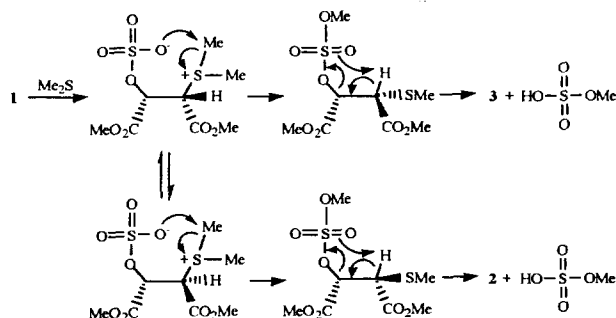


The present reactions of cyclic sulfates **1** with dimethyl sulfide and with pyridine are very special ones. Other cyclic sulfates never showed same reaction patterns as **1**. Further studies are required for the elucidation of the reaction mechanisms.

Acknowledgement. This work was supported by the Organic Chemistry Research Center.

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- Compound **2**: TLC (SiO₂, 1 : 1 ethyl acetate/hexanes) R_f = 0.68; ¹H NMR (CDCl₃, 300 MHz) δ 2.34 (s, 3H), 3.60 (s, 3H), 3.86 (s, 3H), 5.62 (s, 1H); GC MS m/e 190 (M⁺), 159, 131, 130, 105, 85, 72, 59.
- Compound **3**: TLC (SiO₂, 1 : 1 ethyl acetate/hexanes) R_f = 0.59; ¹H NMR (CDCl₃, 300 MHz) δ 2.32 (s, 3H), 3.74 (s, 3H), 3.84 (s, 3H), 6.28 (s, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 15.6, 51.6, 52.6, 110.0, 150.7, 165.0, 166.0.
- A plausible mechanism for the formation of **2** and **3** can be suggested as follows:



- Compound **6**: ¹H NMR (DMSO-d₆, 80 MHz) δ 3.27 (s, 6H), 3.67 (s, 3H), 3.83 (s, 3H), 7.11 (d, 2H, J=8.0 Hz), 7.25 (s, 1H), 8.24 (d, 2H, J=8.0 Hz).
- For example, see: (a) L. D. Brown, K. Itoh, H. Suzuki, K. Hirai, and J. A. Ibers, *J. Am. Chem. Soc.*, **100**, 8232 (1978); (b) H. Suzuki, K. Itoh, Y. Ishii, K. Simon, and J. A. Ibers, *J. Am. Chem. Soc.*, **98**, 8494 (1976); (c) R. J. Crawford, *U. S. Patent*, 3 746 745 (1973).

One-Pot Preparation of Xanthone Derivatives from Aromatic α-Diketones

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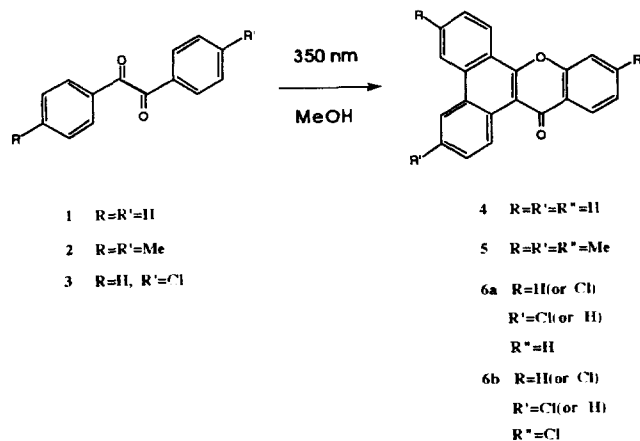
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The photochemistry of α-diketones has been a subject of interest for a century. Since the appearance of comprehensive review articles^{1,2} in 1969 and 1972, activity in this area has continued with investigation of a number of new systems.³⁻¹² The classical photochemistry of saturated and aryl diketones is well known. It has been known that irradiation of benzil in solution gives rise to a variety of reaction products, such as benzaldehyde, benzoic acid, benzoin, benzil pinacol and benzoin benzoate.¹²⁻¹⁵ Irradiation of benzil in ethylene glycol gave α,α'-dihydrostilbene.^{11,15} Irradiation of benzil in cyclohexane yielded benzoic acid, benzoin, desyl benzoyloxyethyl ether and unknown compound.¹⁶ When 2-propanol is used as the solvent, a new product appears which is most probably the dimer of ketyl radical which is formed when an excited benzil abstracts a hydrogen atom.¹² Irradiation of benzil in tetrahydrofuran gave a mixture of product containing benzaldehyde, a small amount of benzoin and unidentified photoproduct.¹⁴

