Specific Photoreactions of Flavanones Typical of n,π^* and π,π^* Characters in Lowest Triplet States

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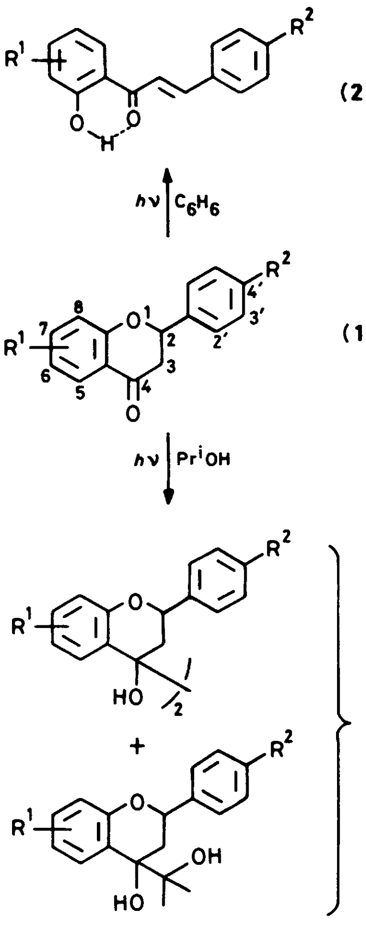
On irradiation with u.v. light, flavanones undergo photochemical opening of the dihydropyranone ring ($\varphi_2 < 0.2$) and/or bimolecular photoreduction ($\varphi_3 < 0.8$). The relative occurrence of these processes markedly depends on the substituents as well as on the solvent. Triplet mechanisms are implied for both reactions by the results of quenching experiments, as well as by fluoroescence and phosphorescence spectra. A Hammett ρ value of *ca.* -1.2 suggests the intermediacy of radicals in the ring-opening reaction. The marked variations in φ_2, φ_3, and φ_f with substituents are explicable in terms of relative contributions of n,π^* and π,π^* character in lowest triplet states.

Much work has been done on specific reactions of n,π^* *versus* π,π^* triplet states,[1–3] particularly with unsaturated cyclic ketones[2] and phenyl ketones.[3] Effects of solvent and ring substituents on relative contributions of n,π^* and π,π^* character in low lying triplets have been studied extensively with a series of substituted phenyl ketones.[3] Recently, it has been implied that the photochemical ring-opening reaction of flavanones takes place from π,π^* triplet states on u.v. irradiation,[4] whereas the reverse photoreaction (cyclisation) occurs from excited singlet states on irradiation with visible light.[5]

Photochemical C–O bond fission in cyclic aryl ethers has received considerable attention. Thus, benzodihydrofurans have been shown to undergo stereospecific photorearrangements to phenols by a concerted process,[6] whereas photorearrangements of chroman-3-ones occur by a stepwise process.[7] Much less work has been done on the photoreaction mechanisms of benzodihydropyranones (flavanones and chroman-4-ones),[4,8,9] though excited-state properties of some chroman-4-ones have been studied.[10] The present work was undertaken to elucidate structure–reactivity relationships for the specific photoreactions of the benzodihydropyranone system, using flavanones with a wide variety of substituents (Scheme 1). Variation in R^1 (ring *A* substituent) was expected to alter substantially the excited-state properties, such as ordering and/or mixing of the low lying excited states, whereas changes in R^2 (ring *B* substituent) would alter the stabilities of chemical intermediates without substantial influence on the excited-state properties.



(3)

		R1	R2
(2)	a	H	H
	b	H	Me
	c	H	OMe
	d	H	F
	e	H	Cl
	f	H	Br
	g	H	NO_2
	h	H	NMe_2
	i	6-Me	H
	j	6-Me	OMe
(1)	k	6-OMe	H
	l	6-OMe	Br
	m	6-OMe	OMe
	n	6-Cl	H
	o	6-NO_2	H
	p	7-OMe	H
	q	7-Cl	H
	r	7,8-(CH:CH·CH:CH)	H

Scheme 1.

Results and Discussion

Ring-opening Reaction.—In a poor H-atom-donating solvent, such as benzene or 2-methylpropan-2-ol, most of the flavanones (**1**) underwent photochemical opening of the dihydropyranone ring to give 2′-hydroxychalcones (**2**) as the major products on irradiation with 313—366 nm light (Table 1). In a good H-atom-donating solvent, such as propan-2-ol, drastic effects of R^1 were found. With (**1a**—**f**, **n**, and **q**) (R^1 = H or Cl) no significant amounts of (**2**) were formed but instead reductive coupling products [(**3**) as mixtures][4b] were the major products, whereas significant amounts of (**2**) were formed with (**1i**—**k** and **m**) (R^1 = 6-Me or -OMe). It is notable that (**1j**) and (**1m**) exhibit particularly clean ring-opening reactions both in benzene and in propan-2-ol. Since the photochemical ring-opening reaction of (**1**) with u.v. light is apparently the reverse of the photocyclisation of (**2**), which occurs cleanly on irradiation with visible light,[5] together they may be regarded as a photochromic system. The benzoflavanone (**1r**) also gave the chalcone (**2r**), both in benzene and in propan-2-ol, but 6-nitroflavanone (**1o**) was photochemically inert in all solvents tested. Thus, electron-donating or conjugative substituents at the 6-position tend to favour the ring-opening reaction, while electron-withdrawing groups favour photoreduction, on irradiation in propan-2-ol.

