Pergamon

Tetrahedron Letters 43 (2002) 5161–5163

TETRAHEDRON
LETTERS

A new type of photodimerization reaction for coumarin derivatives

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Received 3 April 2002; accepted 17 May 2002

Abstract—Irradiation (λ >300 nm) of coumarin-3-carboxylic acid gives the decarboxylated 4,4′-dimer of chroman-2-one, the structure of which is quite different from that of [π2s+π2s] cycloaddition dimer as is observed in the past in the photoreaction of coumarin or some of its derivatives. © 2002 Elsevier Science Ltd. All rights reserved.

The photoreaction of coumarin is well-known to give *cis*-head-to-head (**I**) or *trans*-head-to-head (**II**) dimers via the [π2s+π2s] cycloaddition reaction.[1–6] This reaction depends on the multiplicity of the excited state of coumarin, that is, **I** is formed from the excited singlet state in ethanol solution and **II** from the excited triplet state which is performed by a photosensitizer such as benzophenone in benzene solution, respectively. In 1995, Shim[7] and Chen[8] reported the photocleavage of the cycloaddition dimer of coumarin derivatives with UV light. We have found a new type photodimerization reaction for coumarin-3-carboxylic acid (**1**). Irradiation of **1** in ethanol solution gives three kinds of products, 4,4′-dimer of chroman-2-one (**2**), 3-(1′-hydroxyethyl)-coumarin (**3**) and coumarin itself (**4**). The main photoproduct is **2**. Further, these are decarboxylated compounds. In this paper, we report the photodimerization and decarboxylation reaction of **1** by the detection of the transients using the flash apparatus.

Using a 500 W Xe lamp with a Pyrex filter, irradiation of **1** (Aldrich Chem. Co., recrystallized twice from ethanol) in argon saturated ethanol solution (40 mg in 200 cm^3 cylindrical quartz cell, 1×10^{-3} mol dm^{-3}) for 8 h afforded the three kinds of products. The above procedure was repeated four times and finally, compounds **2**[9] (56 mg, yield 45.2%), **3**[10] (8 mg, 5.0%) and **4**[11] (12 mg, 9.8%) were obtained for each run. The reaction was monitored by HPLC with acetonitrile/water (6:4 in volume) solvent. Compound **2** is obtained as follows: after evaporation of the solvent of the photolysis mixture under reduced pressure, the precipitate appears. It is filtered and recrystallized from acetic acid. With the TLC procedure (silica gel 60 with benzene/methanol, 8:2) of the filtrate, **3** and **4** were obtained, respectively. The quantum yield for the disappearance of **1** (1.0×10^{-4} mol dm^{-3}) is 0.05 with a 150 W Xe lamp equipped with a 313 nm interference filter. The light intensity of the lamp was measured with a chemical actinometer. The value of 0.05 seems to be very high compared with that for the cycloaddition-type dimer because a few days irradiation was needed to obtain the cycloaddition-type dimer even for the diluted solution.[6,7] In the aerated solution of **1**, no changes in the UV absorption spectrum or HPLC on the irradiation are observed. Schenk[3] and Hammond[4] reported the photoreaction of coumarin proceeded under very high concentration, ~0.5 mol dm^{-3}, and the excited singlet and the triplet state coumarin reacted with the ground state coumarin to yield **I** and **II**, respectively. In contrast, **1** does not dissolve so much in ethanol, the maximum concentration being ~1.5×10^{-3} mol dm^{-3} at room temperature. So, we had to experiment under lower concentration of **1** than in the case of the literature. However, it should be noted that even the 1×10^{-2} mol dm^{-3} solution of coumarin[4,5] or the 1×10^{-3} mol dm^{-3} solution of coumarin derivative[7] also gave the cycloaddition-type dimer with the irradiation. The photoreaction for the cycloaddition-type dimer formation seems not to depend on the concentration of coumarin or its derivatives. Further, irradiation of argon saturated ethanol solution of **4** (1×10^{-3} mol dm^{-3}) for 10 h gives no products. This means that under our experimental light intensities of the Xe lamp and the irradia-

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Keywords: coumarin-3-carboxylic acid; photodimerization; decarboxylation; hydrogen abstraction.

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PII: S0040-4039(02)00969-3

tion time, we do not have to consider the possibility of the photoisomerization of the primary product **4**. Thus, the contribution of **I** and **II** type photoproducts of **1** is ruled out.