We have reported that irradiation of benzil in methanol gave the unexpected photoproduct, *i.e.*, xanthone derivatives in 18% yield.¹⁷ Here we now describe the photochemical formation of xanthone derivatives from α-diketones, such as benzil **1**, 4,4'-dimethylbenzil **2** and 4-chlorobenzil **3** in methanol (Scheme 1).

Normal scale preparations of the new photoproducts were conducted in a photoreactor composed of water-cooled pyrex reaction vessel, which is equipped with a nitrogen gas inlet.



Scheme 1.

Irradiation was carried out with 350 nm UV lamps in a Rayonet Photoreactor (Model RPR-208). A gentle stream of nitrogen gas was maintained through the irradiation period. A solution of 100 mg of 4,4'-dimethyl benzil **2** in 250 mL of methanol was irradiated in the apparatus described above. The filtrate yielded solid precipitate after removal of the solvent and washing. The residue was chromatographed over silica gel (70-230 mesh) with *n*-hexane and ethyl acetate as the eluent. Early fraction gave xanthone derivative **5** in 24% yield, which was recrystallized from methanol.

The novel photochemical reactions of α -diketones were interpreted as follows. The mechanism for the classical photochemistry of saturated and aryl diketones may be applied in these photoreactions.¹² These compounds, *i.e.*, α -diketones, can undergo efficient intersystem crossing (very weak fluorescence and strong phosphorescence) to the chemically reactive triplet state (n, π^*) which may (inter- or intramolecularly) abstract a hydrogen atom of a variety of types or add to a multiple bond.¹² The photochemical formation of xanthone derivatives may be rationalized on the basis of a mechanism involving the formation of biradical, α -cleavage of diketone, cyclization, addition of benzoyl radical, and second cyclization followed by aromatization to give the final photoproduct.

The structure of the photoproduct **5** was characterized by spectral data. The IR spectrum showed $\nu_{C=O}$ at 1648 cm^{-1} (1679 cm^{-1} for **4**) ν_{C-O} at 1243 cm^{-1} , and ν_{C-H} (aromatic) at 3070-3020 cm^{-1} . The stretching and bending vibrations for the methyl group were not observed. ¹H-NMR spectrum showed phenyl protons at 9.98 ppm (1H, m, aromatic, intramolecularly hydrogen-bonded) and 8.50-7.18 ppm (8H, m, aromatic). Three methyl protons of **5** appeared at 2.78 ppm, 2.58 ppm and 2.51 ppm in ¹H-NMR spectrum (CDCl_3), and 22.2 ppm, 21.9 ppm and 21.7 ppm in ¹³C-NMR spectrum (CDCl_3).¹⁸ The carbonyl carbon of **5** was found at 178.1 ppm. The molecular ion peak at *m/e* 338 was found as a base peak in EI mass spectrum, which may be due to the rigid cyclic structure of the product **5**. The M-CO peak was also observed at *m/e* 310. The new absorption bands in methanol observed at 367, 331, 315 and 296 nm are due to the phenanthrene moiety.

The similarity of the UV absorption bands certified the structure of the photoproducts. The longest absorption band (367 nm) of **5** are red-shifted in comparison with that (363 nm) of the product **4**, which is due to the electron-donating effect of the methyl groups.

4-Chlorobenzil **3** was also irradiated in methanol to give the same type of photoproducts **6** in 32% yield, in which monochloro compound **6a** and dichlorocompound **6b** were obtained in the molar ratio of 1.0 : 1.0.¹⁹ The xanthone-like photoproduct was not found in the photoreaction of 4,4'-dimethoxybenzil, in which only methyl 4-methoxybenzoate was isolated.²⁰

Studies on the syntheses of asymmetric aromatic α -diketones, *i.e.*, Ar-COCO-Ar', are in progress to understand the exact mechanism and to extend the utility of these novel photochemical reactions.

