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Photoreduction of flavone: identification of the photoproducts and reaction mechanism

Hiroki Kawata [a,*], Tsutomu Kumagai [b], Eiichi Suzuki [c], Shigeya Niizuma [a]

[a] *Faculty of Humanities and Social Sciences, Iwate University, Morioka 020, Japan*
[b] *Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan*
[c] *Department of Applied Chemistry, Faculty of Engineering, Iwate University, Morioka 020, Japan*

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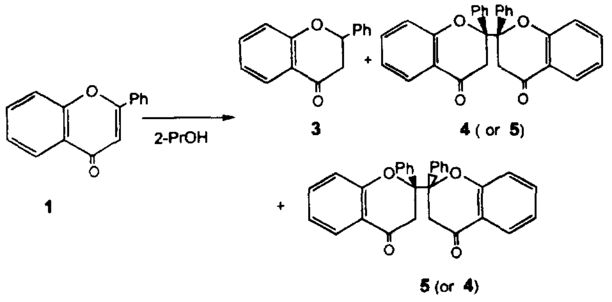
Abstract

The photoreduction of flavone was investigated in 2-propanol or in benzene containing N,N-dimethylaniline by a continuous light irradiation ($\lambda = 300$ nm), a flash photolysis and CIDEP methods. The photoreaction proceeds via the triplet state of flavone and gives the dimers of flavanon in 2-propanol, the diastereoisomers, which are different from the pinacol-type dimer.

Keywords: Flavone; Photoreduction; Diastereoisomer; Hydrogen abstraction; CIDEP

1. Introduction

The photochemistry of flavones has been largely restricted to that of 3-hydroxy derivatives and has concentrated on the photoisomerization of the intramolecular proton transfer in the excited state [1–4]. The photoreactions of flavones so far reported are also confined to the reactions of 3-hydroxy or 3-methoxyflavone which undergoes photorearrangement or photo-oxygenation [5,6]. We now report on the photolysis of flavone **1** by steady-state irradiation, flash photolysis and CIDEP in deoxygenated 2-propanol and benzene containing *N,N*-dimethylaniline.



Scheme 1.

Table 1
Photolysis of **1** at various times

Irradiation time (min)	Conversion of **1** (%)	Yield (%)		
		3	4 (or 5)	5 (or 4)
30	19.6	6.5	4.2	5.8
55	29.4	10.5	6.3	9.1
75	52.0	18.3	10.2	15.8

170 mg of **1** in 200 ml 2-propanol was irradiated.

2. Steady state irradiation

Irradiation (500 W Xe lamp with a UV-31 filter) of **1** in argon saturated 2-propanol (170 mg in 200 cm^3) afforded the three main products flavanone **3** (see Section 4) and its dimers, diastereoisomers **4** and **5** as shown in Scheme 1 and Table 1, the time course of the reaction being monitored by HPLC. These products are formed unequivocally by irradiation, not by the dark reaction. Trace amounts of another photoproduct were obtained with a molecular weight of 448, but we could not determine its structure. **4** and **5** were isolated by TLC in hexane–benzene (1:4 in volume), though their R_F values are relatively close. We named the compound with the larger R_F as **4** in TLC because we cannot specify which structure corresponds to **4** or **5** in Scheme 1 and Table 1. In aerated 2-propanol and deaerated benzene solution, changes in the absorption spectra on irradiation are rarely observed, while the reaction occurs in deaerated ethanol and benzene–2-propanol 1:1 mixed solvent. The yields of **3**, **4** and **5** in ethanol are somewhat low compared with those in 2-pro-

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* Corresponding author.

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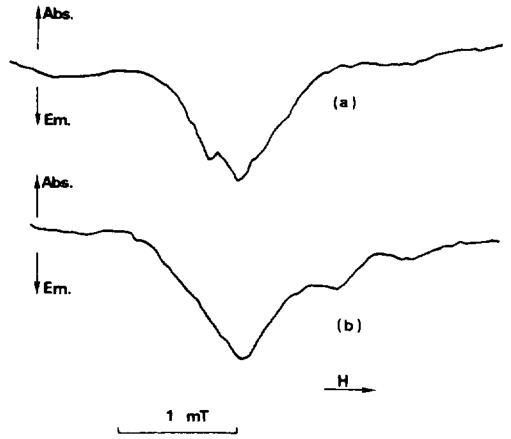
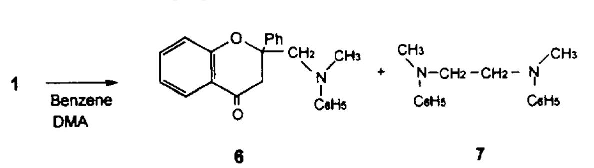
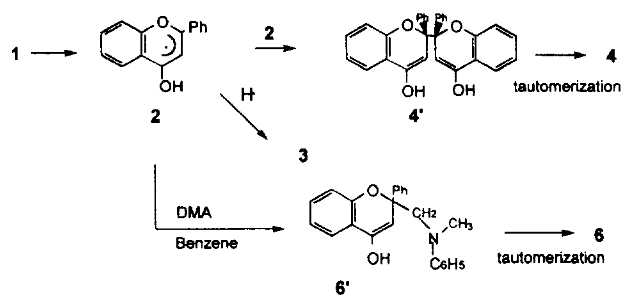