Table 2 lists relative rates of formation of (**2**) on irradiation with 254 nm light in 2-methylpropan-2-ol, which provide some insight into the effects of R^2 on the ring-opening reaction. Since each solution of (**1**) showed complete absorption of the incident

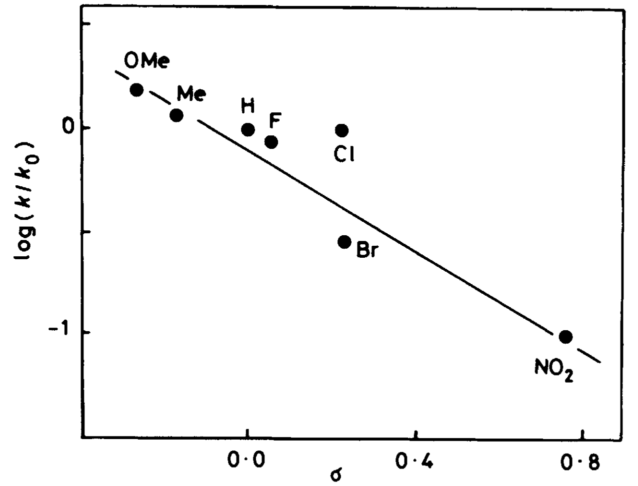


Figure 1. Plot of log(k/k_0) *versus* ordinary Hammett σ of R^2 for the photochemical ring opening of (1) in 2-methylpropan-2-ol with 254 nm light

Table 1. Photochemical ring-opening of flavanones with 313—366 nm light[a]

Flavanone	Solvent	Time (min)	Δ[(1)]/mM[b]	[(2)]/mM	[(2)]/Δ[(1)]
(1a)	Benzene	8	0.21	0.12	0.57
	Bu^{t}OH	8	0.15	0.11	0.70
(1b)	Benzene	15	0.28	0.20	0.71
	Bu^{t}OH	8	0.20	0.12	0.60
(1c)	Benzene	8	0.25	0.19	0.76
	Bu^{t}OH	4	0.13	0.11	0.85
(1d)	Benzene	15	0.20	0.11	0.56
	Bu^{t}OH	16	0.19	0.14	0.74
(1e)	Benzene	8	0.25	0.14	0.55
	Bu^{t}OH	8	0.16	0.07	0.44
(1f)	Bu^{t}OH	16	0.20	0.09	0.45
(1i)	Benzene	8	0.10	0.07	0.70
	Bu^{t}OH	20[c]	0.25	0.17	0.68
	Pr^{i}OH	10	0.16	0.07	0.47
(1j)	Benzene	8	0.15	0.13	0.87
	Pr^{i}OH	10	0.17	0.17	1.0
(1k)	Benzene	60	0.17	0.09	0.53
	Bu^{t}OH	20[c]	0.37	0.13	0.35
	Pr^{i}OH	120	0.27	0.08	0.30
(1m)	Benzene	60	0.26	0.26	1.0
	Pr^{i}OH	120	0.18	0.18	1.0
(1n)	Benzene	12[c]	0.17	0.14	0.83
(1p)	Benzene	40[c]	0.17	0.08	0.49
(1r)	Benzene	180[c]	0.19	0.04	0.21
	Pr^{i}OH	60[c]	0.22	0.05	0.23

[a] Each flavanone (1.0mM-solution) was irradiated at 25 ± 1 °C under nitrogen with a 400 W high-pressure Hg lamp through an aqueous $NiSO_4$ solution filter. [b] Consumption of (1). [c] Irradiated with a 100 W high-pressure Hg lamp through Pyrex glass.

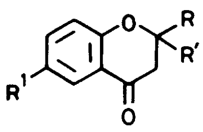
light at 254 nm, the relative rates in Table 2 provide relative quantum yields. A plot of the rates as a function of the ordinary Hammett constants (σ_p)[11] of R^2 showed a linear free energy relationship with a slope (ρ) of −1.2 ± 0.2 (Figure 1). The ρ value, in the neighbourhood of −1, is consistent with a typical homolytic bond fission or free-radical reactions.[12] Since excited-state properties are considered to be little affected by R^2, which is out of conjugation with the major chromophore, the observed substituent effects of R^2 may reflect the relative stabilities of some chemical intermediate.

