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Photochemical Reaction of 2,4-Dimethyl-1-phenylpentane-1,3-dione in the Presence of Oxygen. Formation of Furan-3(2*H*)-one and Peroxide

Michikazu Yoshioka,*a Masashi Oka,a Yuko Ishikawa,a Hideo Tomita,a and Tadashi Hasegawa*b

^a Department of Chemistry, Saitama University, Shimo-okubo, Urawa, Saitama 338, Japan

^b Department of Chemistry, Tokyo Gakugei University, Nukuikitamachi, Koganei, Tokyo 184, Japan

Photolysis of 2,4-dimethyl-1-phenylpentane-1,3-dione (1) in the presence of oxygen gave 2,2,4-trimethyl-5-phenylfuran-3(2*H*)-one (2) and 6-hydroxy-3,3,5-trimethyl-6-phenyl-1,2-dioxan-4-one (3) *via* the interaction of the type II biradical with oxygen.

The effect of oxygen on type II photoprocesses has received considerable attention.^{1,2} It is known that oxygen serves not only as the quencher of carbonyl triplets³ but also as a scavenger of the biradicals¹ generated in the type II reaction. The interaction of the biradicals with oxygen gives an intermediate complex which decays giving type II products

with regeneration of oxygen or cyclizes to yield a hydroperoxide.¹ We have previously reported that the photolysis of 1-phenylpentane-1,3-diones under nitrogen gave type II cyclization products from their triplet states.⁴ We now report the photoreaction of 1,3-diketone (1) in the presence of oxygen to yield the furan-3(2*H*)-one (2) and the peroxide (3).



Irradiation of 2,4-dimethyl-1-phenylpentane-1,3-dione (1) in acetonitrile under oxygen gave 2,2,4-trimethyl-5phenylfuran-3(2H)-one (**2**) (m.p. 59—60 °C. 34%). 6-hydroxy-3,3,5-trimethyl-6-phenyl-1,2-dioxan-4-one (3)(m.p. 95–96 °C, 7%), and benzoic acid (15%). Irradiation of (1) in pentane under the same conditions gave (2), (3), and benzoic acid in 31, 28, and 9% yields, respectively. Irradiation of 4-methyl-1-phenylpentane-1,3-dione which exists in the enol form in solution resulted in no reaction in the absence or presence of oxygen. The structures of (2) and (3) were assigned from their analytical and spectral data and chemical evidence. The u.v. spectrum of (2) $[\lambda_{max}]$ (EtOH) 242 and 304 nm (log ε 4.06 and 4.27)] closely resembled that of bullatenone [2,2-dimethyl-5-phenylfuran-3(2H)-one],⁵ suggesting a conjugated structure of (2) analogous to that of bullatenone. The

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compound (3) gave a positive peroxide test (starch-iodine). Deoxygenation of (3) by triphenylphosphine gave 5-hydroxy-2,2,4-trimethyl-5-phenyloxolan-3-one (4) which was easily dehydrated to give (2) on brief heating or by treatment with acid. The structure of (4) was based on its i.r. and n.m.r. spectra. The i.r. spectrum showed a five-peak carbonyl band at 1775 cm⁻¹. The peroxide (3) was stable at room temperature but decomposed at 150 °C to yield benzoic acid and (2) in 47 and 17% yields, respectively. The peroxide (3) was photolabile to yield benzoic acid upon irradiation.

The formation of (2) and (3) is reasonably explained in terms of the interaction of the biradical generated in the type II reaction with oxygen to give an intermediate complex which may be transformed into (2) probably *via* (4) or may close the ring to (3).

Scaiano reported that about 75% of the complexes resulting from the interaction between the biradicals from phenyl alkyl ketones and oxygen decayed giving type II products with regeneration of oxygen, while the other 25% yielded a hydroperoxide.¹ We could not detect any type II products in the present work; the complex resulting from the interaction between the biradical from (1) and oxygen seemed to give (2) and (3) in its main decay path. It is well-known that dienes react with singlet oxygen to yield 1,4-peroxides. The formation of (3) by the reaction of the dienol form of (1) with singlet oxygen was unlikely because irradiation of an oxygenated solution of (1) in methanol in the presence of dye (Rose Bengal or Methylene Blue) resulted in no reaction.

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