With a conventional microsecond flash apparatus, the photolysis of **1** in argon saturated ethanol solution gives a relatively long-lived transient which decays in the second order with the rate constant of $1.4\times\varepsilon\times10^4$ $dm^3\ mol^{-1}\ s^{-1}$, where ε is the molar extinction coefficient of the transient at 420 nm. This transient is observed below the wavelength of 600 nm (λ_{max} 420 and 540 nm). No transient was observed in the aerated ethanol or the argon saturated benzene solution of **1**. Nanosecond laser flash photolysis (266 nm light pulse excitation of Nd^{3+}–YAG laser with a full width at half-maximum intensity of 5 ns) of **1** in argon saturated ethanol solution also gives a transient which decays in the first order with the rate constant of $2.4\times10^5\ s^{-1}$, while no transient is observed in the aerated system. Fig. 1 shows the time-dependent transient absorption spectra at various delay times, 300 ns, 1.5 μs and 2.5 μs after flashing, respectively. This should be a T–T absorption spectrum of **1** because it is quenched by ferrocene or oxygen molecule, a good triplet quencher. The quenching rate constant by ferrocene is 3.4×10^9 $dm^3\ mol^{-1}\ s^{-1}$. The amount of the long-lived transient by a dose observed in a microsecond flash photolysis decreases with increasing the concentration of ferrocene, though the additive does not affect its decay rate. Thus the photoreactive state of **1** is inferred to be the excited triplet state (^{3}**1***) and the long-lived transient is a subsequent product after the decay of ^{3}**1***. We interpret this transient as a precursor of **4**, a ketyl radical formed by the hydrogen abstraction from the solvent, ethanol. This is also detected in a benzene solution containing *N*,*N*-dimethylaniline, a hydrogen atom donor, but not detected in a benzene only solution as mentioned above. Unfortunately, we could not obtain the CIDEP signals for the ketyl radical as were observed in the photolysis of chromone-2-carboxylic acid.[12]

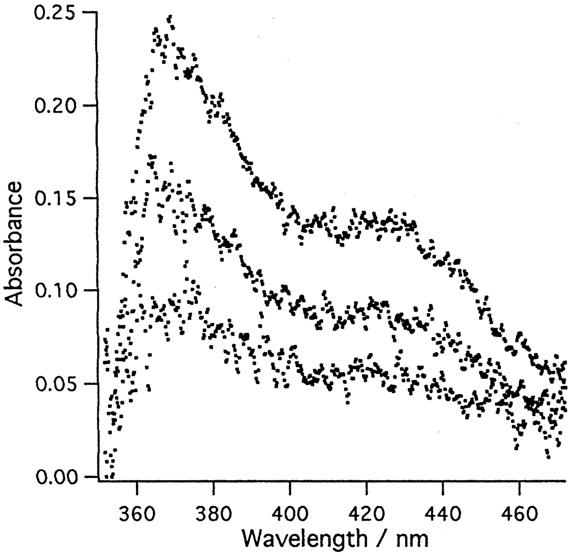
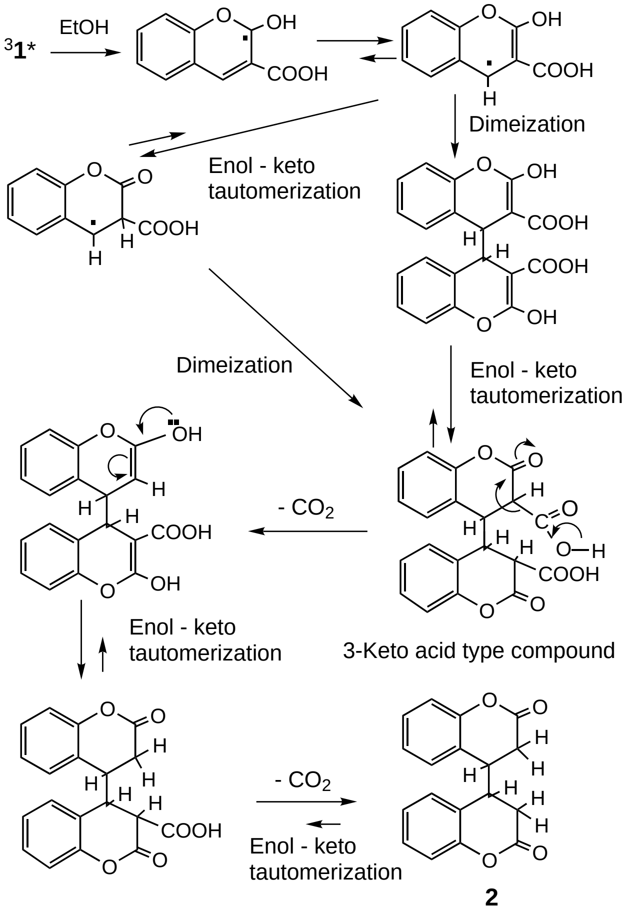
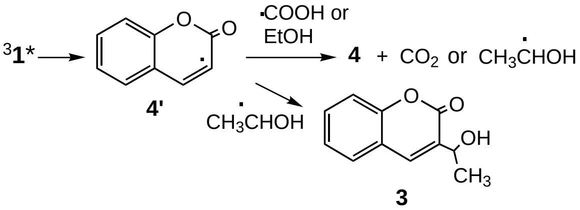