Table 2. Photochemical ring-opening of flavanones with 254 nm light[a]

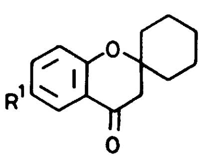
Flavanone	Time (h)	Δ[(1)]/mM	[(2)]/mM	[(2)]/Δ[(1)]	σ[b]
(1a)	4	0.25	0.18	0.72	0.00
(1b)	4	0.32	0.20	0.63	−0.17
(1c)	4	0.36	0.26	0.72	−0.27
(1d)	4	0.23	0.17	0.74	+0.06
(1e)	4	0.34	0.20	0.59	+0.23
(1f)	8	0.24	0.13	0.54	+0.23
(1g)	32	0.27	0.16	0.59	+0.78
(1i)	8	0.22	0.18	0.82	
(1k)	8	0.06	0.05	0.83	
(1n)	4	0.17	0.13	0.76	
(1p)	8	0.15	0.09	0.60	

[a] Each flavanone (1.0mM-solution) in 2-methylpropan-2-ol was irradiated with a 10 W low-pressure Hg lamp at 26 ± 2 °C. [b] Ordinary Hammett constants for the ring *B* substitutents (R^2).

Table 3. Effects of substituents and solvent on relative rates for the photoreduction of flavanones and chroman-4-ones[a]



(1) s; R = R′ = R^1 = H
u; R = R′ = Me, R^1 = MeO



(1) t; R^1 = Me
v; R^1 = MeO

Substrate	Irrad. time (min.)	Relative photoreduction rates[b] Methanol	Ethanol	Propan-2-ol
(1s)	1	31	35	38
(1a)	1	20	32	37
(1t)	10	1.1	3.0	5.6
(1u)	120	0.044	0.080	0.1.7
(1v)	120	0.048	0.083	0.24

[a] Each substrate (1.0mM-solution) was irradiated with a 400 W high-pressure Hg lamp through Pyrex glass. [b] [(3)] × 100 (mmol l^{-1} min^{-1}).

Photoreduction of H-*atom-donating Alcohols*.—Table 3 exemplifies the effects of substituents and solvents (alcohols) on photoreduction rates. In these alcohols photoreduction products (3) were formed exclusively [with only traces of (2)]. Marked effects of R^1 on the photoreduction rates are noted, but the chromanone 2-substituents seem to have little effect, which is in contrast to the substituent effects on the ring-opening reaction. While (**1a** and **s**) (R^1 = H) show high reactivities and little dependence on solvents (or H-atom-donating ability), (**1t**—**v**) exhibit much lower reactivities and high H-donor dependences. Since it has been well established that the photoreactivities of acetophenones and benzophenones in bimolecular H-atom abstraction are essentially attributable to the n,π^* character in the lowest triplet state (T_1),[13] the marked effects of R^1 must be related to the variation in n,π^* *versus* π,π^* character in T_1. The solvent dependence of the photoreduction rates may reflect relative stabilities of the radicals $Me_2\dot{C}OH > Me\dot{C}HOH > H_2\dot{C}OH \gg \dot{C}H_2CMe_2OH$. The lack of effect of the chromanone 2-substitutents is expected, since neither the excited states nor the chemical intermediates [ketyl radicals (5)] of photoreduction would be affected by these.

Quantum Efficiencies.—Since the substrates (1) do not show complete absorption of u.v. light, and absorptivities vary according to R^1, quantum yields are required for quantitative

Table 4. Quantum efficiencies for the photoreactions and fluorescence[a]

Flavanone		In benzene[b]	In propan-2-ol			
No.	R^1	φ_2	φ_2	φ_3	φ_f[c]	($\lambda_{f\ max.}$/nm)
(1a)	H	0.07	0.00	0.40	$<10^{-3}$	(390)
(1c)	H	0.14	0.00	0.46	$<10^{-3}$	(390)
(1i)	6-Me	0.09	0.05	0.04	0.002	(400)
(1j)	6-Me	0.18	0.10	0.00	0.002	(400)
(1k)	6-OMe	0.04	0.005	0.01	0.25	(450)
(1l)	6-OMe		0.01	*d*	0.25	(450)
(1m)	6-OMe	0.12	0.01	0.00	0.25	(450)
(1n)	6-Cl	0.14	0.00	0.78	$<10^{-3}$	(400)
(1r)	7,8-(CH:CH·CH:CH)		0.002	0.007	0.12	(425)

[a] Formation quantum yields of **(2)** (φ_2) and **(3)** (φ_3) at 313 nm; φ_3 was estimated as the difference between φ_2 and the consumption quantum yield of **(1)** (φ_{-1}). [b] No fluorescence was observed in benzene. [c] Room-temperature fluorescence quantum yield on excitation at 334 nm. [d] Could not be estimated since significant amounts of unknown products were formed as well as **(1)** and **(3)**.

