shifted. The remarkable bathochromic shifts by the electron-donating groups allow more complete absorption of the incident light of the wavelengths longer than 350 nm. On the other hand, the shoulder at *ca.* 350 nm was extensively red-shifted by electron-donating substituents at the 6'-position in ring A, *e.g.*, *ca.* 370 for 2'-hydroxy-6'-methylchalcone and 390 nm (weak and broad band) for 2'-hydroxy-6'-methoxychalcone while the 316 nm band was not shifted at all. Further, change in the solvent polarity from cyclohexane to ethanol gives rise to considerable red shifts (250—1 500 cm^{-1}) of the intense bands (Table 4), implying π,π^* or intramolecular charge-transfer transition. The contrast band shifts by the rings A and B substituents suggest that the intense bands are due to the cinnamoyl moiety and the shoulders or weak bands to the hydroxybenzoyl moiety.

The difference may cause a large wavelength dependence of the quantum yield for the photocyclization reaction.

The intense band of chalcone at *ca.* 300 nm has been interpreted in terms of the conjugation of the whole molecule,[9a] which may correspond to intramolecular charge-transfer or a π,π^* transition,[9b] (Scheme 1) while the reverse or different assignments[9c–e] have also been proposed. Since the relative positions of the u.v. bands of chalcones and flavones are often

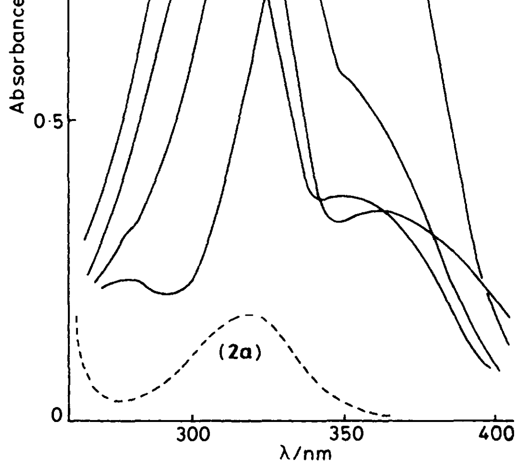
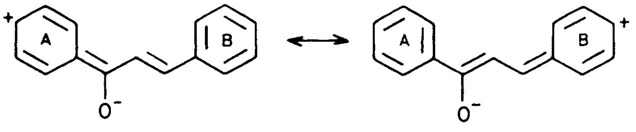


Figure 1. U.v. absorption spectra of some 2'-hydroxychalcones (4×10^{-5}M) in cyclohexane. Broken line: flavanone (4×10^{-5}M) for comparison

Table 1. Photocyclization of 2′-hydroxychalcones with visible light[a]

Compound						
No.	Ar	Solvent	Irrad. time (h)	Consumption of (1) (mM)	Formation of (2) (mM)	(2)/ − (1)[b]
(**1a**)	Phenyl	Ethyl acetate	10	0.79	0.72	0.91
		Benzene	10	0.24	0.12	0.50
		THF	5	0.30	0.25	0.83
(**1b**)	*p*-Tolyl	Ethyl acetate	10	0.67	0.64	0.93
		Benzene	10	0.18	0.14	0.77
		THF	5	0.34	0.22	0.63
(**1c**)	*p*-Methoxyphenyl	Ethyl acetate	10	1.0	0.93	0.93
		Benzene	10	0.40	0.33	0.83
		THF	5	0.34	0.32	0.94
(**1d**)	*p*-Fluorophenyl	Ethyl acetate	5	0.59	*c*	
(**1e**)	*p*-Chlorophenyl	Ethyl acetate	10	0.93	0.82	0.88
		Benzene	10	0.17	0.18	1.0
		THF	5	0.49	0.37	0.75
(**1f**)	*p*-Bromophenyl	Ethyl acetate	10	1.0	0.74	0.74
		Benzene	10	0.17	0.16	0.94
		THF	5	0.24	0.18	0.75
(**1g**)	*p*-Nitrophenyl	Ethyl acetate	5	0.84	*c*	
(**1h**)	*o,p*-Dimethoxyphenyl	Ethyl acetate	10	1.0	0.96	0.96
		Benzene	10	0.62	0.50	0.81
		THF	10	0.77	0.70	0.91
(**1i**)	α-Naphthyl	Ethyl acetate	10	1.0	0.94	0.94
		Benzene	10	0.45	0.32	0.71
		THF	10	0.65	0.61	0.94
(**1j**)	Styryl[d]	Ethyl acetate	10	0.45	0.31	0.69
		Benzene	10	0.15	0.06	0.40
		THF	10	0.15	0.09	0.60

[a] Initial concentration of each chalcone was 1mM. [b] Yield of flavanone (**2**) based on the consumption of chalcone (**1**). [c] Not determined. [d] 1-(2-Hydroxyphenyl)-5-phenylpenta-2,4-dien-1-one for comparison, though not a chalcone.



