

Photoreaction of 1-Aryl 1,3-Diketones. Trapping Reaction of the Biradicals Generated in the Type II Reaction with Oxygen

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The biradicals generated in the type II photoreaction of 1-aryl-2,4-dimethylpentane-1,3-diones (**1**) were trapped by oxygen to form biradical-oxygen complexes. In acetonitrile, pentane, or benzene, 5-aryl-2,2,4-trimethylfuran-3(2*H*)-ones (**2**), 6-aryl-6-hydroxy-3,3,4-trimethyl-1,2-dioxan-4-ones (**3**), and arene carboxylic acids (**4**) were produced *via* the biradical-oxygen complexes, whereas in alcoholic solvents, 4-aryl-4-hydroxy-3,5,5-trimethyl-4,5-dihydrofuran-2(3*H*)-ones (**5**) were produced in addition to (**2**), (**3**), and (**4**).

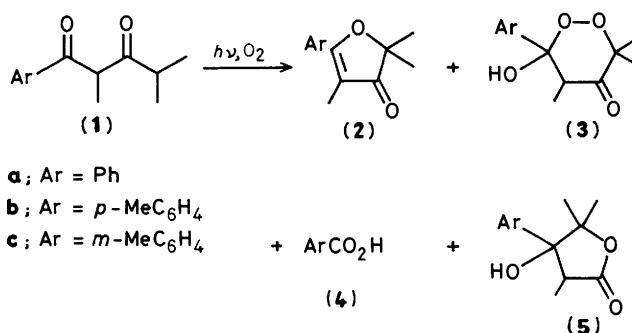
The behaviour of the 1,4-biradicals involved in type II photoreactions of ketones has received much attention.¹ Successful trapping of these biradicals by thiols,² hydrogen bromide,³ di-*n*-butyl selenoketone,⁴ hydrogen selenide,⁵ and several oxidants⁶ has been reported. It is known that oxygen serves not only as a quencher of ketone triplets⁷ but also as a scavenger of the biradicals generated in the type II reaction.⁸ The rate of quenching of ketone triplets with oxygen is reported to be $\sim 4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.^{8b} This rate is somewhat slower than the diffusion rate, and so the interaction of oxygen with very short lived ketone triplets is insignificant for the wide range of oxygen concentrations in solution. The ketones with short lived triplet states undergo type II photoreaction even in the presence of oxygen to produce 1,4-biradicals which may react with oxygen.⁸

We have recently reported that 1-aryl 1,3-diketones bearing a weak $\gamma\text{C-H}$ bond undergo type II cyclization from their triplet states to give 3-hydroxycyclobutanones.⁹ We now report the photoreaction of 1-aryl-2,4-dimethylpentane-1,3-diones (**1**) in the presence of oxygen to give furan-3(2*H*)-ones (**2**), peroxides (**3**), and tetrahydrofuran-2-ones (**5**) through type II photoreaction and subsequent trapping of the resulting biradicals with oxygen.

Results and Discussion

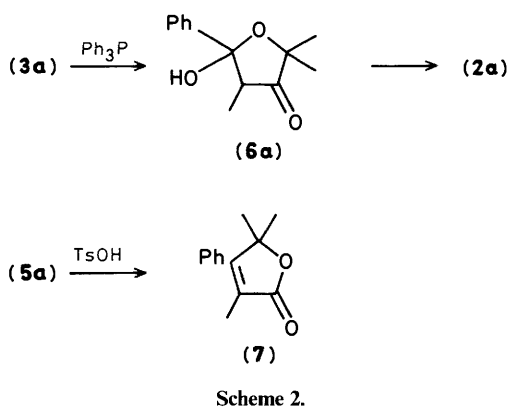
Irradiation of 2,4-dimethyl-1-phenylpentane-1,3-dione (**1a**) with a high-pressure mercury lamp with a Pyrex filter in acetonitrile under bubbling air gave 2,2,4-trimethyl-5-phenylfuran-3(2*H*)-one (**2a**) and benzoic acid (**4a**).¹⁰ Irradiation of (**1a**) in pentane under the same conditions gave 6-hydroxy-3,3,5-trimethyl-6-phenyl-1,2-dioxan-4-one (**3a**) in addition to the furanone (**2a**) and benzoic acid (**4a**). In methanol or propan-2-ol under the same conditions, (**1a**) underwent unexpected photochemical reaction giving 4-hydroxy-3,5,5-trimethyl-4-phenyl-4,5-dihydrofuran-2(3*H*)-one (**5a**), the product arising from an insertion of an oxygen atom in the C³-C⁴ bond of (**1a**), along with (**2a**), (**3a**), and (**4a**) (Scheme 1).