Table 5. Effects of additives[a]

		In benzene	In propan-2-ol	
Flavanone	Additive	[(2)]/[(2)]$_0$	[(2)]/[(2)]$_0$	[(3)]/[(3)]$_0$
(1a)	Air	0.43	0.20	
	Ferrocene	0.36		0.40[b]
	trans-Stilbene	0.17		0.35
	Fumaronitrile			0.43
(1i)	Air	0.42	0.34	0.27
	Ferrocene	0.41[c]	0.14[d]	0.13[e]
	trans-Stilbene	0.16	0.16	0.14
	Fumaronitrile	0.34		
(1k)	Air		0.54	0.65
	Ferrocene	0.37	0.60[g]	0.71
	trans-Stilbene	0.16[f]	0.53[g]	0.55
	Fumaronitrile		0.48	0.50
	Nitrosobenzene	0.18		

[a] The ratio of the yields of **(2)** in the presence [ ] and absence [ ]$_0$ of additive (1.0mM), on parallel irradiation at 25 ± 1 °C. Concentrations of the dissolved oxygen in aerated solution are assumed to be in the 10^{-3}M region though not determined. [b] Stern–Volmer plot gave a straight line with a slope $K_{SV} = (1.36 \pm 0.09) \times 10^3\ l\ mol^{-1}$. [c] $K_{SV} = (1.60 \pm 0.30) \times 10^3\ l\ mol^{-1}$. [d] $K_{SV} = (6.3 \pm 0.3) \times 10^3\ l\ mol^{-1}$. [e] $K_{SV} = (5.2 \pm 0.9) \times 10^3\ l\ mol^{-1}$. [f] $K_{SV} = (4.3 \pm 0.2) \times 10^3\ l\ mol^{-1}$. [g] Stern–Volmer plots were not linear.

examination of photoreactivities in this wavelength region. The formation quantum yields have been measured for selected substrates with different substituents R^1 (Table 4). In benzene solution, where fluorescence and photoreduction are less important, φ_2 values are mainly affected by R^2, suggesting that the nature of stability of a chemical intermediate [such as **(4)**] is altered by R^2. On the other hand, in propan-2-ol where fluorescence and/or photoreduction are important, φ_2 values vary drastically with R^1 rather than with R^2. Thus, when R^1 = H or Cl, φ_2 values are zero, owing to efficient photoreduction (high φ_3), whereas when R^1 = 6-OMe or a 7,8-benzofusion both φ_2 and φ_3 are low, at least partly owing to efficient fluorescence (high φ_f). When R^1 = 6-Me, both φ_f and φ_3 are low, and φ_2 values are highest. Thus, the substituent R^1 profoundly affects the relative efficiences for fluorescence *versus* intersystem crossing as well as the rates and relative occurrence of the photoreduction and ring-opening reactions.

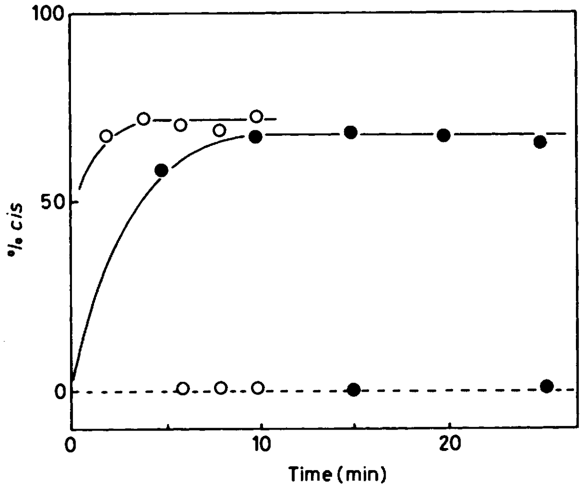


Figure 2. Photostationary states of stilbenes obtained by **(1k)**-sensitised isomerisation of *trans*-stilbene in benzene (○) and in propan-2-ol (●); each solution contained **(1k)** (1.0mM) and *trans*-stilbene (1.0mM) and was irradiated with 365—366 nm light at 25 °C [broken line: similarly irradiated in the absence of **(1k)**]