Scheme 1.

reversed upon substitution, their assignments may differ as the case may be.

Selective Photocyclization with Visible Light.—Figure 2 illustrates, as a preliminary experiment, the effect of the excitation wavelength on the yield of flavanone and the consumption of chalcone in ethyl acetate. Comparison of (A)—(D) reveals that irradiation with visible light only is preferable for selective and high conversion of chalcone into flavanone, though the rate is lowered. A similar tendency was found in 1,3-dioxane, tetrahydrofuran (THF), ether, and dimethylformamide. Irradiation with u.v. light may cause secondary photoreactions of flavanone, such as hydrogen-atom abstraction from solvents and a ring-opening reaction leading back to chalcone.[10] These effects become serious at higher conversion [(A) and (B)] where the yield of flavanone is poor. Visible irradiation of chalcones in aprotic solvents led to selective photocyclization to give flavanones as the main products (Table 1).

With the time of irradiation, the u.v. absorption spectrum of (**1a**) gradually changed until it almost coincided with that of (**2a**) after 10 h, with an isosbestic point at 260 nm. The yields of flavanones based on the consumption of chalcones, (**2**)/ − (**1**), are fairly close to 100%, thus showing high selectivity of the reaction. Methoxy and phenyl substituents tend to facilitate the apparent rate (**1c**, **h**, i) as expected from the increased absorptivities, whereas halogen atoms and the nitro group (**1e**—**g**) have little effect.

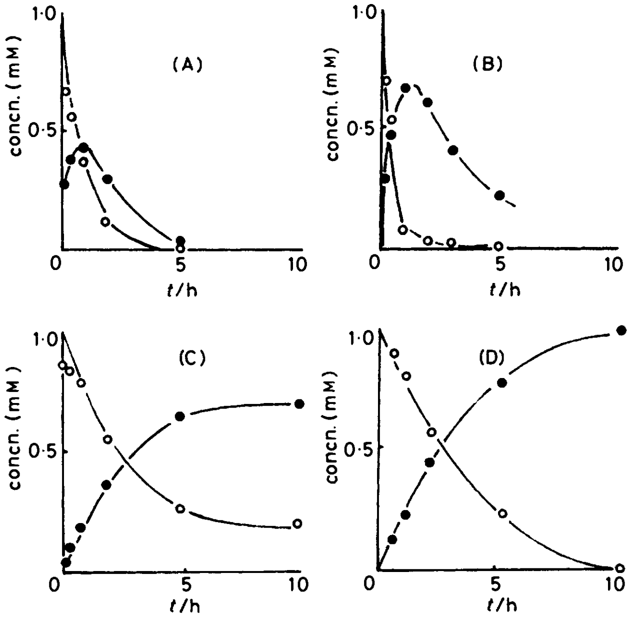


Figure 2. Effects of excitation wavelength on the photocyclization of (**1a**) in ethyl acetate. (○) Recovery of (**1a**); (●) formation of (**2a**). Excitation wavelengths were (A), ≧313 nm; (B), ≧334 nm; (C), ≧365 nm; and (D) ≧405 nm

Solvent Effects.—The relative rates of consumption of (**1a**) were compared in different solvents (Table 2). The rates are

Table 2. Solvent effects on the consumption rate of (**1a**)[a]

Solvent	Irrad. time (h)	Consumption (%)	Rate (% h^{-1}[b])
Ethyl acetate	0.5	7.0	14
Dioxane[c]	2	14	7.0
Dioxane–H_2O (95:5)	20	12	0.6
Dioxane–D_2O (95:5)	20	13	0.65
THF[c]	2	11	5.4
THF–H_2O (90:10)	5	6.4	1.3
THF–H_2O (40:60)	5	7.0	1.4
t-Butyl alcohol	2	4.7	2.4
Dimethylformamide	5	11	2.2
Cyclohexane	3	6.1	2.0
Acetonitrile	5	8.7	1.7
Acetonitrile–H_2O (95:5)	50	0.0	0.0
Acetonitrile–H_2O (40:60)	50	6.9	0.1
Benzene	14	8.1	0.6
Carbon tetrachloride	40	11	0.3
Ethanol	90	9.8	0.1
Methanol	90	7.7	0.1
Chloroform	40	0.0	0.0

[a] Initial concentration of (**1a**) was 1mM, on visible irradiation. Irradiation times were controlled so that the conversions were close to or below 10%. [b] Relative rate for the consumption of (**1a**). Solvent effects on the absorption at $\lambda \geqq 400$ nm were nil, hence the rate can be regarded as the relative quantum yield. [c] Distilled over fresh sodium.