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18. Spectral data of **5**: ¹H-NMR (CDCl_3), δ 2.51 (s, 3H, methyl), 2.58 (s, 3H, methyl), 2.78 (s, 3H, methyl), 7.18-8.49 (m, 8H, aromatic) and 10.0 ppm (d, 1H, $J=8$ Hz, aromatic, intramolecularly hydrogen-bonded); ¹³C-NMR (CDCl_3), δ 21.7 (methyl), 21.9 (methyl), 22.3 (methyl), 117.2, 122.2, 122.7, 123.9, 126.0, 126.4, 127.6, 128.8 and 129.0 (9 C's, with hydrogen atom), 112.1, 121.8, 122.0, 127.0, 127.4, 133.8, 135.0, 140.7, 144.8, 154.7, and 154.8 (11 C's, with no hydrogen atom), and 178.1 ppm (1C, carbonyl); UV (MeOH), λ_{max} 367, 331, 314, 296, 269 and 254 nm; Mass (EI), *m/e* 386 (M), 368 (M-CO).
19. Compounds, **6a** and **6b**, could not be separated, but were observed in the ratio of 1.0 : 1.0 in 400 MHz ¹H-NMR spectrum. ¹H-NMR (CDCl_3) of **6** (mixture of **6a** and **6b**), $\delta=10.19$ (d, 1H, $J=6.3$ Hz), 10.16 (d, 1H, $J=6.3$ Hz) and 8.82-7.50 ppm; Mass (EI), **6a**, *m/e* 330 (M), 332 (M+2), 302 (M-CO), 295 (M-Cl); **6b**, *m/e* 364 (M, 100%), 366 (M+2), 368 (M+4), 336 (M-CO), 329 (M-Cl), 294 (M-2 Cl), 266 (294-CO); UV (cyclohexane), λ_{max} 367, 348, 331, 312 and 298 nm.
20. Spectral data of methyl 4-methoxybenzoate: ¹H-NMR (CDCl_3), δ 3.86 (s, 3H, MeOAr), 3.88 (s, 3H, COOMe),

6.92 (d, 2H, aromatic, $J=9$ Hz) and 8.00 ppm (d, 2H, aromatic, $J=9$ Hz), Mass (EI), m/e 166 (M), 135 (M-OMe, 100%) and 107 (M-COOMe), IR (KBr), 1700 ($\nu_{C=O}$) and 846 cm^{-1} ($\delta_{\text{CH(OOP)}}$, aromatic).

Photochemistry of Anthrone and Its Derivatives

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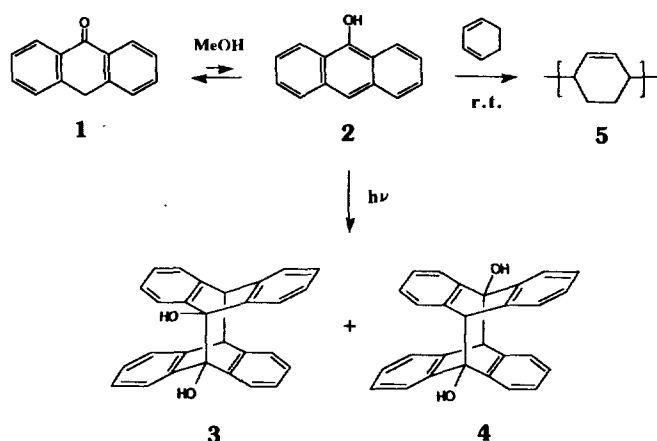
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There has been special interest in the energy-rich cyclodimers of aromatic hydrocarbons.¹⁻⁵ The synthesis of both the $4\pi_s + 4\pi_s$ and $4\pi_s + 2\pi_s$ adducts of arenes has allowed a study of orbital and state symmetry control in their thermal and photochemical cycloreversion.^{5,6} The photochemistry of anthracene derivatives had enriched organic photochemistry with some remarkable novel structures, namely 9,9'-didehydrodianthracene and 9,9',10,10'-tetrahydrodianthracene, etc.⁷⁻¹⁰ For some substituted anthracenes, the course of their intramolecular photolytic transformations is governed by the nature of the substituent and by their excited state interactions with the π system of anthrone. The photochemistry of 9-hydroxyanthracene (or anthranol **2**) is complicated not only because of the solvent-dependent ground-state equilibrium with anthrone **1**, but also by the facile formation of various autoxidation products.¹¹⁻¹³ Irradiation of anthranol **2** yielded $4\pi_s + 4\pi_s$ dimers, *i.e.*, head-to-head and head-to-tail dimers.¹⁴ Anthranol **2** can also be formed when anthrone **1** is dissolved in methanol.¹⁵ In that case, enol content (*i.e.*, % **2**) is about 11% in methanol solution at room temperature.