Effects of Additives.—Suppression effects of additives have been measured for selected flavanones with different substituents R^1 (Table 5). Both photoreduction and ring-opening reactions were subject to efficient quenching by triplet quenchers and free-radical inhibitors. Stern–Volmer quenching constants, K_{SV}, are included in the footnote to Table 5. The fluorescence intensities of these flavanones in propan-2-ol were virtually unaffected by these additives. The results imply that both photoreduction and ring-opening take place *via* triplet states and/or radical intermediates. Quenching efficiencies for the two photoreactions are similar in propan-2-ol, suggesting that the two reactions occur from common triplets, presumably lowest triplets of strongly mixed orbital character. Since some of the quenchers (olefins and molecular oxygen) may also act as free radical inhibitors, and since fumaronitrile (a free-radical inhibitor) may also act as triplet quencher, there remains some uncertainty as to the identity of the species actually quenched. To remove this uncertainty and to obtain more insight into the nature of the relevant excited states, photostationary compositions of the *cis–trans*-isomers (%*cis* p.s.s.) have been determined in the flavonone-sensitised isomerization of *trans*-stilbene. Figure 2 illustrates the rapid attainment of the photostationary states in both photoreactions. From the %*cis* p.s.s. values thus obtained and the plot of %*cis* p.s.s. *versus* T_1 of sensitizer,[14] some T_1 levels of **(1)** were estimated (Table 6). These values are similar to those obtained from the low-temperature phosphorescence spectra, implying that triplets are the active states pertinent to the photoreactions and quenching.

Absorption and Emission Spectra.—U.v. absorption spectra of selected flavanones with different substituents R^1 are listed in Table 7, showing strong bands at 310—350 nm and weak shoulders in the longer wavelength region. The spectra were little changed with R^2 but changed significantly with R^1 as well as with solvent. The long-wavelength shoulders were observed with all these flavanones in dilute solution in cyclohexane as well as in ethanol solution in higher concentrations. On changing solvent from cyclohexane to ethanol or on exchanging R^1 (at the 6-position) for electron-donating groups, the strong bands were significantly red-shifted, but solvent shifts of the weak shoulders were not clear owing to substantial overlapping with the strong bands, particularly in polar solvents. The strong

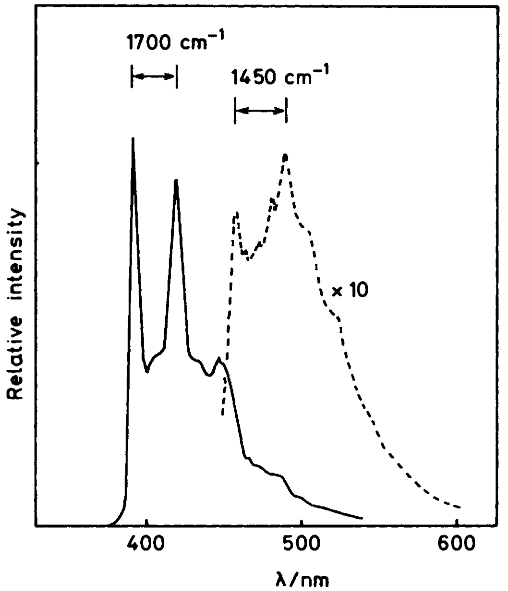


Figure 3. Phosphorescence spectra of (**1a**) in 2-methyltetrahydrofuran (solid line) and (**1k**) in ethanol (broken line) at 77 K

Table 6. Triplet properties of flavanones[a]

Flavanone	Solvent†	%*cis* p.s.s.	T_1[b]/kcal mol^{-1}	T_1[c]/kcal mol^{-1}	Character[e]
(**1a**)[d]	MTHF or MP			73	n,π^*
(**1i**)	Benzene	53	>70		
	Propan-2-ol	62	63		
	MTHF			68	n,π^*
(**1k**)	Benzene	72	59		
	Propan-2-ol	69	58		
	Ethanol			62	π,π^*
(**1r**)	Benzene	91	52		
	MTHF			59	π,π^*

[a] Solution containing 1.0mM (**1**) and 1.0mM *trans*-stilbene was irradiated with 365—366 nm light at 25 ± 1 °C. [b] Obtained from %*cis* p.s.s. at room temperature. [c] From 0–0 band of the phosphorescence in solid matrix glass at 77 K. [d] Could not be obtained because of the extensive consumption of (**1a**) before p.s.s. was attained in benzene or in propan-2-ol. [e] Dominant character T_1 assigned from vibrational modes of the low-temperature phosphorescence spectra.

† MTHF = 2-methyltetrahydrofuran; MP = 3-methylpentane.

Table 7. U.v. absorption spectra of some flavanones[a]

Flavanone	Solvent[b]	λ/nm (ε/l mol^{-1} cm^{-1})
(**1a**)	C	365sh (15 ± 5), 347sh (25 ± 10) 312 (3 600), 245 (8 800)
	E	317 (3 600), 250 (9 600)
(**1i**)	C	365sh (30 ± 10), 320 (3 700) 247 (8 900)
	E	330 (3 400), 250 (7 700)
(**1k**)	C	357sh (10 ± 5), 343 (4 400) 248 (7 400)
	E	350 (4 000), 254 (7 400)
(**1n**)	C	368sh (10 ± 5), 324 (3 500) 245 (8 000)
	E	328 (3 200), 250 (6 500)

[a] Values of ε_{sh} involve substantial uncertainty (as indicated) because of the underlying absorption from the tail of the strong band. [b] C: cyclohexane, E: ethanol.