Table 3. Quantum yields for the consumption of 2′-hydroxychalcones in ethyl acetate at different wavelengths[a]

Chalcone	λ/nm	Irrad. time (min)	Quantum yield (%)[b]
(**1a**)	313	15	1.2 ± 0.1
	365—366	15	0.51 ± 0.07
	405	30	0.15
(**1e**)	365—366	15	0.45 ± 0.01
	405	30	0.10 ± 0.01
(**1f**)	365—366	15	0.63 ± 0.06
	405	30	0.13 ± 0.02
(**1b**)	365—366	15	0.56 ± 0.06
	405	30	0.14 ± 0.01
(**1c**)	365—366	15	0.57 ± 0.01
	405	30	0.24 ± 0.03

[a] Initial concentration of each chalcone was 1mM. Irradiation times were controlled so that the conversion of chalcones was below 5%. [b] Each value is the average over three independent measurements, with the mean deviations as indicated.

higher in polar aprotic solvents, but low in non-polar solvents and extremely low in hydroxylic solvents (except for t-butyl alcohol). The effects of solvent polarity suggest some polar nature of the intermediates or active excited states. The remarkable interference by hydroxylic media is of particular interest since it seems relevant to the breakdown or weakening of the intramolecular cyclic hydrogen bonding of the phenolic proton to the carbonyl oxygen, in the excited and/or ground states. In the ground-state n.m.r. spectrum of (**1a**) the phenolic proton in dry THF (and in most organic solvents) appeared at δ *ca.* 12.8 as a sharp singlet (halfwidth *ca.* 0.03 p.p.m.), implying fairly stable intramolecular hydrogen bonding of a six-membered cyclic conformation. In the presence of water, *e.g.*, in THF–H_2O (90:10), the phenolic proton of (**1a**) appeared as a broad singlet (halfwidth *ca.* 0.25 p.p.m.) at δ 12.8, suggesting that the cyclic intermolecular hydrogen bond was significantly weakened by solute–solvent interaction.

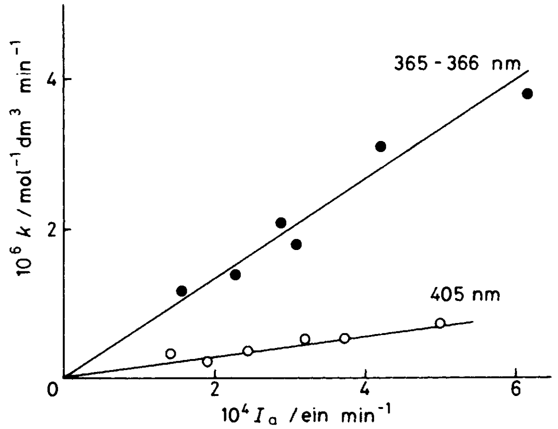


Figure 3. Effects of the light intensity on the rate of the photocyclization of (**1a**) in ethyl acetate

Effects of Additives.—Photocyclization of (**1a**) was not depressed by the addition of 2,6-di-t-butylphenol (6.5—54mM), nitrosobenzene (0.05—1.0mM), or acrylonitrile (15—60mM), as free-radical inhibitors. This suggests the involvement of non-radical mechanisms such as ionic or polar ones, consistent with the solvent effects. The addition of ferrocene (0.5—10mM), cyclohexa-1,3-diene (6.5—60mM), anthracene (0.5—2.5mM), phenanthrene (0.5—2.5mM), or acenaphthylene, as triplet quenchers, affected neither the yield of (**2a**) nor the consumption rate of (**1a**) within experimental error (±5%). The results suggest the involvement of either excited singlet states or extremely short lived (and/or low lying) triplet states. Further investigation on the active excited states is in progress.