We describe here the $4\pi_s + 4\pi_s$ photodimers of 9-hydroxyanthracene derivatives using keto-enol tautomerization.¹⁶ Anthrone **1** is not fluorescent, on the other hand, when dissolved in methanol, strong fluorescence bands of anthranol **2** were observed at 433.3 nm and 452.5 nm at room temperature. The fluorescence was quenched by some olefins, such as 1,3-cyclopentadiene, furan and thiophene. When a solution of 150 mg (7.7×10^{-4} mole) of anthrone **1** and 10.0 mL (excess amount) of furan in 200 mL of dichloromethane was irradiated with 350 nm UV light, a dimer of anthrone, *i.e.*, 10,10'-bianthrone¹⁷ was obtained as the major product. When the irradiation was carried out in methanol, the $4\pi_s + 4\pi_s$ dimers (HH dimer **3** and HT dimer **4**) of anthranol and 1:1 adduct¹⁸ of anthrone and furan, as well as bianthrone, were found in good yields (26, 15 and 35%, respectively). The photoproducts were isolated by column chromatography on



Scheme 1.

silica gel (70-230 mesh) using *n*-hexane and ethyl acetate as the eluent. R_f values of **3** and **4** were 0.23 and 0.49, respectively, in *n*-hexane and ethyl acetate (4 : 1, v/v). Hydroxyl protons and benzylic protons of HH dimer (and HT dimer) were observed at 2.36 ppm (and 2.41 ppm) and 4.42 ppm (and 4.60 ppm) in ¹H-NMR spectrum (CDCl_3), respectively. The molecular ion peak was also found at m/e 388 in EI mass spectrum. It is interesting to note that anthranol is formed *via* keto-enol tautomerization of anthrone in methanol solution. In fact, simply mixing anthrone **1** and 1,3-cyclohexadiene in methanol gave rise to white precipitate at room temperature, which was identified as heptamer **5** of 1,3-cyclohexadiene.¹⁹ The formation of anthranol dimers, such as **3** and **4**, and heptamer **5** suggests that anthranol **2** is formed *via* keto-enol tautomerization, and also demonstrates that the protons produced during the tautomerization initiate the cationic polymerization reaction²⁰ of 1,3-cyclohexadiene to yield the heptamer **5**.

The irradiation (350 nm) of 100 mg of 10-nitroanthrone in 200 mL of dichloromethane gave only anthraquinone as the major product and 10,10'-bianthrone¹⁷. When the irradiation was carried out in methanol with visible light, the major product produced was 10,10'-bianthrone. As the nitro group was actually labile during the photoreaction, *i.e.*, photochemically unstable, visible light was used instead of UV light source. The $4\pi_s + 4\pi_s$ dimer was not found in the reason of the photochemically unstable property.

When the irradiation of 1,8-dihydroxyanthrone (or dithranol or anthralin) was carried out in methanol, all the starting material was consumed. But only an unidentified compound was obtained in which benzylic protons were disappeared in ¹H-NMR spectrum (CDCl_3). Irradiation of anthralin in dichloromethane gave bianthralin.²¹

In contrast to blue fluorescence of anthranol, very weak fluorescence emission bands of anthralin were observed at 497.5 nm, 525.0 nm and 565.0 nm in methanol. The ratio of fluorescence intensity, *i.e.*, $I_f(\text{anthranol})/I_f(\text{anthralin})$, was 13.6.²² 10-Nitroanthrone was not fluorescent in the same experimental condition.

While the $4\pi_s + 4\pi_s$ dimers could not be isolated from 10-nitroanthrone and anthralin at room temperature, the participation of enol form of anthrone **1** in the photoreaction could be used to the synthesis and application of highly unstable compounds such as 9,9',10,10'-tetrahydrodianthracene and