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Photoreactions of Flavanones

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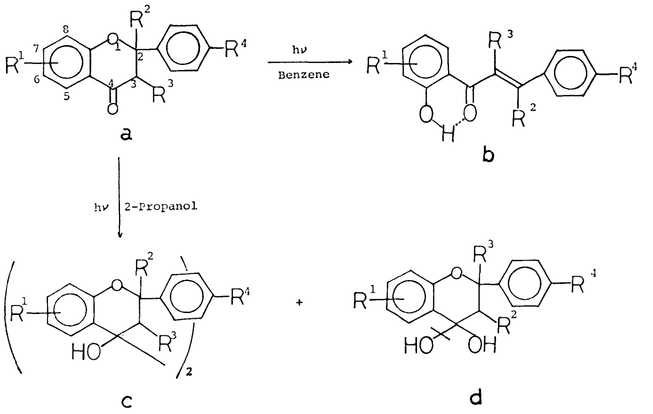
Parent and substituted flavanones undergo photochemical opening of the pyrone ring to give corresponding 2′-hydroxychalcones in benzene, pyridine, acetonitrile *etc.*, the yields varying from 0 to 70% with substituents. The reaction is depressed by the addition of 1,3-pentadiene, nitrosobenzene, or acrylonitrile. On the other hand, flavanone and 4-chromanone undergo photoreduction in 2-propanol to give reductive coupling products and solvent adducts as isomeric mixtures. 7,8-Benzoflavanone does not undergo photoreduction in 2-propanol but the ring opening reaction instead. Mechanisms have been discussed in terms of the relative contribution of n,π* and π,π* character in the lowest triplet states.

Flavanones have been shown to undergo photochemical ring opening reaction to give 2′-hydroxychalcones in inert solvents such as benzene[1—4] and photoreduction to give reductive coupling products in hydrogen-donating solvents.[2,3] Both biradical[1,2] and concerted[3] mechanisms have been suggested for the photochemical ring opening reaction, though not proved.

On the other hand, photoisomerization of substituted 3-chromanones have extensively been studied and the mechanism has been shown to involve prior photochemical enolization.[5] In this view, interesting mechanisms involving enolization followed by 6π-electrocyclic reactions have been postulated for the photochemical ring opening reaction of flavanones[3] and for the photochemical cyclization of 2′-hydroxychalcones to flavanones.[6]

The present work reports on the photochemistry of parent and substituted flavanones, with discussion on the mechanisms in terms of n,π* and π,π* character in the lowest triplet states.



Scheme 1.

Results

Photochemical Ring Opening Reaction. Dilute solutions of parent or substituted flavanones in benzene underwent photochemical ring opening reaction to give corresponding 2′-hydroxychalcones, on irradiation under a nitrogen atmosphere at room temperature with a high pressure mercury lamp (Scheme 1). The products proved identical with independently prepared authentic samples of 2′-hydroxychalcones. Irradiation of **5a**, **7a**, **8a**, **11a**, **12a**, and 4-chromanone **14a** resulted in the recovery of the starting materials: their NMR spectra remained unchanged. The yields for the reaction depended on the substituents (Table 1). Thus, electron-

Table 1. Substituent effects on the photochemical ring opening of flavanones in benzene[a)]

Flavanone	Substituent				2′-Hydroxychalcone	Yield[b)]
	R^1	R^2	R^3	R^4		%
1a	H	H	H	H	**1b**	14
2a	H	H	H	OMe	**2b**	40
3a	H	H	H	OCOMe	**3b**	70
4a	6-OMe	H	H	H	**4b**	15
5a	6-OCOMe	H	H	H	**5b**	0
6a	7-OMe	H	H	H	**6b**	11
7a	5-OH, 7-OMe	H	H	H	**7b**	0
8a	5,6-Benzo	H	H	H	**8b**	0
9a	7,8-Benzo	H	H	H	**9b**	5
10a	7-OMe	Me	H	H	**10b**	13
11a	7-OMe	H	*cis*-Me	H	**11b**	0
12a	7-OMe	H	*trans*-Me	H	**12b**	0
13a	7-Cl	H	H	H	**13b**	2

a) Each flavanone solution (8.8×10^{-3} mol/dm^3) was irradiated under a nitrogen atmosphere for 16.5 h at room temperature with a 100-W high pressure mercury lamp. b) Estimated from the NMR signal intensities of the phenolic protons at δ 12—15 ppm.

withdrawing groups in R^1 seem to depress the reaction (**5a**, **13a**), while electron donating groups do not (**4a**, **6a**, **10a**).