bands are assigned to $\pi\rightarrow\pi^*$ transitions in view of their solvent shifts and large extinction coefficients, while the weak shoulders are assigned to $n\rightarrow\pi^*$ transitions in view of the small extinction coefficients. Consistent with the results, it has been shown that the lowest singlet state of (**1s**) is of n,π^* character and that the state ordering remains unchanged with changes in solvent polarity.[10]

Fluorescence spectra also varied markedly with R^1 as well as with solvent: (**1k**—**m**, **u**, and **v**) (R^1 = 6-OMe) were strongly fluorescent in alcohols but showed zero fluorescence in benzene and cyclohexane, while (**1a** and **s**) (R^1 = H) were very weakly fluorescent in alcohols. Table 4 includes the fluorescence quantum yields (φ_f) and the maximum bands of some flavanones in propan-2-ol. On change in solvent from propan-2-ol to 2-methylpropan-2-ol, φ_f values of (**1v** and **t**) were not increased, implying that the excited singlets are not directly involved in the photoreduction. Since the lowest singlet states (S_1) are mainly of n,π^* character and essentially unchanged, the marked changes in φ_f with R^1 may be attributable to the variation of the $S_1 \longrightarrow T$ intersystem crossing efficiencies, depending on the electronic character of the relevant triplets.[15]

Figure 3 illustrates the phosphorescence spectra of (**1a**) and (**1k**) at 77 K. The former is similar to the spectrum of (**1s**) reported by Gallivan.[10] Thus, the prominent vibrational progression at *ca.* 1 700 cm^{-1} is ascribable to carbonyl stretching and implies that T_1 of (**1a** and **s**) is predominantly of n,π^* character, in both 2-methyltetrahydrofuran and 3-methylpentane glasses. This assignment may apply to all the substrates with R^1 = H because the chromophores are identical, and hence T_1 of (**1a**—**h** and **s**) are of n,π^* character (*ca.* 73 kcal mol^{-1}). On the other hand, the *ca.* 1 450 cm^{-1} vibrational progression of (**1k**) is ascribable to ring vibration, implying that the T_1 state is dominantly of π,π^* character. Because of the identical chromophores, T_1 of (**1k**—**m**, **u**, and **v**) are dominantly of π,π^* character (*ca.* 62 kcal mol^{-1}). Also (**1r**) exhibited a vibrational progression at *ca.* 1 500 cm^{-1}, implying a π,π^* nature for T_1. Though much less prominent than (**1a**), (**1i**) showed a *ca.* 1 650 cm^{-1} vibrational progression, implying n,π^* character in methyltetrahydrofuran glass. The energy levels and orbital configurations of T_1 states, estimated from the phosphorescence spectra, are included in Table 6 for comparison with T_1 obtained from the %*cis* p.s.s. in the sensitised reactions. The much weaker phosphorescence intensity of (**1k**) suggests inefficient $S_1 \longrightarrow T$ intersystem crossing. The discrepancy in the E_T values of (**1r**) cannot be accounted for as yet.

Discussion of the Mechanisms.—Triplet mechanisms are strongly implied for both photoreduction and ring-opening by the following observations: (i) efficient quenching of both reactions by triplet quenchers without quenching of fluorescence; (ii) the agreement in the T_1 levels, except for (**1r**), from phosphorescence spectra and sensitised isomerisation of stilbenes; and (iii) the competition between $\varphi_2 + \varphi_3$ and φ_f (in propan-2-ol). Similar quenching efficiencies for the two photoreactions suggest that both occur from the same triplets T_1 and relative occurrence of the two reactions reflects the fractions of n,π^* and π,π^* character in T_1. Thus, with R^1 = H or Cl, a dominant n,π^* character in T_1 leads to photoreduction (in an H-atom-donating solvent) while with R^1 = 6-OMe a dominant π,π^* character leads mainly to ring-opening. Low-temperature phosphorescence spectra support this idea.

A simplified schematic profile may be proposed in terms of a single reactive triplet state (T_1) the electronic character of which varies from one compound to another: $T_1 = a(n,\pi^*) + b(\pi,\pi^*)$. Two extreme cases are illustrated in Figure 4. Many of the flavanones produce both types of product, depending on the degree of mixing of electronic character in T_1. At one extreme