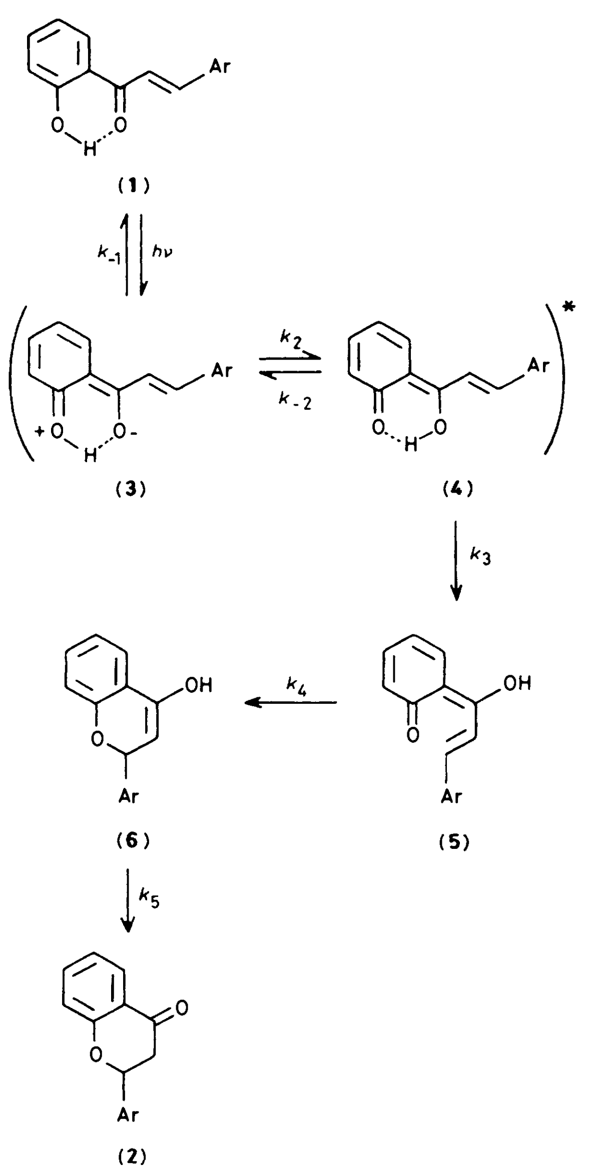
Quantum Yields.—The quantum yields were measured for the photoreaction of (**1a—f**) in ethyl acetate at some different wavelengths (Table 3). They were measured at low conversions (below 5%) to minimize the secondary photoreactions. The values are low and vary markedly with the wavelength of irradiation, *e.g.*, $\varphi_{313}/\varphi_{405}$ is 8. On the other hand, the quantum yields are unexpectedly little affected by the substituents, *e.g.*, $\varphi_{365-366}$ *ca.* 0.5 ± 0.1%. The lack of an internal heavy-atom effect is also notable [(**1f**)].

The effects of the light intensity on the quantum yield were measured for (**1a**). Figure 3 shows the constancy of the quantum yield against the light intensity, implying that photocyclization proceeds by way of a single-photon excitation mechanism.

Discussion on the Mechanism.—In the ground states, a strong intramolecular hydrogen bond of the phenolic proton to the carbonyl oxygen, a six-membered cyclic conformation (**1**), occurs as implied by the n.m.r. spectra. In π, π* excited states, phenolic groups usually become more acidic and carbonyl groups more basic, enhancing proton transfer.[2,6,7]

Thus, our results can be accounted for by the mechanism in Scheme 2 where excited π, π* or charge-transfer singlet states are tentatively assumed, though triplet states cannot be ruled out yet on the basis of the quenching experiments alone. Here, (**3**)* and (**4**)* correspond to the two minima in the excited singlet states, according to Weller's postulate of a dynamic equilibrium in a proton-transfer double-minimum potential, for salicyclic acid derivatives,[6] *o*-hydroxycarbonyl compounds,[7] and other related substrates.[8] The postulate of the excited-state equilibrium, $(\mathbf{3})^* \rightleftharpoons (\mathbf{4})^*$, is consistent with the one-photon nature of the photoreaction (Figure 3).