Substitution of methyl group at the C_3-position retards the reaction (**11a**, **12a**), whereas methyl substitution at the C_2-position permits the reaction (**10a**). The photochemical intertness of **11a**, **12a**, and **7a** is ascribable to a reversible intramolecular hydrogen transfer *via* a five-membered (**11a**, **12a**) or six-membered (**7a**) cyclic configuration. The low or nil reactivity of **8a** and **9a** may, at least partly, be relevant to their low-lying or less reactive π,π^* triplet states.

TABLE 2. PHOTOCHEMICAL RING OPENING OF **2a** IN DIFFERENT SOLVENTS[a]

Solvent	Yield of **2b**/%
Carbon tetrachloride	31
Benzene	69
Benzene (air)[b]	49
Pyridine	66
Acetonitrile	48

a) Irradiated in ampule with a 400 W high pressure mercury lamp for 3 h at 15 °C; $[\mathbf{2a}]=10^{-3}$ mol/dm^3. b) Without deoxygenation.

Table 2 lists the solvent effects on the photochemical ring opening reaction of **2a**. No simple correlation with solvent polarity or basicity is found. Dissolved oxygen seems to depress the reaction to some extent.

Addition of 1,3-pentadiene (1.5×10^{-3} mol/dm^3) to a benzene solution of **2a** (10^{-3} mol/dm^3) resulted in significant depression of the photoreaction (Table 3). Both acrylonitrile and nitrosobenzene, which are known to inhibit a free radical reaction, significantly depress the photoreaction.

TABLE 3. EFFECTS OF ADDITIVES ON THE PHOTOCHEMICAL RING OPENING OF **2a**

Additive	Concn of additive 10^{-3} mol dm^{-3}	Yield of **2b** %
1,3-Pentadiene	0.0	64[a]
	1.5	35[a]
Acrylonitrile	0.0	40[b]
	4.5	5[b]
Nitrosobenzene	0.0	46[c]
	6.4	5[c]

a) Benzene solution of **2a** (10^{-3} mol/dm^3) was irradiated in ampule with a 400-W high pressure mercury lamp for 70 min. b) A 50 ml benzene solution of **2a** (3×10^{-4} mol/dm^3) was irradiated with a 100-W high pressure mercury lamp for 16 h. c) A 6 ml benzene solution of **2a** (10^{-3} mol/dm^3) was irradiated in ampule with a 400-W high pressure mercury lamp for 40 min.

Photolysis of Flavanones and 4-Chromanone in 2-Propanol. A deoxygenated solution of flavanone **1a** (4.5×10^{-3} mol/dm^3) in 2-propanol gave reductive coupling product **1c** (as isomeric mixture) and solvent adduct **1d** (as 1 : 1 isomeric mixture) besides unidentified products, on irradiation with a 100 W high pressure mercury lamp at room temperature (Scheme 1 and Table 4).

TABLE 4. PHOTOLYSES OF FLAVANONES AND 4-CHROMANONE IN 2-PROPANOL

Starting material	Concentration 10^{-3} mol/dm^3	Irrad. time h	Products	$\phi_{\rm dis}$[a]
1a	4.5	5	**1c**(39%)[b] **1d**(8%)[c] Unknown (20%)	0.43
7a	7.4	5	None[d]	0.00
8a	10	12	None[d]	0.00
9a	9.4	16	**9b** (33%)	0.02
14a	4.8	5.5	**14c** (89%)[e]	0.24

a) Quantum yield for the disappearance of each starting material during 10 min irradiation. b) Sum of the meso and the racemic mixtures of 4,4′-biflavanol isomers. c) Sum of 1 : 1 *cis*- and *trans*-4-hydroxy-4-(1-methyl-1-hydroxyethyl)flavanes. d) The NMR spectra remained unchanged and no TLC spot was detected other than that of the starting material. e) The sum of the meso (53%) and the racemic (36%) forms of 4,4′-bichromanol isomers.

Similar photolysis of 4-chromanone **14a** gave corresponding coupling product **14c** in a high yield. Photolysis of **6a**, **13a**, and 5,7-dimethylflavanone **15a** gave too complex mixtures to permit their analyses, while **7a** and **8a** did not react. The results are summarized in Table 4, together with the quantum yield for the disappearance of each starting material at an initial stage of the reaction. Interestingly, 7,8-benzoflavanone **9a** underwent ring opening reaction to give **9b** in 2-propanol, instead of the photoreductive coupling reaction. In addition, the yield for the ring opening reaction of **9a** is higher in 2-propanol than in benzene by a factor of 6.