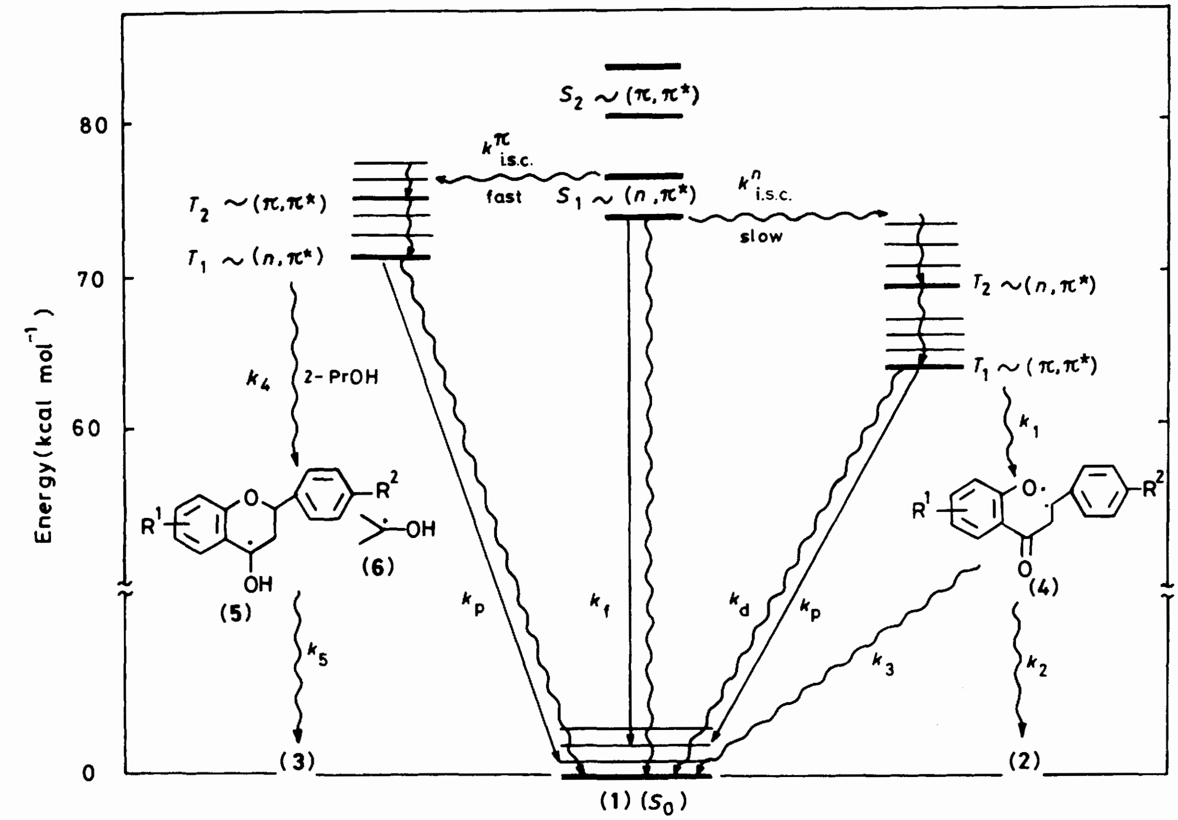
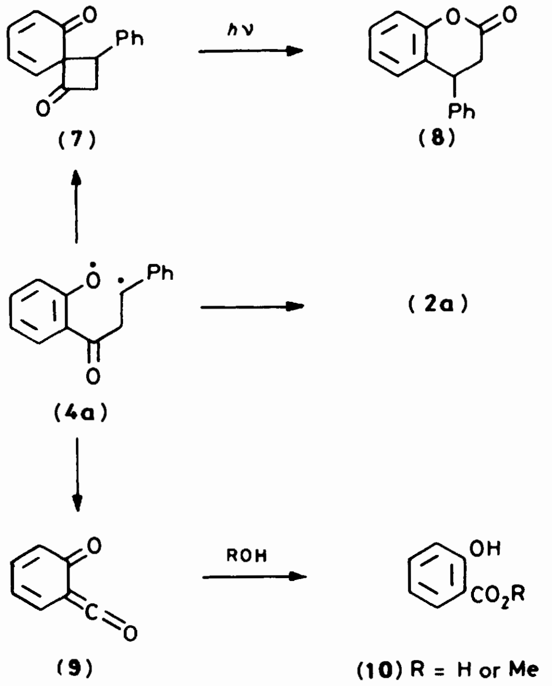


Figure 4. Simplified schematic profile illustrating two extremes with $T_1 \sim n,\pi^*$ [left-hand side: for (**1a**—**h**)] and with $T_1 \sim \pi,\pi^*$ [right-hand side: for (**1k**—**m**)]. Many of the flavonones produce both (**2**) and (**3**) depending on the mixing of these electronic characters in T_1, since we are dealing with approximate models using a single electron configuration which makes the major contribution to that state



Scheme 2.

