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Photochemical Addition of Methanol to Chromones

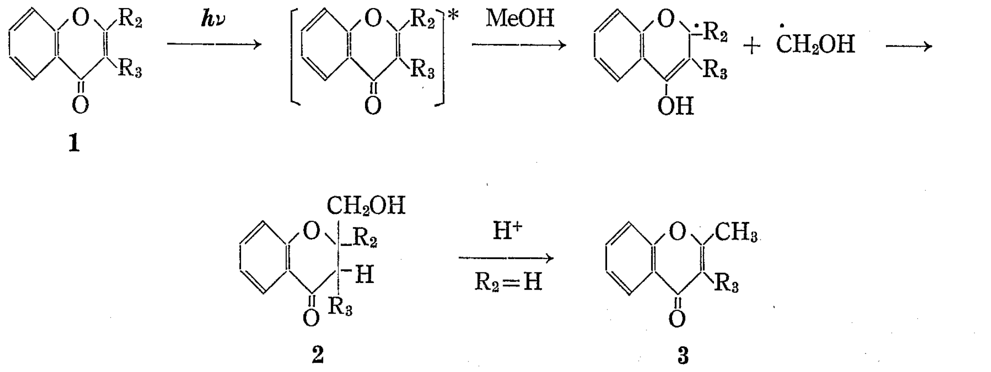
Irradiation of chromones in MeOH-HCl induced the homolytic addition of methanol to the double bond in the pyrone ring to give the 2-hydroxymethylated chromanones.

Keywords——photochemical addition; chromones; 2-hydroxymethylchromanone; 2-methylchromone; n-π^* triplet state

Flavonoids were found in many plants and their photochemical reactions have been studied in detail.[1] In connection with our studies on flavonoids,[2] we have examined the photochemical behavior of chromones in acidic media.

Irradiation of 2-methylchromone (**1a**) in methanol containing 5% hydrochloric acid by 400 W high-pressure mercury lamp (Toshiba H-400 P) with a pyrex filter until all of the starting material had been consumed, resulted in the formation of **2a**, mp 86—87°, in 70% yield. The physical data of **2a** [*m/e* 192 ($M^+=C_{11}H_{12}O_3$); infrared spectrum (IR) $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3340 (OH), 1680 (C=O); ultraviolet spectrum (UV) $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 223 (2.24), 252 (2.78), 324 (1.40); proton magnetic resonance (PMR) δ ($CDCl_3$): 1.15 (3H, s, 2-CH_3), 2.50 (1H, d, J=16 Hz, 3-CH_2), 3.13 (1H, d, J=16 Hz, 3-CH_2), 3.67 (2H, s, 2-CH_2O), 6.7—7.9 (4H, m, aromatic-H)] indicated it to be 2-hydroxymethyl-2-methylchromanone.

By the irradiation of **1b** under the same condition, 2-hydroxymethyl-2,3-dimethylchromanone (**2b**): [*m/e* 206 ($M^+=C_{12}H_{14}O_3$); IR $\nu_{\max}^{\mathrm{Liquid}}$ cm^{-1}: 3320 (OH), 1680 (C=O); PMR δ ($CDCl_3$): 1.15 (3H, s, 2-CH_3), 1.20 (3H, d, J=7 Hz, 3-CH_3), 3.30 (1H, q, J=7 Hz, 3-CH), 3.70 (2H, s, 2-CH_2O), and 6.7—7.9 (4H, m, aromatic-H)] was obtained as an oil in 70% yield.



	R₂	R₃
a:	CH₃	H
b:	CH₃	CH₃
c:	H	CH₃
d:	H	H

Fig. 1

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1) T. Matsuura, H. Matsushima and H. Sakamoto, *J. Am. Chem. Soc.*, **86**, 6370 (1967); T. Matsuura, T. Takemoto, and R. Nakashima, *Tetrahedron Lett.*, **1971**, 1539; A.C. Waiss, R.E. Ludin, A. Lee, and J. Corse, *J. Am. Chem. Soc.*, **89**, 6213 (1967).

2) M. Komatsu, I. Yokoe, and Y. Shirataki, *Chem. Pharm. Bull.* (Tokyo), **26**, 1274 (1978).

Irradiation of **1c** and **1d**, which have no substituent at the 2 position under the same conditions afforded in good yields the methylated chromones (**3c**, mp 71°, and **3d**, mp 97°) whose structures were determined by the direct comparison with the authentic samples.[3] The formation of **3c** and **3d** is reasonably explained by the acid catalyzed dehydration of the initially formed 2-hydroxymethylated chromanones (**2c** and **2d**).

No reaction of **1** was observed either by the irradiation in methanol in the absence of hydrochloric acid or in *t*-butanol containing hydrochloric acid.

While a detail mechanism of this photoaddition reaction was not clear at present, we tentatively propose the following mechanism.

Thus, a hydrogen atom was abstracted from methanol by the excited chromone and so formed $^{\bullet}CH_2OH$ was coupled with chromone to afford the compound **2**.

In accordance with this proposal, this reaction was sensitized by benzophenone and this fact indicated that the excited species was not the n-π^* singlet state of the chromone,[4] but the n-π^* triplet.[5]

While photochemical hydroxymethylation and C-alkylation reaction were reported in many N-heterocyclic compounds,[6] the present results seem to be the first example of photoaddition of methanol to benzopyrone derivatives. The further application of this reaction to the related system is in progress.

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[3] S. Biniecki and E. Kesler, *Acta Polon. Pharm.*, **13**, 503 (1956) [*Chem. Abstr.*, **51**, 9607 (1957)]; I. Manta, T. Berger, and E. Silghi, *Rev. Chim.*, **10**, 69 (1959) [*Chem. Abstr.*, **57**, 15059 (1962)].

[4] The n-π^* absorption of chromone is at 360 nm ($\varepsilon = 25$) in 3-methylpentane; J.W. Hanifin and E. Cohen, *J. Am. Chem. Soc.*, 91, 4494 (1969).

[5] The n-π^* triplet state of carbonyl group is known to be a good hydrogen abstractor; P.J. Wagner and G.S. Hammond, "Advances in Photochemistry," John Wiley and Sons, Inc., New York, Vol. 5, 1968, p. 93.

[6] O. Buchardt, "Photochemistry of Heterocyclic Compounds," John Wiley and Sons, Inc., New York, 1976, p. 524.