Discussion

Owing to the rapid and efficient intersystem crossing, the singlet lifetimes of aromatic carbonyl compounds are usually too short ($\leq10^{-8}$ s)[7] to permit bimolecular singlet quenching in low concentrations of donor and quencher. The significant quenching effect of 1,3-pentadiene (1.5 mmol/dm^3) supports for a triplet mechanism.[2] The depression effects of acrylonitrile and nitrosobenzene favors for radical processes,[1] in accord with the triplet mechanism.

The variation in the relative reactivities in Table 1 may simply be interpreted as due to the inductive and electromeric effects of substituents in some cases (**4a**—**6a**, **10a**, **13a**); such simple interpretation, however, does not hold for some others (**1a**—**3a**).

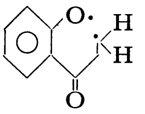
It seems more reasonable to interpret as due to the relative contribution (importance) of n,π^* and π,π^* character: the ring opening reaction takes place from π,π^* triplet states while reductive coupling reaction from n,π^* triplet states. Benzoflavanones **8a** and **9a**, for example, are expected to have a dominant π,π^* character in the lowest triplet states in any solvents, because of the extended π-conjugation in the molecules. Thus, the lack of the photoreduction of **8a** and **9a** in 2-propanol is ascribable to nil or insufficient contribution of n,π^* character in the lowest triplet states.

Instead, **9a** undergoes photochemical ring opening reaction in 2-propanol, reflecting a dominant contribution of π,π^* character.

The higher efficiency for the ring opening reaction of **9a** in 2-propanol than in benzene may be attributable at least partly, to the more stabilization and contribution of the π,π^* state.

All other flavanones in Table 1 are also assumed to have considerable π,π^* character in their lowest triplet states, since the lowest triplet states of methoxy-substituted acetophenones are mostly of π,π^* in nature.[8] Relative importance of n,π^* and π,π^* character depends on solvent and substituents. Thus, reductive coupling reaction, as a reflection of n,π^* character, dominates in a hydrogen-donating solvent such as 2-propanol. In benzene, the n,π^* character in the lowest triplet states would increase (the π,π^* would decrease) in favor of hydrogen atom abstraction. However, the C–H bond of benzene is much stronger (*e.g.*, by 22 kcal/mol or more in the gas phase) than the C_2–H bond of 2-propanol, and hydrogen atom abstraction from benzene is unfavorable even though the n,π^* character is somewhat increased. Thus, the alternative pathway which does not involve hydrogen atom abstraction, *i.e.*, the ring opening reaction, would become dominant in benzene even though the π,π^* character is somewhat decreased.

The lack of the photochemical ring opening reaction of **14a** is ascribable to the less stability of the intermediate species, *e.g.*, biradical **16** as compared with **17** having benzyl radical stability.



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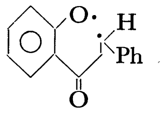

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On the other hand, the high efficiency for the reductive coupling reaction of **14a** in 2-propanol is due partly to a small steric hindrance of the chromanone ketyl radicals compared to that of the flavanone ketyl radicals in bimolecular coupling processes, and partly to the essential n,π^* character in its lowest triplet state.

As an alternative to the unimolecular mechanism above discussed it might be thought that the photochemical ring opening reaction proceeds *via* bimolecular hydrogen atom abstraction. Hydrogen atoms at the C_3-position of ground state flavanones could be abstracted by n,π^* triplets of another flavanone molecules, followed by β-cleavage or hydrogen atom transfer of radical intermediates giving eventually 2′-hydroxychalcones. However, such mechanism seems less likely.

The recovery of each starting isomer **11a** or **12a** without *cis-trans* isomerization, or the lack of inversion at the C_3-center, suggests that hydrogen atom abstraction from the C_3-position is less important.

Bimolecular hydrogen atom abstraction from the C_2-position (the weakest C–H bond) might be thought to occur and affect the ring opening reaction. However, substitution of the hydrogen atom at the C_2-position by methyl group did not affect the efficiency (compare **10a** with **6a**), thus bimolecular C_2–H abstraction seems irrelevant to the ring opening reaction.