Fig. 1. CIDEP spectra 1.2 μs after 308 nm pulse irradiation of the solution of **1** in (a) benzene containing DMA ([**1**] = 0.01 mol dm^{-3}, [DMA] = 0.1 mol dm^{-3}) and (b) 2-propanol (0.8 mW).



Scheme 2.



Scheme 3.

panol. More noticeable of the reaction in ethanol is the reverse of the yield ratio of **4** to **5** compared with those in 2-propanol and benzene–2-propanol. The process of formation of **4** and **5** is affected by the surrounding atmosphere.

In general the hydrogen abstraction reaction of aromatic carbonyl compounds has been shown to give ketyl radicals through the n–π* triplet state. Especially, in the photochemistry of enones [7], hydrogen abstraction occurs either at the carbonyl oxygen atom or at the β-olefinic carbon atom according to the triplet species of the n–π* or π–π* state respectively. Sakaguchi et al. [8] found that direct hydrogen abstraction occurred through the π–π* triplet state in CIDEP studies of flavone for the first time when tri-*n*-butyltin hydride was used as a reducing agent. They distinguish the reactions by the character of the hydrogen donors between the hydride-type and the usual proton- and CT-type, in the former the benzyl type radical and in the latter the ketyl radical being formed respectively. At first glance, our experimental results appear to show the benzyl-type radical as judged by the structure of the products.

We successfully observed the CIDEP signal of the radical from **1** in benzene solution (10^{-2} mol dm^{-3}) containing *N*,*N*-dimethylaniline (DMA, 10^{-1} mol dm^{-3}) as shown in Fig. 1(a). It is a broad singlet line with E phase pattern induced by the triplet mechanism, analogously to the case of the photoreaction of **1** in 2-propanol containing *N*,*N*-diethylaniline [8]. This transient is a flavone ketyl radical. On steady state irradiation of **1** in benzene–DMA solution ([**1**] = 4.5 × 10^{-3} mol dm^{-3}, [DMA] = 5.0 × 10^{-1} mol dm^{-3}), the main photoproducts are the adduct of DMA to **1** (**6**) and the dimer of DMA (**7**, see Section 5) as shown in Scheme 2, though very small amounts of **4** and **5** are produced at the same time from the analysis of the NMR spectrum of the photoproducts. The CIDEP spectrum observed in the system of **1** in 2-propanol shows the same pattern (Fig. 1(b)) as that in benzene solution containing DMA, being different from the benzyl radical type signal [8] obviously. This means that the first transient of the photoreaction both in 2-propanol and in benzene containing DMA is the flavone ketyl radical and then the reaction proceeds by the coupling of radicals. Further, hydrogen abstraction from the solvents occurs at the phenyl substituted C-atom position as shown in Scheme 3, which is commonly observed in the photoreaction of heterocyclic enones [9,10]. Finally, it goes to diketon or keton by tautomerization of bisenol.

3. Flash photolysis

Fig. 2 shows the time-dependent transient absorption spectra obtained by laser flash photolysis of **1** in argon saturated 2-propanol at various delay times. The decay is of first order with the rate constant 2.1 × 10^5 s^{-1}. It is quenched by ferrocene with quenching rate constant 3.2 × 10^9 dm^3 mol^{-1} s^{-1}. In aerated solution, no transient was observed. This should be the T-T absorption of **1**. After 20 μs flashing, a new

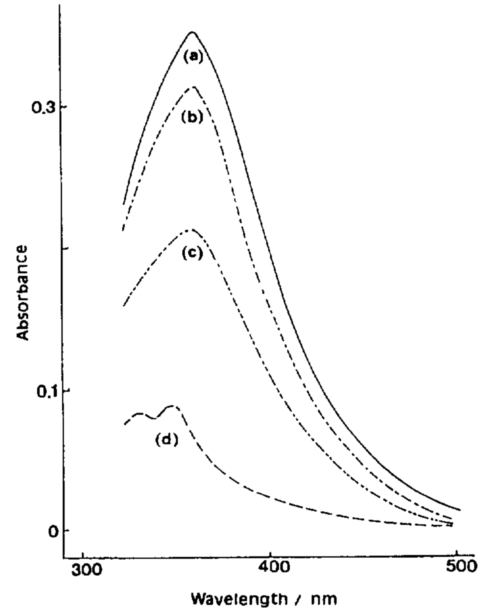


Fig. 2. Transient absorption spectra (a) 50 ns, (b) 100 ns, (c) 1 μs, and (d) 20 μs after laser flashing.

