

PHOTOCHEMICAL REACTIONS OF AROMATIC α -DIKETONES

SUNG SIK KIM,* DONG YEOL YOO, MI HYUN SO and KWANG JOONG O
Department of Chemistry, Chonbuk National University, Chonju 560-756, Korea

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Abstract — Irradiation of aromatic α -diketones, such as benzil, 4,4'-dimethylbenzil, 4-chlorobenzil, 4,4'-diisopropylbenzil, 3,3'-dimethylbenzil, in methanol gives rise to xanthone derivatives, in addition to α -hydroxyketones. Irradiation of 4,4'-dibromobenzil, 2,2'-pyridil, 2,2'-naphthil and 9,9'-anthril yields only α -hydroxyketones, whereas 4,4'-dimethoxybenzil yields methyl 4-methoxybenzoate.

INTRODUCTION

The photochemistry of α -diketones has been a subject of interest for about a century.¹ Since the appearance of comprehensive review articles in 1969 and 1971, activity of this area has continued with investigation of a number of new systems.²⁻⁸ It has been known that irradiation of benzil in solution yields a variety of products, benzaldehyde, benzoic acid, benzoin, benzil pinacol, *etc.*¹

We found that irradiation of aromatic α -diketones in methanol yields the unexpected photoproducts, *i.e.*, xanthone derivatives, in addition to α -hydroxyketones.

EXPERIMENTAL SECTION

Aromatic α -diketones, such as benzil, 4,4'-dimethylbenzil, dimethylbenzil, 4,4'-diisopropylbenzil, 3,3'-dimethylbenzil, 4,4'-dimethoxybenzil, 2,2'-naphthil and 9,9'-anthril, were synthesized by the oxidation of the corresponding α -hydroxy ketones prepared from the benzoin condensation of aromatic aldehydes.⁹ 4,4'-Dibromobenzil, 4-chlorobenzil and 2,2'-pyridil were purchased from Aldrich Chemical Company and used without further purification. Methanol, *n*-hexane, ethyl acetate, dichloromethane, cyclohexane and benzene were freshly distilled before use. Analytical TLC was performed on commercial plates coated with silica gel Kieselgel 60 F254 (0.25-mm thick, Merck). Silca gel for flash chromatography was Merck Kieselgel 60 (230-400 mesh).

Ultraviolet spectra were recorded on Hitachi 556 Spectrophotometer. Infrared spectra were recorded on a Nicolet 5-DX13 Spectrophotometer. NMR spectra

were recorded on a Jeol JMN EX Spectrometer. Mass spectra were obtained on a Hewlett Packard 5985 GC/MS system using electron impact (EI) method. Fluorescence spectra were recorded on a Jasco Spectrofluorometer (Model FP-770).

Normal scale preparations of the photoproducts were conducted in a photoreactor composed of water-cooled pyrex reaction vessel, which is equipped with a nitrogen gas inlet. Irradiation was carried out in a Rayonet Photochemical Reactor (The Southern New England Ultraviolet Company, Model RPR-208) with 350 nm UV lamps. The progress of the photoreactions was monitored by the pre-coated TLC plates.

Benzil (500 mg) was dissolved in methanol (200 mL) and degassed with dry nitrogen gas for 1 h. The solution was irradiated with 350 nm UV light for 28 h. Filtration and recrystallization gave a xanthone derivative **2** in 18% yield: UV (MeOH), λ_{\max} 363, 343, 324, 311, 289, 262, 246 nm; IR (KBr), 3070-3020, 1648, 1243 cm^{-1} ; ¹H-NMR (CDCl_3), δ 10.2 (1H, d, $J=7\text{Hz}$, aromatic, intramolecularly hydrogen-bonded), 8.68-7.30 ppm (11H, m, aromatic); Mass (EI), m/e 120, 176, 268 (M-CO), 296 (M); Fluorescence (MeOH), λ_{em} 382, 402 nm.