Experimental

Chemicals. Flavanones and 4-chromanone were prepared according to the reported methods as summarized in Table 5 together with the UV absorption maxima. Typical methods for the preparation of 2′-hydroxychalcones are shown in Table 6 together with their melting points and spectral data. Solvents and other chemicals were of guaranteed grade without further purification, except that acrylonitrile was purified just before use to eliminate polymerization inhibitors.[28]

TABLE 5. UV ABSORPTION MAXIMA OF FLAVANONES AND 4-CHROMANONE

Compound	Method of preparation[a]	Solvent[b]	λ_{max} / nm	($\varepsilon_{max}\times 0.01$ / $mol^{-1}dm^2$)
1a	10, 11	E	320(3.53),	252(8.98)
2a	10, 12	E	320(33.2)	
3a	10, 13	E	310(1.09)	
4a	10, 14	E	352(3.53),	254(6.16)
5a	15	E	319(6.91),	233(83.2)
6a	10, 16	P	310(5.69),	272(11.8)
7a	10, 17	P	320(3.01),	285(17.0)
8a	18	P	340(4.20),	312(7.57)
9a	19	P	360(4.74),	280(7.08)
10a	10, 20	E	314(6.94),	277(13.2)
14a	10, 21	E	320(3.67),	250(8.81)

a) Indicated are the Reference numbers. b) Solvent used for the measurements of UV spectra; E: ethanol, P: 2-propanol.

TABLE 6. PHOTOCHEMICAL RING OPENING PRODUCTS OF FLAVANONES

Product	Mp / °C	Vinyl-H / δ	Ar–OH[a] / δ	IR(C=O) / cm^{-1}	Method of preparation[b]
1b	90—91	5.40	12.8	1630	10, 22
2b	71	5.45	13.8	1700	10, 23
3b	143—146	5.45	12.7	1720	10, 13
4b		5.50	12.0		10, 24
6b	102—105	5.45	13.6		10, 25
9b	115—125	5.45	14.8		26
10b	92—98	6.40	13.2	1680	10, 19

a) The NMR signals of the phenolic protons disappeared on addition of D_2O. b) Indicated are the Reference numbers.

Apparatus and Procedures. The IR, UV, and NMR spectra were measured by means of a JASCO IRA-I spectrometer, a Hitachi 124 spectrometer, and a Hitachi R-24 NMR spectrometer, respectivery. The light source was a 100 W high pressure mercury lamp (Riko) immersed in the reaction vessel, for preparative photoreactions; or a 400 W high pressure mercury lamp with a merry-go-round irradiation apparatus thermostated at 20 °C, for small scale experiments. Quantum yields were measured by the usual method[29] using aqueous tris(oxalato)ferrate(III) solution and with the light beams of 313 and 334 nm paralleled and through a glass filter (Toshiba UV-D2).

Photochemical Ring Opening Reaction. Typical procedures are as follows. A 100 ml benzene solution of **1a** (197 mg, 0.88 mmol) was irradiated with a 100 W high pressure mercury

Table 7. Photoreductive coupling products of flavanone and 4-chromanone in 2-propanol

Product	Mp[a] °C	Found (Calcd) %	IR (KBr) ν/cm^{-1}	NMR (CDCl$_3$)[b] δ
1c (*meso*-I)[c]	270—272	C: 80.41 (79.98) H: 5.92 (5.82)	3550	1.41—2.41 (m, H_3H_3', 4H), 3.03 (s, OH, 1H),[d] 3.67 (s, OH, 1H),[d] 4.86—5.41 (m, H_2H_2', 2H), 6.86—7.50 (m, Ar, 16H), 7.70—8.30 (m, Ar, 2H)
1c (*meso*-II)	78—80		3380	1.55—2.40 (m, H_3H_3', 4H), 3.32 (s, OH, 1H),[d] 3.86 (s, OH, 1H)[d], 4.88—5.35 (m, H_2H_2', 2H), 6.94—7.45 (m, Ar, 16H), 7.65—810 (m, Ar, 2H)
1c (racemic)[c]	237—238	C: 79.40 (79.98) H: 5.80 (5.82)	3590, 3445	2.39—3.90 (m, H_3H_3', 4H), 5.24 (s, OH, 2H)[d], 5.80—6.22 (m, H_2H_2', 2H), 6.50—7.50 (m, Ar, 16H)
1d (*cis*)	125—128		3520, 3450	1.35 (s, CH_3, 3H), 1.43 (s, CH_3, 3H), 2.1—2.2 (m, OH, 2H)[d], 2.20, 2.80 (each dd, $J_{2,3}=3.7$ and 12.3 Hz, H_3, 2H), 5.60 (dd, $J_{2,3}=3.7$ and 12.7 Hz, H_2, 1H), 6.76—7.75 (m, Ar, 9H)
1d (*trans*)	125—130		3400	1.00 (s, CH_3, 3H), 1.30 (s, CH_3, 3H), 1.90—2.24 (m, H_3, 2H), 2.45—3.20 (m broad, OH, 2H),[d] 4.78—5.20 (m, H_2, 1H), 6.68—7.58 (m, Ar, 9H)
14c (*meso*)[c]	201—204	C: 72.21 (72.46) H: 6.12 (6.08)	3550	1.50—2.35 (m, H_3H_3', 4H), 2.68 (s, OH, 1H),[d] 3.28 (s, OH, 1H),[d] 3.88—4.20 (m, H_2H_2', 4H), 6.5—7.4 (m, Ar, 7H), 8.00—8.12 (m, Ar, 1H)
14c (racemic)[c]	184—186	C: 72.51 (72.46) H: 6.17 (6.08)	3500, 3450	1.82—2.32 (m, H_3H_3', 4H), 3.87—4.27 (m, H_2H_2', 4H) 5.24 (s, OH, 1H),[d] 6.32—7.32 (m, Ar, 8H)

