

Novel Photochemical Reactions of Benzil

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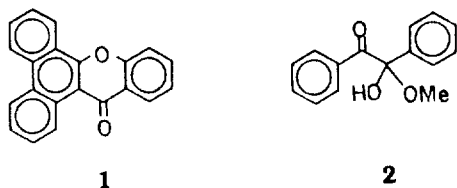
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The photochemistry of α -diketones has been the subject of interest for about a century. It has been known that photoirradiation of benzil in solution produces a variety of reaction products, i.e., benzaldehyde, benzoic acid, benzoin, benzil pinacol, benzoin benzoate, and α, α' -dihydroxystilbene.¹⁻⁷

We now report that irradiation of benzil ($\lambda_{max} = 370$ nm) in methanol gave the unexpected photoproduct **1** as the major product, not α -hydroxyketone **2**.⁸⁻¹⁰

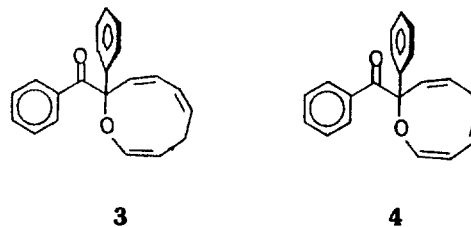
A solution of benzil in methanol was irradiated with 350 nm UV light under nitrogen gas for 28 h to obtain a solid product.



The infrared spectrum showed $\nu_{C=O}$ at 1648 cm^{-1} (1670 cm^{-1} for benzil), ν_{C-O} at 1243 cm^{-1} , and ν_{C-H} (aromatic) at $3070\text{--}3020\text{ cm}^{-1}$. The stretching and bending vibrations for the methyl group were not observed. ¹H-NMR spectrum (CDCl_3) showed phenyl protons at $\delta 8.68\text{--}8.35$ ppm (4H, m) and $\delta 7.80\text{--}7.30$ ppm (8H, m). The molecular ion peak (m/e 296, $\text{C}_{21}\text{H}_{12}\text{O}_2$, base peak) was observed in the mass spectrum (EI method), which may be due to the rigid cyclic structure of the product **1**. A peak at m/e 176 is good diagnostic peak for phenanthrene moiety. The M-CO peak was also observed at m/e 268 (relative abundance 18.6). The new absorption bands observed at 363, 346, 330, 317, 300, and 277 nm are due to the phenanthrene moiety. The product **1** was not obtained in benzene or dichloromethane. This reaction can be explained on the basis of a mechanism involving the formation of biradical, α -cleavage of diketone, and hydrogen atom abstraction from solvent.⁸ Cyclization prior to the formation of biradical can not be excluded in this reaction.

Irradiation of a solution of benzil and cycloheptatriene in dichloromethane for 25 h gave a photoadduct **3** via (2+2)-cycloaddition as follow.

The adduct was isolated by the column chromatography (silica gel) using chloroform as an eluting solvent ($R_f = 0.59$, TLC solvent; CHCl_3). The structure for the adduct **3** is supported by the spectroscopic data. An alternative structure **4** has



been ruled out by means of the ¹H-NMR spectrum. The methylene protons were observed at $\delta 2.72$ ppm ($\delta 2.25$ ppm for cycloheptatriene). The infrared spectrum showed $\nu_{C=O}$ (1680 cm^{-1}), ν_{C-O} (1250 cm^{-1}), δ_{C-H} (1450 cm^{-1} , methylene group), and ν_{C-H} (aromatic and aliphatic, ca. 3000 cm^{-1}). The ¹H-NMR spectrum (CDCl_3) showed methylene protons ($\delta 2.72$ ppm, 2H, m), vinyl protons ($\delta 6.78\text{--}5.25$ ppm, 6H, m), and phenyl protons ($\delta 8.13\text{--}7.25$ ppm, 10H, m). The mass spectrum (EI method) showed m/e 77 (C_6H_5 , phenyl group), 105 ($\text{C}_6\text{H}_5\text{CO}$, base peak), and 197 ($\text{M-C}_6\text{H}_5\text{CO}$, $\text{C}_{14}\text{H}_{13}\text{O}$).

Studies on the mechanism and scope of the reaction are in progress.

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