4,4'-Dimethylbenzil (300 mg) was dissolved in methanol (150 mL) and degassed with dry nitrogen gas for 1 h. The solution was irradiated with 350 nm UV light for 40 h. Filtration and recrystallization gave the resulting photoproduct **3a** ($a = \text{me}$) in 20% yield: UV (MeOH), λ_{\max} 367, 346, 330, 314, 297, 267, 255 nm; IR (KBr), 3080-3020, 2980-2880, 1650 cm^{-1} ; ¹H-NMR (CDCl_3), δ 10.0 (1H, d, $J = 8\text{Hz}$, intramolecularly hydrogen-bonded), 8.20-7.00 (9H, m, aromatic), 2.60 (3H, s), 2.47 (3H, s), 2.36 ppm (3H, s); Mass (EI), m/e 338 (M).

Irradiation (350 nm) of 4,4'-diisopropylbenzil (200 mg) in methanol (150 mL) for 12 h also gave **3b** ($R = i\text{-Pr}$) in 30% yield: UV (MeOH), λ_{\max} 365, 350, 331,

* To whom correspondence should be addressed.

314 nm; IR(KBr), 3057, 2966, 1623, 1433, 1046, 828 cm^{-1} ; $^1\text{H-NMR}(\text{CDCl}_3)$, δ 10.14(1H, d, $J=8.8$ Hz), 8.74-7.34 (8H, m), 3.26 (1H, septet, CHMe_2), 3.23 (1H, septet, CHMe_2), 3.13 (1H, septet, CHMe_2), 1.46 (6H, d, CHMe_2), 1.44 (6H, d, CHMe_2), 1.39 ppm (6H, d, CHMe_2).

4-Chlorobenzil (100 mg) was dissolved in methanol (150 mL) and degassed with dry nitrogen gas for 1 h. The solution was irradiated with 350 nm UV light for 12 h. The filtrate yielded solid precipitate after removal of the solvent and washing. The residue was chromatographed over silica gel (230-400 mesh) with *n*-hexane and ethyl acetate as eluents. Early fraction gave xanthone derivative **4** (**4a** and **4b**) in 24% yield, which was recrystallized from methanol: Two isomeric products could not be isolated, but were observed in the ratio of 1.0 : 1.0 in 400 MHz $^1\text{H-NMR}$ spectrum. $^1\text{H-NMR}(\text{CDCl}_3)$ of the isomeric **4** (**4a** and **4b**), δ 10.19 (1H, d, $J=6.3\text{Hz}$), 10.16 (1H, d, $J=6.3\text{Hz}$), 8.82 - 7.50 ppm; Mass (EI), **4a**, m/e 330 (M), 332(M+2), 302 (M-CO), 295 (M-Cl); **4b**, m/e 364 (M, 100%), 366 (M+2), 368 (M+4), 336 (M-CO), 329 (M-Cl), 294 (M-2Cl), 266 (294-CO); UV (cyclohexane), λ_{max} 367, 348, 331, 312, 298 nm.

3,3'-Dimethylbenzil (200 mg) was dissolved in methanol (200 mL) and degassed with dry nitrogen gas for 1 h. The solution was irradiated with 350 nm UV light for 24 h. The photoproduct **5** was isolated, in 25% yield, by column chromatography using *n*-hexane and ethyl acetate as eluents: UV (cyclohexane), λ_{max} 368, 352, 334, 321, 271, 254 nm; IR (KBr), 3070-3020, 2917, 1630, 1482, 1398, 807, 751 cm^{-1} ; $^1\text{H-NMR}(\text{CDCl}_3)$, δ 9.98 (1H, s), 8.50 (2H, m), 8.40 (1H, s), 8.27 (1H, d), 7.60 (2H, m), 7.48 (1H, d), 7.35 (1H, t), 2.77 (3H, s), 2.65 (3H, s), 2.63 ppm (3H, s); $^{13}\text{C-NMR}(\text{CDCl}_3)$, 178.48 (CO), 134.27, 131.89, 127.79, 127.31, 124.00, 123.94, 123.06, 122.34 and 121.75 (8 CH's, aromatic), 22.03, 21.69 and 21.55 ppm (3 Me's); Mass (EI), m/e 338 (M).

Irradiation of 4,4'-dimethoxybenzil gave methyl 4-methoxybenzoate **6** as a major product: IR (KBr), 1700, 846 cm^{-1} ; $^1\text{H-NMR}(\text{CDCl}_3)$, δ 3.86 (s, 3H, MeOAr), 3.88 (s, 3H, COOMe), 6.92 (d, 2H, aromatic, $J=9$ Hz), 8.00 ppm (d, 2H, aromatic, $J=9\text{Hz}$); Mass (EI), m/e 166 (M), 135 (M-OMe, 100%), 107 (M-COOMe).