Figure 1. T–T absorption spectra of 2×10^{-4} mol dm^{-3} ethanol solution of **1**: (a) 300 ns, (b) 1.5 μs and (c) 2.5 μs after 266 nm laser flashing.



Scheme 1.

We propose the Scheme 1 for the formation of **2**. The photoreactive state is ^{3}**1*** from the flash photolysis. The fate of the ketyl radical is as follows. The equilibrium between the 2-position and 4-position radical should shift to the latter judging from the structure of the end product. Two pathways for the formation of 3-keto acid-type compounds can be depicted as in Scheme 1; the dimerization of radicals followed by the enol-keto tautomerization or quite the reverse. However, it is uncertain which way is plausible to give the 3-keto acid-type compound. 3-Keto acids, especially free carboxylic acids, are known to decompose very easily to give carbon dioxide and ketone by a concerted reaction involving a cyclic transition state.[13] Similarly, 3-keto acid-type dimer in Scheme 1 can be thought to undergo the two-step reaction through the decarboxylation and the enol-keto tautomerization in the dark, and finally to yield **2**. Further, photoillumination of 4-hydroxycoumarin or 4-methyl-3-phenylcoumarin in argon saturated ethanol solution gives no transients and no photoproducts. The hydrogen abstraction and the following decarboxylation reaction in this paper seem to be characteristic of the carboxylic group of coumarin.



Scheme 2.

The reaction mechanism for the minor photoproducts, **3** and **4**, is represented in Scheme 2. First, the direct homolytic cleavage of the carboxyl group should occur from ^{3}**1*** as is also observed in the photo-decarboxylation reaction of pyridine carboxylic acid.[14] A hydrogen atom in the 3-position of **4** most likely comes from the carboxyl group, though the hydrogen abstraction from ethanol cannot be ruled out. As a result, the 1-hydroxyethyl radical, which is formed in Scheme 1 or in both Schemes 1 and 2, attacks **4**′ to yield **3**.

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9. Compound **2**: Mp 278–280°C. Anal. found: C, 73.29; H, 4.44. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.79%. HRMS: 294.0892 (calcd for $C_{18}H_{14}O_4$; 294.3014). IR (KBr): 1771, 1760 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 2.73 (1H, ddd, J=2.0, 5.2, 16.0 Hz), 2.85 (1H, dd, J=2.0, 16.0 Hz), 2.91 (1H, dd, J=2.0, 2.0 Hz), 7.14 (dd, J=1.2, 8.0 Hz), 7.22 (ddd, J=1.2, 7.6, 7.6 Hz), 7.29 (dd, J=1.6, 7.6 Hz), 7.37 (ddd, J=1.6, 7.6, 8.0 Hz). ^{13}C NMR (CDCl$_3$, 150 MHz): δ 32.981 (CH2), 38.681 (CH), 117.64 (C4), 124.844 (C6), 129.542 (C5), 129.709 (C7), 167.733 (C1).
10. Compound **3**: Colorless oil. IR (KBr): 3424, 1718, 1699, 1610 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 1.55 (3H, d, J=6.5 Hz), 3.23 (OH, brs), 4.93 (1H, dq, J=0.8, 6.5 Hz), 7.29 (ddd, J=1.0, 7.6, 8.0 Hz), 7.32 (dd, 1.0, 8.7 Hz), 7.506 (dd, J=1.7, 7.6 Hz), 7.508 (ddd, 1.7, 8.0, 8.7 Hz), 7.78 (1H, s). ^{13}C NMR (CDCl$_3$, 150 MHz): δ 21.860 (CH3), 65.919 (CH), 116.397 (C4), 124.539 (C6), 127.904 (C7), 131.249 (C5), 137.237 (C3).
11. Mp, mass and NMR spectra of **4** are identical with those of the authentic sample, coumarin.
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