If the ground-state enol (**4**), instead of (**4**)*, were involved, then a second photo-excitation would be required to rotate about the enol double bond (k_3) and hence the overall process should have a two-photon nature. Polar aprotic solvents can stabilize the zwitterion to facilitate the reaction. In hydroxylic

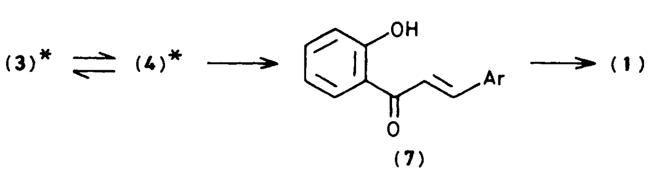


Scheme 2.

or protic solvents, on the other hand, the phenolic proton and/or the carbonyl oxygen are externally hydrogen-bonded,[5,6,7f] and are unfavourable for the cyclization reaction. The low quantum efficiencies may be due to the rapid deactivation process (k_{-1}) and intersystem crossing (i.s.c.) or internal conversion (i.c.) to inactive states, as well as the energy-wasting *cis–trans* photoisomerization about the $C_\alpha{=}C_\beta$ double bond.[9d]

In photophysical dynamic studies,[6–8] the short life-times ($\geqq 10$ ps) and highly efficient radiation processes of the internally hydrogen-bonded excited states have been discussed in terms of the rapid i.c.[8a] or i.s.c.[6f,7f] to inactive states, the state mixing,[7c,f] and vibrationally hot excited states,[6b,e,8b,c] though the nature of the deactivation processes remains open to clarification.

A number of factors can cause a wavelength dependence of organic photoreactions.[11] The marked wavelength dependence of the quantum yields (Table 3) may be related to the differences in (i) the ground-state species present in solution prior to excitation, such as the keto–enol tautomers or closed and open conformers,[5,6] (ii) the chromophores primarily relevant to the



Scheme 3.

Table 4. M.p.s and u.v. absorption spectral data[a]

Chalcone	M.p. (°C)	$\lambda_{max.}$ or λ_{sh}/nm	10^{-4} ε/l mol^{-1} cm^{-1}	$\Delta\nu^{b}$/cm^{-1}
(**1a**)	86—87	316	2.35	−308
		350 sh	1.20	
(**1b**)	148—149	330	2.57	−804
		360 sh	1.79	
(**1c**)	88—89	366	2.83	−1 500
		355 sh	2.74	
(**1d**)	77—78	316	2.29	−303
		355 sh	1.27	
(**1e**)	146—149	319	2.64	−298
		360 sh	1.28	
(**1f**)	146—148	320	2.78	−245
		360 sh	1.37	
(**1g**)	200[c]	318	2.81	−505
		360 sh	1.10	
(**1h**)	95—96	385	2.40	−625
(**1i**)	112—113	370	2.29	
(**1j**)[d]	136—137	360	2.24	
2′-Methoxy	36—37	303	2.09	
2′-Nitro	124—125	295	2.19	

[a] M.p.s were uncorrected. Absorption spectra were measured in ethanol. Approximate positions of the shoulders (λ_{sh}) are also included. [b] The shifts of the maximal bands due to the increase in the solvent polarity from cyclohexane to ethanol. [c] Sublimed. [d] Not a chalcone. No shoulders appeared for (**1h**—**j**).

photoexcitation in the molecule (the cinnamoyl and hydroxybenzoyl moieties),[9] and (iii) the electronic and vibrational states which can affect the relative efficiencies of the forward and/or dissipative processes.[5–8] The ground-state equilibria of the chalcones are considered to lie exclusively toward the closed keto form (**1**), on the basis of relative stabilities and the unit intensities of the n.m.r. phenolic protons in non-polar and polar aprotic solvents. Thus, possibility (i) seems to be low. From the substituent effects on the u.v. absorption spectra of chalcones, it is implied that the intense bands (mostly at *ca.* 315—330 nm) are primarily due to the cinnamoyl group and the shoulders (at *ca.* 360 nm) are due to the hydroxybenzoyl group. Then, it may be expected that the selective excitation of the cinnamoyl group (with 313 nm light) would be less effective than that of the hydroxybenzoyl group (with longer wavelength light) for photocyclization, since the cinnamoyl group is rather distant from the proton-transfer reaction centre and since it has a $C_\alpha{=}C_\beta$ double bond capable of energy-wasting *cis–trans* photoisomerization. The facts, however, argue against expectations and hence (ii) is uncertain, although this point deserves more in-depth study combined with more detailed examination of the u.v. spectra. The dissipative pathways *via* i.c. and i.s.c. to inactive states[6–8] would be facilitated when the energy levels of the excited singlet states are lowered and become closer to the triplet states, *e.g.*, T_2 (*n*, π*), or the ground states. The highly efficient i.s.c. of aromatic ketones,[12] $k_{\text{i.s.c.}}$ *ca.* 10^{10}—10^{11} s^{-1}, is compatible with decay rates for the excited singlet states of the internally hydrogen-bonded conformers of aromatic *o*-hydroxy-