a) Uncorrected. b) DMSO-d_6 was used for **1c** ((racemic) and **14c** (racemic). c) Treatment with lead tetraacetate in acetic acid gave starting material at room temperature. d) Disappeared on addition of D_2O.

lamp for 16.5 h. Oxygen-free nitrogen current was passed through the solution before and during the photolysis.

The products were separated on silica gel–benzene. Similarly the photochemical ring opening products of other flavanones were isolated. They were identified by comparing their mp, IR, and NMR spectra (Table 6) with those of authentic samples independently prepared. The amounts of the products were determined by measurement of either the UV absorption at near 360 nm after separation on silica gel or the NMR signal intensities of the phenolic protons at near 13 ppm as mixture solutions.

*Photoreduction of **1a** and **14a** in 2-Propanol.* A 100 ml solution of **14a** (1 g, 4.8 mmol) in 2-propanol was irradiated with a 100 W high-pressure mercury lamp for 5.5 h. Separation of the products on silica gel–benzene and crystalization from methanol yielded colorless crystals A (53%) and B (36%).

The spectral and CH analysis data in Table 7 show that A and B are 4,4′-bichromanol isomers. Relative rates of oxidative decomposition with lead tetraacetate can serve as a method of identification of a series of isomeric 1,2-diols: the rate is rapid for gauche structure (with respect to the two hydroxyl groups) and slow for anti one.[27] Both A and B gave **14a** on treatment with lead tetraacetate with relative rates A : B = 1 : 4 in acetic acid at room temperature. Thus, A and B are ascribable to anti (meso) and gauche (racemic) forms, respectively.

Molecular models implied that the racemic form favors for intramolecular hydrogen bonding while the meso form is sterically unfavorable. Thus, the O–H streching absorption appearing in two bands (3500 and 3450 cm^{-1}) and the low-field shift of the hydroxyl protons (5.24 ppm as compared to 2.3—3.3 ppm for A) of B are ascribable to intramolecular hydrogen bonding of the racemic isomer.[30,31]

Similar photolysis of **1a** (1 g, 4.5 mmol) in 2-propanol for 5 h gave a mixture of 4,4′-biflavanols **1c** and 4-hydroxy-4-(1-hydroxy-1-methylethyl)flavanones **1d**. By separation on silica gel and crystallization, **1c** gave colorless crystals E (from benzene), F (from acetone), and G (from ligroin), while **1d** gave K and L (both from petroleum benzine).

The product E is assumed to have racemic form since the low-field shift of the hydroxyl protons (5.24 ppm) and the O–H streching appearing in two bands (3590 and 3445 cm^{-1}) are comparable with those of the racemic isomer of **14c**. On the other hand, F and G are assumed to have meso forms since their IR and NMR spectra are comparable to those of the meso isomer of **14c**.

According to Bolger *et al.*,[32] the coupling constants of the C_3-methylene protons of 4-flavanols are generally large for isomers with equatrial 4-hydroxyl group but small for isomers with axial 4-hydroxyl group: $J_{eq}=15—17$, $J_{ax}=5—6$ Hz. Thus, relatively large coupling constant of K (12.3 Hz) is ascribable to the *cis* isomer (in which 4-hydroxyl group is equatrial) of **1d**. Molecular models of the isomers of **1d** implied that the *cis* form is favorable but the *trans* form is sterically unfavorable for intramolecular hydrogen bonding between two hydroxyl groups. Thus, the O–H stretching absorption (3520 and 3450 cm^{-1}) is ascribable to the *cis* isomer.

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