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Photoreactions of Flavanones[1]

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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 Pinhey[7] 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.

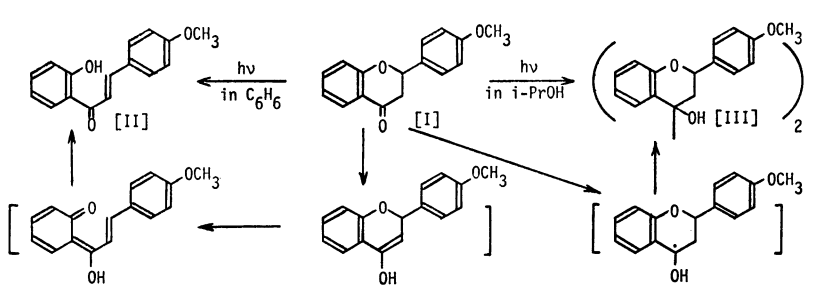
Irradiation of 4′-methoxyflavanone (I) with a high-pressure mercury lamp (Pyrex) in benzene and 2-propanol gave 4-methoxy-2′-hydroxychalcone (II; 14%) with the recovered I (18%) and a mixture of pinacols III[8] in 23% yield, respectively, similarly to the other flavanones.[6] In both solvents, the remaining part of products was intractable polymers. The formation of II may be recognized as a 6π-electrocyclic reaction of the enolic form of I. A similar type of photochemical electrocyclic reaction has been observed for 2*H*-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.

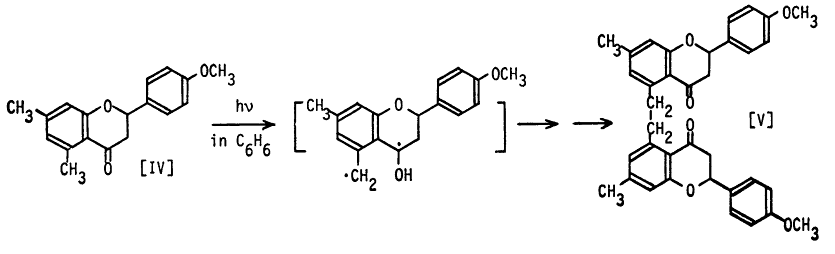
5,7-Dimethyl-4′-methoxyflavanone (IV), which was photochemically rather unreactive in 2-propanol underwent oxidative coupling by irradiation in benzene to give V in 8% yield. The structure of V was assigned by elemental and NMR (with decoupling) spectral analyses. On longer irradiation, V suffered further 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 h[14] to 4′-methoxyflavanone (I); mp 89—90 °C (lit,[15] mp 97 °C); NMR ($CDCl_3$), 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, $-\overset{\cdot}{C}H_2-\overset{\cdot}{C}H-$), 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-dimethoxyacetophenone[18] and *p*-anisaldehyde.

4′-Methoxy-5,7-dimethylflavanone (IV) was prepared by the following sequence of reactions applying the known method[14]: 3,5-xylenol→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 ($CDCl_3$), 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-CH_2), 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 $C_{18}H_{18}O_3$: 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-CH_2), 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 $C_{32}H_{30}O_6$: 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 ($CDCl_3$), 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, -CH_2CH-), 3.30 (m, 2H, -CH_2-), 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 $C_{36}H_{34}O_6$: 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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