Irradiation of 4,4'-dibromobenzil, pyridil, 2,2'-naphthil and 9,9'-anthril were also irradiated in methanol, but only α -hydroxyketones, **7**, were isolated, which were characterized by $^1\text{H-NMR}$, IR, UV and Mass spectra.

RESULTS AND DISCUSSION

It has been known that irradiation of benzil in solution produces a variety of reaction products, i. e., ben-

zaldehyde, benzoic acid, benzoin, benzil pinacol, *etc.*¹ Photochemical reactions of aromatic α -diketones in alcohol solvent, in general, yield α -hydroxyketones.

We now report that irradiation of some aromatic α -diketones, such as benzil,^{10,11} 4,4'-dimethylbenzil,¹¹ 4,4'-diisopropylbenzil, 3,3'-dimethylbenzil, and 4-chlorobenzil,¹¹ in methanol gives rise to xanthone derivatives, such as **2**, **3**, **4**, and **5**, as shown in Figure 1.

Irradiation (350 nm) of benzil in methanol gives rise to **2**. EI mass spectrum of **2** shows molecular ion peak at m/e 296 ($\text{C}_{12}\text{H}_{12}\text{O}_2$, base peak), which may be due to the rigid cyclic structure of the product **2**. The M-CO peak was also observed at m/e 268. $^1\text{H-NMR}$ spectrum (CDCl_3) shows an aromatic proton at 10.2 ppm (d, $J=7\text{Hz}$, intramolecularly hydrogen-bonded with oxygen atom of C=O group). The new absorption bands observed at 363, 343, 324, 311, 289, and 246 nm are due to the phenanthrene moiety.

Irradiation of 4,4'-dimethylbenzil also gave the same type of photoproduct, **3a** ($\text{R} = \text{Me}$). $^1\text{H-NMR}$ spectrum (CDCl_3) of **3a** shows an aromatic proton at 10.0 ppm (d, $J=8\text{Hz}$, intramolecularly hydrogen bonded). Three methyl protons of **3a** appear at 2.89 ppm, 2.58 ppm and 2.51 ppm in $^1\text{H-NMR}$ spectrum (CDCl_3), and 22.2 ppm, 21.9 ppm and 21.7 ppm in $^{13}\text{C-NMR}$ spectrum (CDCl_3). The carbonyl carbon of **3a** was found at 178.1 ppm. The molecular ion peak at m/e 338 was observed as a base peak in EI mass spectrum, which may be due to the rigid structure of **3a**. The M-CO peak was also found at m/e 310. The new absorption bands at 367, 331, 315, and 296 nm are due to the phenanthrene moiety. The longest absorption band (367 nm) of **3a** is red-shifted in comparison with that (363 nm) of the product **2**, which is due to the electron-donating effect of the methyl groups. The similarity of the UV absorption bands certifies the structure of the photoproducts.

Irradiation (350 nm) of 4,4'-diisopropylbenzil in methanol also gave rise to the same type of photoproduct **3b** ($\text{R} = i\text{-Pr}$) in 30 % yield. $^1\text{H-NMR}$ spectrum (CDCl_3) of **3b** shows an aromatic proton (s, intramolecularly hydrogen-bonded) at 10.14 ppm. Three septets of three isopropyl groups of the photoproduct **3b** were found at 3.25, 3.23, and 3.13 ppm.

4-Chlorobenzil was also irradiated in methanol to give the same type of photoproducts, **4** (**4a**; $\text{R} = \text{H}$ (or Cl), $\text{R}' = \text{Cl}$ (or H), $\text{R}'' = \text{H}$, and **4b**; $\text{R} = \text{H}$ (or Cl), $\text{R}' = \text{Cl}$ (or H), $\text{R}'' = \text{Cl}$), in which the isomeric products could not be separated, but were observed in the ratio of 1.0:1.0 in 400 MHz $^1\text{H-NMR}$ spectrum (CDCl_3). Two intramolecularly hydrogen-bonded protons were observed at 10.19 ppm and 10.16 ppm. EI mass spectrum of monochloro compound **4a** shows peaks at m/e 330 (M), m/e 332 (M+2), m/e 302 (M-CO),

m/e 295 (M-Cl), and that of dichloro compound **4b** shows peaks at m/e 364 (M, 100%), m/e 366 (M+2), m/e 368 (M+4), 336 (M-CO), m/e 329 (M-Cl), m/e 294 (M-2Cl), 266 (m/e 294-CO). The UV absorption bands of **4a** (mixed with **4b**) were observed at 367, 348, 331, 313, and 298 nm in cyclohexane.

