Faculty of Pharmaceutical
Science, Higashi Nippon
Gakuen University,
Ishikari-Tobetsu, Hokkaido,
061-02, Japan

YOSHIHISA YAMAMOTO
EIKO TOYOTA

Received March 6, 1978

[Chem. Pharm. Bull.
26(7)2277-2278(1978)]

UDC 547.814.1.04 : 547.261.04

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; $n-\pi^*$ 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) $\nu_{\max}^{KBr}$ cm^{-1} : 3340 (OH), 1680 (C=O); ultraviolet spectrum (UV) $\lambda_{\max}^{MeOH}$ nm (log ϵ): 223 (2.24), 252 (2.78), 324 (1.40); proton magnetic resonance (PMR) δ ($CDCl_3$): 1.15 (3H, s, 2-CH₃), 2.50 (1H, d, $J=16$ Hz, 3-CH₂), 3.13 (1H, d, $J=16$ Hz, 3-CH₂), 3.67 (2H, s, 2-CH₂O), 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 $\nu_{\max}^{Liquid}$ cm^{-1} : 3320 (OH), 1680 (C=O); PMR δ ($CDCl_3$): 1.15 (3H, s, 2-CH₃), 1.20 (3H, d, $J=7$ Hz, 3-CH₃), 3.30 (1H, q, $J=7$ Hz, 3-CH), 3.70 (2H, s, 2-CH₂O), and 6.7–7.9 (4H, m, aromatic-H)] was obtained as an oil in 70% yield.

Fig. 1

- 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 $\cdot\text{CH}_2\text{OH}$ 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 $n\text{-}\pi^*$ singlet state of the chromone,⁴⁾ but the $n\text{-}\pi^*$ 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.

Faculty of Pharmaceutical Sciences
Josai University
Keyakidai, Sakado, Saitama
350-02, Japan

ICHIRO YOKOE
YOSHIKI SHIRATAKI
MANKI KOMATSU

Received March 22, 1978

- 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 $n\text{-}\pi^*$ absorption of chromone is at 360 nm ($\epsilon=25$) in 3-methylpentane; J.W. Hanifin and E. Cohen, *J. Am. Chem. Soc.*, **91**, 4494 (1969).
- 5) The $n\text{-}\pi^*$ 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.