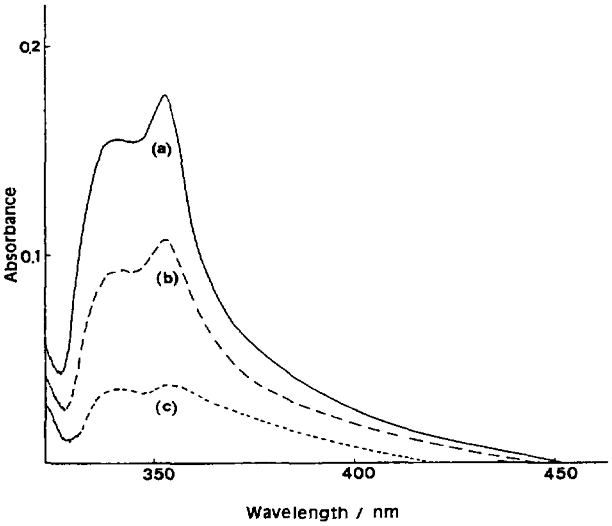


Fig. 3. Transient absorption spectra observed with microsecond flash apparatus (a) 100 μs, (b) 400 μs, and (c) 1 ms after flashing.

absorption could be observed. Fig. 3 shows the long lived transient (**I**) absorption spectra at various delay times observed by microsecond flash photolysis. The amount of this transient by dose decreases with ferrocene, but its decay is not affected. However, 60% of the photoreaction of **1** under steady-state irradiation is quenched by ferrocene under the condition that the concentrations of **1** and ferrocene are 1.5×10^{-4} and 7.5×10^{-5} mol dm^{-3} respectively. Thus, the photoreactive state of **1** is inferred to be the excited triplet state as shown in Scheme 3 and **I** is the subsequent product after the decay of ^{3}**1***. The decay of the ketyl radical **2** should be the superposition of the first and second orders if the above Scheme 3 is valid. Under this assumption, the decay of **I** was analyzed satisfactorily to give the value of $(k'/\epsilon d-k)$ as 2.0×10^3 s^{-1}, where k', k, ϵ and d are the second-order rate constant for the formation of **4** and **5**, the first-order rate constant for the formation of **3**, the molar extinction coefficient of **2** at the wavelength of 355 nm and the pathlength of light respectively. Thus, **I** seems to be **2** considering the CIDEP spectrum and the structure of the photoproducts. In benzene solution of **1**, only T-T absorption is observed. When DMA is added to the solution, a transient (λ_{max} 356 nm) appears just as is the case in 2-propanol. This must be **2** produced through a CT complex between **1** and DMA because of the results mentioned above. The confirmation of ketyl radical formation by flash photolysis and CIDEP techniques ensures the validity of Scheme 3.

4. Spectral data for 3, 4, 5

3, white needles, mp 74–75 °C (literature 75 °C); ^{1}H-NMR (600 MHz, CDCl$_3$) δ 2.474 (dd, J = 16.70, 2.99 Hz), 2.579 (dd, J = 16.70, 13.28 Hz), 4.839 (dd, J = 13.28, 2.99 Hz), 6.702 (ddd, J = 7.85, 6.91, 1.04 Hz), 6.864 (dd, J = 8.32, 1.09 Hz), 7.030 (ddd, J = 8.28, 7.15, 1.81 Hz), 7.04–7.21 (m, 5H), 8.137 (dd, J = 7.85, 1.82 Hz); ^{13}C-NMR (150 MHz, CDCl$_3$) δ 190.649 (C_1), 44.738 (C_2), 79.615 (C_3), 161.770 (C_4), 118.129 (C_5), 135.755 (C_6), 121.644 (C_7), 127.280 (C_8), 121.640 (C_9).

4, colorless powder, mp 220–221 °C; HRMS m/z 446.1513 (calculated for $C_{30}H_{22}O_4$ (M^+) 446.1518) and 223.0768 (calculated for $C_{15}H_{11}O_2$ ($M^+/2$) 223.0760); IR (KBr) 1686, 1603, 1460, 1306, 1224 cm^{-1}; ^{1}H-NMR (600 MHz, CDCl$_3$) δ 3.348 (H_{2a}, d, J = 16.32 Hz), 3.962 (H_{2b}, d, J = 16.32 Hz), 6.921 (H_6, ddd, J = 7.82, 6.91, 0.99 Hz), 6.93 (2H (orth), br m), 7.097 (2H (meta), br t, J = 7.4 Hz), 7,151 (H_4, dd, J = 8.36, 0.74 Hz), 7.179 (1H (para), tt, J = 7.35, 1.14 Hz), 7.484 (H_5, ddd J = 8.36, 7.20, 1.76 Hz), 7.664 (H_7, dd, J = 7.82, 1.76 Hz); ^{13}C-NMR (150 MHz, CDCl$_3$) δ 41.041 (C_2), 87.977 (C_3), 118.241 (C_4), 121.412 (C_{7a}), 121.475 (C_6), 126.481 (C_7), 127.741 ($C_{3'}$), 128.612 ($C_{4'}$), 128.858 ($C_{2'}$), 135.026 ($C_{1'}$), 136.184 (C_5), 159.278 (C_{3a}), 191.246 (C_1); UV λ_{max} 253 (ϵ 6.2×10^3) and 320 nm (ϵ 2.2×10^3) in EtOH.