(with R^1 = H) T_1 is mainly of n,π* character and predominantly undergoes H-atom abstraction [the left-hand side of the Figure, *e.g.* for (**1a**—**h**)]. Because of the allowed spin-orbit coupling (and smaller energy separation), intersystem crossing from $S_1 \sim (n,\pi^*)$ to $T_2 \sim (\pi,\pi^*)$ occurs efficiently,[15] followed by rapid internal conversion to $T_1 \sim (n,\pi^*)$. As a result, φ_f is low and φ_2 is high in a good H-atom-donating solvent, or phosphorescence intensity is high in low-temperature rigid glass. In the other extreme case (with R^1 = 6-OMe), π,π* character in T_1 becomes larger or dominant and ring-opening becomes significant or dominant [the righ-hand side of the Figure, *e.g.* for (**1k**—**m**)]. Because of the forbidden spin-orbit coupling for intersystem crossing (i.s.c.) from $S_1 \sim (n,\pi^*)$ to $T_2 \sim (n,\pi^*)$ and/or as a result of larger energy separation between S_1 and $T_1 \sim (\pi,\pi^*)$, $\varphi_{\text{i.s.c.}}$ is low, thus resulting in high φ_f and low $\varphi_2 + \varphi_3$ and weaker phosphorescence in low-temperature rigid glass.

The Hammett ρ value of *ca.* −1.2 (effect of R^2) is consistent with a radical mechanism. The diradical (**4**) has been postulated as the key intermediate in the photoreactions of (**1a**) in benzene with 254 nm light (Scheme 2),[8] though the relevant excited state has not been specified. Although not analysed in the present work, some minor products were detected (t.l.c.) on irradiation in benzene and we believe they included (**8**) and (**9**) or derivatives. Homolytic C–O bond fission and the intermediacy of spirocyclohexa-2,4-dienones such as (**7**) have been often encountered in aryl ether photochemistry.[6–8] It seems reasonable to assume that species (**4**) are generated as triplet diradicals from T_1,[16] thereby making it difficult to discriminate between triplet quenching and radical trapping.

The overall efficiency for the formation of (**2**), or the

$$\varphi_2 = \varphi_{\text{i.s.c.}}\left(\frac{k_1}{k_1 + k_d + k_p}\right)\left(\frac{k_2}{k_2 + k_3}\right) \qquad \text{(i)}$$

formation quantum yield (φ_2), may be represented by three terms [equation (i)]. The middle term, involving the primary C–O bond fission, would be substantially affected by the relative stability of (**4**), and the last term, including relative rates for back recombination *versus* product formation, might also be sensitive to the properties of (**4**). Thus every term in the equation could be susceptible to the substituents, and hence the ρ value (effects of R^2 on φ_2) cannot be related to the primary C–O bond fission (k_1) unless the other two terms are unchanged. This point seem to deserve further investigation (*e.g.* e.s.r. measurements). The rather low values of φ_2 may be partly due to the back recombination (k_3) of (**4**) as well as low $\varphi_{\text{i.s.c.}}$.

Experimental

Apparatus.—The u.v. absorption and fluorescence spectra were recorded with a Hitachi 200-10 spectrophotometer and a 204 fluorescence spectrometer, respectively. High-performance t.l.c. analysis was carried out with an Iatoroscan YH-10 TLC/FID analyser (Iatron Lab. Inc.). The light source for irradiation with 313—366 nm light was a high-pressure mercury lamp (100 or 400 W) with a merry-go-round irradiation apparatus; a 10 W low-pressure mercury lamp was immersed in a reaction vessel (150 ml) for 254 nm irradiation. Temperature was usually 25 ± 1 °C.

Material and Procedures.—Flavanones,[17] 2′-hydroxychalcones,[18] chroman-4-ones,[19] and 1-(2-hydroxyaryl)butenones[20] were prepared according to the reported methods. Other reagents and solvents were of the purest grade commercially available (Wako Chemicals). Solutions of (**1**) (1.0mM) were purged in identical 10 ml ampoules with pure nitrogen (99.999%) for 40—60 min; the ampoules were then sealed and irradiated under identical conditions. The ring-opening products were identified by comparing their ^1H n.m.r. and u.v. spectra with those of the compounds (**2**) independently prepared.[18,20] Structural analyses of the photoreduction products in propan-2-ol solution have been described previously.[4b]

The amounts of the photoproducts (**2**) and of unchanged starting materials (**1**) were determined by high-performance t.l.c. analysis as well as by u.v. absorption spectroscopy. The amounts of (**3**) (as the totals of the mixtures) were estimated indirectly as the difference between the amounts of consumption of (**1**) and the formation of (**2**), since only (**2**) and (**3**) were the major products in propan-2-ol. On irradiation in benzene some other minor products were detected (t.l.c.), perhaps (**8**) and (**9**)[8] or derivatives.

Quantum yields for the photoproducts were measured using actinometer solutions of benzophenone–diphenylmethanol in deaerated benzene[21] in ampoules. The monochromatic 313 nm mercury line was isolated through a nickel sulphate filter solution. Fluorescence quantum yields were measured using 4 × 10^{-5}M-quinine in aqueous 0.5M-sulphuric acid as a standard. Phosphorescence spectra were measured by Dr. K. Tokumura at Kanazawa University.

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