Table 5. Experimental conditions for the actinometry

λ/nm	Light source	Filter	Actinometer (concentration)	φ_A[a]	Irrad. time	10^4 I_a/ ein min^{-1}
313	HP-Hg 400 W	$NiSO_4$ aqueous solution (3M)	Benzophenone–diphenylmethanol (0.1M)	0.68	60 min	1.3
365—366	HP-Hg 500 W	Glass filters (UV-35 + UV-D2)	$K_3Fe_2(C_2O_4)_3$ (0.15M)	1.15	28 s	6.2
405	HP-Hg 500 W	Interference filter	0.006M	1.14	30 s	5.1
436	HP-Hg 500 W	Glass filter (VY-44)	0.17M	0.89	23 s	10

[a] Reported quantum yields of actinometers.[14]

carbonyl compounds.[7] It has been suggested that i.s.c. can be an important deactivation pathway for the singlet zwitterion *via* reversible proton transfer.[7a] The lack of an internal heavy-atom effect in (**1f**) suggests the minor importance of i.s.c. as a deactivation process. However, it is possible to consider that i.s.c. is so efficient that actual efficiencies are unaffected even when facilitated by heavy atoms. If the reversible proton transfer in the excited states was an important dissipative channel[7] or vibrational factors were relevant in the rate-determining step, then a significant kinetic isotope effect should be found between 2′-OH- and 2′-OD-chalcones. A nil kinetic isotope effect, $k_H/k_D = 1.0 \pm 0.2$, was found in our additional experiments where the photoreaction rates were compared for 2′-OH- and 2′-OD-chalcone (the n.m.r. signal at δ 12.8 was absent), on irradiation with visible light in ethyl acetate. The percentage conversions, 2′-OH chalcone/2′-OD, were 11.3/15.7, 28.9/27.7, and 49.9/53.8, for irradiation for 2, 5, and 10, h respectively. Thus it is unlikely that the rate-determining step involves proton transfer or vibrational factors. Rather, the major deactivation process may take place *via* i.c. (k_{-1}) or by the alternative route involving the formation of the inactive open conformer (7) (Scheme 3).

Experimental

2′-Hydroxychalcones and flavanones were prepared from substituted benzaldehydes and hydroxyacetophenones according to the literature method.[13] Other reagents and solvents were of guaranteed grade (Wako Chemical) and were used without further purification. The contamination of tetrahydrofuran as solvent with water below 0.3% v/v caused no serious interference. Each sample solution to be irradiated was deoxygenated by bubbling through with purified nitrogen gas in a Pyrex ampoule (5—10 ml) and sealed, then irradiated with a 400 W high-pressure mercury lamp (400 W HP-Hg) in a merry-go-round apparatus thermostatted at 20 ± 1 °C. Appropriate solution filters and glass filters (Toshiba) were used to cut off short-wavelength regions. Photolysed mixture solutions were separated on silica gel–benzene after condensation. The photocyclization products were identified by comparing their n.m.r. and u.v. spectra with those of flavanones independently prepared.[13] The amounts of chalcones recovered and flavanones formed were determined from their u.v. absorptions after separation on silica gel–benzene. U.v. and n.m.r. spectra were measured using a Hitachi 200-10 and a Hitachi R-24 n.m.r. spectrometer, respectively.

For the measurement of quantum yields, paralleled and narrow-band light beams were employed by means of an optical train system (Ushio Electric) consisting of a Hg super-high pressure point-source lamp (500 W HP-Hg), parabolic mirror, collimating lens, glass filters, and slits. The sample cell and actinometer cell were cylindrical cells with parallel flat windows (20 mm diameter, 25 mm depth). The light quanta not absorbed by and transmitted through the sample solution were measured in the actinometer cell placed behind the sample cell. Thus, the light quanta absorbed by the sample solution were determined from the difference in the light quanta per unit time in the actinometer cell, in the absence and presence of the reactants in the sample cell. The conversions of the reactants were in the range 3—5%. Because of the low sensitivities of the reactants, irradiation times for the sample solution were relatively long (15—90 min) while those for the actinometer solution[14] were much shorter. Table 5 summarizes the experimental conditions employed for actinometry. Since the intensity of the light source was not highly stable, each quantum yield value was obtained by the average over three or two measurements. The deviations were usually 5% or less. No correction was made, however, for the reflection of the light at the interfaces at the windows of the cells.

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