5, colorless powder, mp 295–297 °C; HRMS m/z 446.1513 (calculated for $C_{30}H_{22}O_4$ (M^+) 446.1518) and 223.0758 (calculated for $C_{15}H_{11}O_2$ ($M^+/2$) 223.0759); IR (KBr) 1699, 1604, 1460, 1304, 1222 cm^{-1}; ^{1}H-NMR (600 MHz, CDCl$_3$) δ 3.123 (H_{2a}, d, J = 16.15 Hz), 3.649 (H_{2b}, d, J = 16.15 Hz), 6.892 (H_6, ddd, J = 7.76, 7.25, 0.5 Hz), 7.117 (H_4, dd, J = 8.40, 0.5 Hz), 7.20–7.25 (3H (meta and para), br m), 7.568 (H_7, dd, J = 7.15 Hz); ^{13}C-NMR (150 MHz, CDCl$_3$) δ 42.412 (C_2), 87.111 (C_3), 117.942 (C_4), 121.338 (C_{7a}), 121,484 (C_6), 126.487 (C_7), 128.095 ($C_{3'}$), 128.468 ($C_{4'}$), 129.082 ($C_{2'}$), 135.900 ($C_{1'}$), 136.211 (C_5), 158.759 (C_{3a}), 190.495 (C_1); UV λ_{max} 253 (ϵ 6.5×10^3) and 320 nm (ϵ 2.3×10^3) in EtOH.

5. Spectral data for 6, 7

6; HRMS m/z 343.1570 (calculated for $C_{23}H_{21}NO_2$ (M^+) 343.1572) and 224.0878 (calculated for $C_{15}H_{12}O_2$ 224.0837); ^{1}H-NMR (CDCl$_3$, 500 MHz) δ 3.326 (1H, d, J = 16.0 Hz), 3.359 (1H, d, J = 16.0 Hz), 3.744 (2H, s), 6.732 (1H, t, 7.3 Hz), 6.880 (1H, td, J = 7.8, 0.8 Hz), 7.078 (1H, dd, J = 70.08 Hz), 7.18–7.24 (3H, m), 7.280 (2H, dd, J = 8.0, 7.3 Hz), 7.420(2H, d, J = 8.5 Hz), 7.845 (1H, ddd, J = 7.8, 7.0, 1.8 Hz), 7.674 (1H, dd, J = 7.8, 1.8 Hz); ^{13}C-NMR (150 MHz, CDCl$_3$) δ 40.116 (CH_3), 43.538 (CH_2), 63.765 (C_3), 87.422 (C_2), 112.271 ($C_{2'}$, $C_{6'}$), 117.050 ($C_{4'}$), 118.210 (C_6), 121.139 (C_8), 121.229 (C_{4a}), 126.189 ($C_{2''}$, $C_{6''}$), 126.485 (C_5), 128.147 ($C_{4''}$), 128.747 ($C_{3''}$, $C_{5''}$), 129.093 ($C_{3'}$,$C_{5'}$), 136.002 (C_4), 139.572 ($C_{1''}$), 149.698 ($C_{1'}$), 159.626 (C_{1a}), 191.615 (C_4), ′ and ″ refer to the N-phenyl and C-phenyl positions respectively; IR (KBr) 1691, 1599 cm^{-1}.

7; HRMS m/z 240.1629 (calculated for $C_{16}H_{20}N_2$ (M^+) 240.1626) and 120.0819 (calculated for $C_8H_{10}N$ ($M^+/2$) 120.0813); ^{1}H-NMR (500 MHz, CDCl$_3$) δ 2.931 (6H, s), 3.531 (4H, s), 6.65–6.75 (6H, m), 7.231 (4H, dd, J = 7.5, 8.5 Hz); ^{13}C-NMR (150 MHz, CDCl$_3$) δ 38.652 (CH_3), 49.724(CH_2), 111.827(C_2, C_6), 116.236(C_4), 129.274 (C_3, C_5), 148.867 (C_1); IR (KBr) 1599, 1506 cm^{-1}.

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