

Photoreactions of Flavanones¹⁾

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Synopsis. On irradiation in benzene, 5,7-dimethyl-4'-methoxyflavanone gave a bis-flavanone V, while in 2-propanol it was largely recovered. Irradiation of 4'-methoxyflavanone in benzene and 2-propanol yielded the corresponding chalcone and pinacols, respectively. 5,7,4'-Trimethoxyflavanone was relatively inert to photolysis in benzene, but gave a complex mixture of products in 2-propanol.

In a series of our investigation on flavonoid photochemistry,²⁻⁵⁾ it has been found that the presence of the 5-hydroxyl group causes photo-resistance to flavonoids such as 3-methoxyflavones,^{4,5)} 3-hydroxyflavones,⁵⁾ and flavanones,⁵⁾ possibly due to the loss of its excitation energy. Among these flavonoids, the photoreaction of flavanones had remained unknown until Kishimoto *et al.*⁶⁾ and Mack and Pinhey⁷⁾ reported that flavanones underwent photoreduction in 2-propanol and photoisomerization to chalcones and 4-phenyl-3,4-dihydrocoumarines in benzene. These reports prompted us to communicate our independent results on the photoreactions of a few flavanone derivatives.

Irradiation of 4'-methoxyflavanone (I) with a high-pressure mercury lamp (Pyrex) in benzene and 2-propanol gave 4-methoxy-2'-hydroxychalcone (II; 14%) with the recovered I (18%) and a mixture of pinacols III⁸⁾ in 23% yield, respectively, similarly to the other flavanones.⁶⁾ In both solvents, the remaining part of products was intractable polymers. The formation of II may be recognized as a 6 π -electrocyclic reaction of the enolic form of I. A similar type of photochemical electrocyclic reaction has been observed for 2H-pyrans.⁹⁾ The reverse reaction of 2'-hydroxychalcone to flavanone is known to occur photochemically.¹⁰⁾ Under similar photolysis conditions, 5,7,4'-trimethoxyflavone was

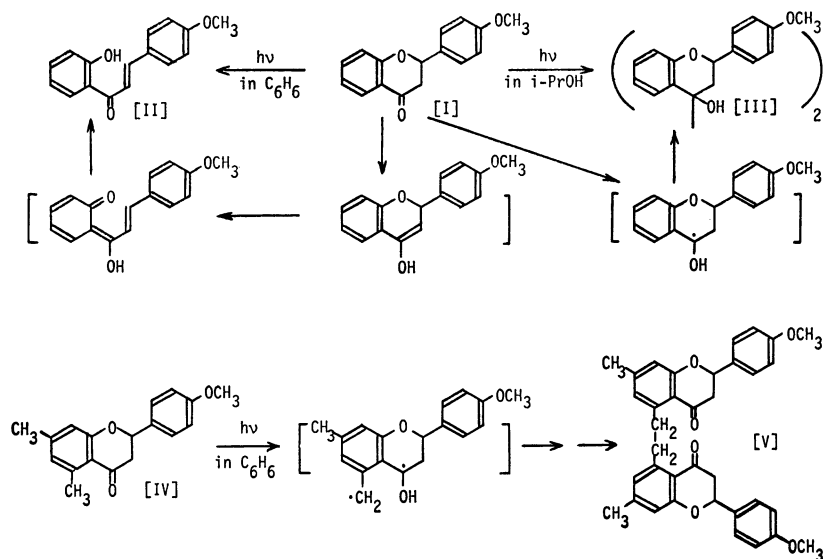
largely recovered under the formation of some resinous material in benzene, while it underwent faster photodecomposition in 2-propanol to give a complex mixture of at least six products.

5,7-Dimethyl-4'-methoxyflavanone (IV), which was photochemically rather unreactive in 2-propanol underwent oxidative coupling by irradiation in benzene to give V in 8% yield. The structure of V was assigned by elemental and NMR (with decoupling) spectral analyses. On longer irradiation, V suffered further photodecomposition to give a resinous material. It may be reasonable to assume that the formation of V involves an intramolecular hydrogen abstraction of the excited IV, similar to that of *o*-alkylphenyl ketone.¹¹⁾ A similar dehydrodimerization has been reported to occur in the photolysis of 5,8-dimethyltetralone.¹²⁾

Experimental

All the melting points are uncorrected. NMR, IR, and mass spectra were measured on an NEVA T-60 or a Varian HA-100 spectrometer with TMS as the internal standard, on a Hitachi EPI-G3 spectrophotometer, and on a Hitachi RMS-4 spectrometer, respectively.

Materials. 4-Methoxy-2'-hydroxychalcone (II) was prepared from *o*-hydroxyacetophenone and *p*-anisaldehyde by the method for the preparation of chalcone.¹³⁾ The product was cyclized by refluxing in a mixture of 1:1:1 ethanol, acetic acid, and water for 10 h¹⁴⁾ to 4'-methoxyflavanone (I); mp 89–90 °C (lit.¹⁵⁾ mp 97 °C); NMR (CDCl₃), δ 2.8–3.2 (m, 2H), 3.80 (s, 3H), an ABX at 2.80, 3.18, and 5.45 (J_{AB} = 17 Hz), J_{AX} = 5 Hz, J_{BX} = 11 Hz, –CH₂–CH–), 6.8–8.0 (m, 8H). 4',5,7-Trimethoxyflavanone, mp 125–126 °C (lit.¹⁶⁾ mp 123 °C), was prepared by the similar method *via* 4,4',6'-trimethoxy-2'-hydroxychalcone, mp 112.5–114 °C (lit.¹⁷⁾ mp 113



°C), which was prepared from 2-hydroxy-4,6-dimethoxyacetophenone¹⁸ and *p*-anisaldehyde.