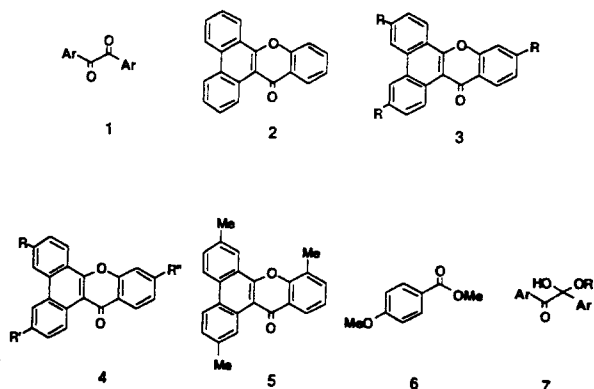


Figure 1

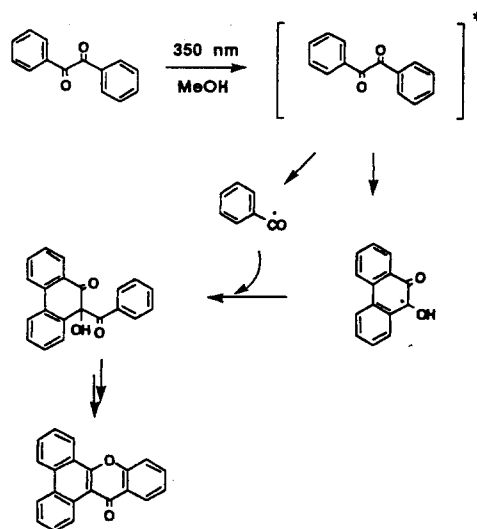
3,3'-Dimethylbenzil was also irradiated in methanol to give **5** in 25% yield. $^1\text{H-NMR}$ spectrum (CDCl_3) of **5** shows an aromatic proton (s, intramolecularly hydrogen-bonded) at 9.98 ppm. The molecular ion peak was also found at m/e 338 in EI mass spectrum. Three methyl protons appears at 2.77 ppm, 2.65 ppm, and 2.63 ppm in $^1\text{H-NMR}$ spectrum (CDCl_3), and 22.03 ppm, 21.69 ppm and 21.55 ppm in $^{13}\text{C-NMR}$ spectrum (CDCl_3). The carbonyl carbon was found at 178.5 ppm.

The xanthone-like photoproduct was not found in the photoreaction of 4,4'-dimethoxybenzil, in which only methyl 4-methoxybenzoate **6** was isolated. 4,4'-Dibromobenzil, 2,2'-pyridil, 2,2'-naphthil and 9,9'-anthril were also irradiated in methanol, in which only α -hydroxyketones, like **7**, were isolated.

Saturated and aryl diketones undergo efficient intersystem crossing to the chemically reactive triplet state (n,π^*) which may (inter- or intramolecularly) abstract a hydrogen atom of a wide variety of types or to a multiple bond.¹ In addition to the common reaction types mentioned above, α -cleavages might occur and will be recognizable by fragmentation or loss of carbon monoxide. The novel photochemical reaction of aromatic α -diketone was interpreted, as suggested in Scheme 1, on the basis of a mechanism involving the formation of biradical, α -cleavage of diketone, and hydrogen atom abstraction from the solvent molecules. Aromatization in the final step may be a driving force in these photochemical reactions.

Irradiation of the α -diketone in molecular oxygen did not yield the xanthone-like photoproducts. Irradiation of the compounds in dichloromethane, in benzene, or in cyclohexane also did not give xanthenes.

The experimental evidence shows that the photoreactions of some aromatic α -diketones in



Scheme 1

methanol provide a convenient entry to xanthone derivatives. Extension of the syntheses of various aromatic α -diketones and of the chemical properties of the xanthenes will be investigated.

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