4-Methoxy-5,7-dimethylflavanone (IV) was prepared by the following sequence of reactions applying the known method¹⁴: 3,5-xyleneol→3,5-xylyl acetate→2-hydroxy-4,6-dimethylacetophenone→4-methoxy-2'-hydroxy-4',6'-dimethylchalcone→IV. Recrystallization from ethanol gave IV as colorless crystals; mp 77–79 °C; IR (KBr), 1680, 1620, 1520 cm⁻¹; *m/e*, 282 (M⁺); NMR (CDCl₃), δ 2.35 (s, 3H, 7-Me); 2.65 (s, 3H, 5-Me), 3.85 (s, 3H, 4'-OMe), 2.8–3.2 (m, 2H, 3-CH₂), 5.40 (dd, 1H, *J*=4 and 11 Hz, 2-CH), 6.30 (broad s, 1H, aromatic H), 6.36 (broad s, 1H, aromatic H), an AB at 7.00 and 7.44 (*J*_{AB}=9 Hz).

Found: C, 76.10; H, 6.58%. Calcd for C₁₈H₁₈O₃: C, 76.57; H, 6.43%.

Photolysis of 4'-Methoxyflavanone (I).

(a) *In Benzene*: A solution of I (500 mg) in benzene (130 ml) was irradiated with a 100-W high-pressure mercury lamp through Pyrex glass under nitrogen for 8 h. After removal of the solvent, the residue was submitted to preparative TLC (silica gel; chloroform) to give I (90 mg) and 4-methoxy-2'-hydroxychalcone (II; 70 mg) identical with an authentic sample (IR).

(b) *In 2-Propanol*: A solution of I (1 g) in 2-propanol (140 ml) was irradiated for 6 h in the same manner. After removal of the solvent, the residue was crystallized four times from ethyl acetate to give a stereoisomeric mixture of 4,4-bi(4-hydroxy-4'-methoxyflavane)s (III; 230 mg) as colorless crystals; mp 229–232 °C; IR (KBr), 3500, 3440, 1620, 1520, 1480 cm⁻¹, 510 (M⁺), 492, 256; NMR (DMSO-*d*₆), δ 1.6–2.7 (m, 2H, 3-CH₂), 3.76 (s, 3H, 4'-OMe), 5.16 (s, 1/2 H, OH), 5.21 (diffused s, 1/2H, OH), 5.8–6.2 (m, 1H, 2-CH), 6.7–7.6 (m, 8H, aromatic H).

Found: C, 74.98; H, 5.97%. Calcd for C₃₂H₃₀O₆: C, 75.27; H, 5.92%.

Photolysis of 4',5,7-Trimethoxyflavanone.

(a) *In Benzene*: A solution of the flavanone (800 mg) in benzene (130 ml) was irradiated in a similar manner for 5 h. TLC analysis (silica gel; ethyl acetate) of the reaction mixture showed that it consisted of the recovered starting material with a small amount of origin substances. The starting material (450 mg) was recovered by preparative TLC.

(b) *In 2-Propanol*: The flavanone (500 mg) in 2-propanol (140 ml) was similarly irradiated for 5 h. The reaction mixture showed a complex TLC pattern in which the presence of at least six products were observed. No pure product was isolated by preparative TLC.

Photolysis of 4'-Methoxy-5,7-dimethylflavanone (IV).

In Benzene: A solution of IV (800 mg) in benzene (130 ml) was irradiated similarly for 2 h. After removal of the solvent, the addition of ethanol to the residue gave insoluble crystals which on two recrystallizations from chloroform yielded 1,2-[bis(4'-methoxy-7-methyl-4-oxo-5-flavanyl)]ethane (V; 60 mg) as colorless crystals; mp 221–223 °C; IR (KBr), 1680, 1620, 1520, 1470 cm⁻¹; *m/e*, 562 (M⁺), 281, 267; NMR (CD-

Cl₃), δ 2.35 (s, 3H, 7-Me), and ABX at 2.80, 3.10, and 5.38 (*J*_{AB}=9 Hz, *J*_{AX}=2 Hz, *J*_{BX}=6 Hz, -CH₂CH-), 3.30 (m, 2H, -CH₂-), 3.81 (s, 3H, 4'-OMe), AB at 6.94 and 7.39 (4H, *J*_{AB}=4.5 Hz, 2',3',5',6'-aromatic H), 6.74 (broad s, 1H, aromatic H), 6.90 (broad s, 1H, aromatic H).

Found: C, 75.63; H, 6.42%. Calcd for C₃₆H₃₄O₆: C, 76.85; H, 6.09%.

(b) *In 2-Propanol*: A solution of IV (300 mg) in 2-propanol (140 ml) was irradiated similarly. TLC analyses of the reaction mixture after 6 and 12 h showed that it consisted mainly of the starting material and some colored polymers.

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