The structures of products (**2a**), (**3a**), and (**5a**) were assigned from their analytical and spectral data and chemical evidence. The u.v. spectrum of (**2a**) showed maxima at 242 and 304 nm (ϵ 11 400 and 18 700). The spectrum closely resembled that of bullatenone [2,2-dimethyl-5-phenylfuran-3(2*H*)-one],¹¹ suggesting a conjugated structure for compound (**2a**) analogous to that of bullatenone. In the i.r. spectrum, the carbonyl absorption for (**2a**) appeared at the same wavenumber as that of bullatenone (1700 cm^{-1}).^{11b} The ¹H n.m.r. spectrum of (**2a**)



Scheme 1.

showed a singlet due to two methyl groups on C-2 at δ 1.43 and a singlet due to the allylic methyl group at δ 1.97. Compound (**3a**) gave a positive peroxide test (starch-iodine). The i.r. spectrum of (**3a**) in chloroform showed hydroxy (3580 cm^{-1}) and carbonyl (1735 cm^{-1}) absorptions. The n.m.r. spectrum of (**3a**) showed two singlets due to C-3 methyl groups at δ 1.32 and 1.70, and a doublet due to a C-5 methyl group at δ 0.68. These spectral data indicate that compound (**3a**) is a single stereoisomer, but its configuration could not be assigned on the basis of these data. Deoxygenation of (**3a**) by triphenylphosphine gave 5-hydroxy-2,2,4-trimethyl-5-phenyl-4,5-dihydrofuran-3(2*H*)-one (**6a**) which was easily dehydrated to give (**2a**) on brief heating or by treatment with acid. Compound (**6a**) showed five-membered carbonyl (1775 cm^{-1}) and hydroxy (3600 cm^{-1}) absorptions in its i.r. spectrum. The peroxide (**3a**) was stable at room temperature but decomposed at 150°C to yield benzoic acid and (**2a**) in 47 and 17% yield, respectively. Peroxide (**3a**) was photolabile to yield benzoic acid upon irradiation. The formation of benzoic acid (**4a**) from (**1a**), therefore, can be explained in terms of the secondary photoreaction of (**3a**). The ¹³C n.m.r. spectrum of compound (**5a**) showed a singlet at δ 176.8 assignable to the lactone carbonyl carbon. The hydroxy and lactone carbonyl absorptions in the i.r. spectrum of (**5a**) appeared at 3600 and 1770 cm^{-1} , respectively. The ¹H n.m.r. spectrum of (**5a**) showed two singlets due to two methyl groups on C-5 at δ 1.02 and 1.53, and a doublet due to the methyl group on C-3 at δ 1.20. These data indicate that compound (**5a**) is one of the two stereoisomers with respect to substituents on C-3 and C-4, but its configuration could not be assigned. Compound (**5a**) was dehydrated to give 3,5,5-trimethyl-4-phenylfuran-2(5*H*)-one (**7**) by refluxing in benzene in the presence of toluene-*p*-sulphonic acid (PTSA) (Scheme 2). Compound (**7**) showed a singlet due to two methyl groups on



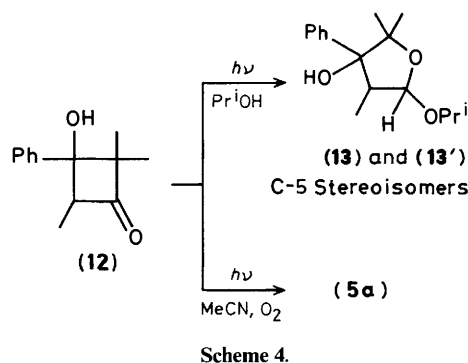
C-5 at δ 1.50 and a singlet due to the allylic methyl group on C-3 at δ 1.78 in its n.m.r. spectrum.

The 2,4-dimethyl-1-tolylpentane-1,3-diones (**1b**) and (**1c**) were irradiated under the same conditions as was (**1a**). In acetonitrile, pentane, or benzene furan-3(2*H*)-ones (**2b**) and (**2c**), peroxides (**3b**) and (**3c**), and toluic acids (**4b**) and (**4c**) were produced. However, in propan-2-ol, tetrahydrofuran-2-ones (**5b**) and (**5c**) were produced along with furan-3(2*H*)-ones, peroxides, and toluic acids. The structures of these photo-products were unambiguously established by the comparison of their spectral data with those of (**2a**), (**3a**), and (**5a**).

The formation of products (**2**) and (**3**) can be rationalized in terms of hydrogen abstraction by the aryl carbonyl from the isopropyl group and subsequent reaction of the resulting biradical (**8**) with oxygen to give an intermediate complex (**9**) which is analogous to that assumed in reactions between type II biradicals from phenyl alkyl ketones and ground-state oxygen.^{8b} The biradical-oxygen complex (**9**) may produce the hydroperoxide (**10**). The complex (**9**) and/or the hydroperoxide (**10**) may be transformed into (**2**) probably *via* (**6**). Compound (**3**) may be formed by ring closure of the complex (**9**) (Scheme 3). Similar peroxide formation from the type II biradical-oxygen complex was reported in the photo-oxygenation of 2,4,6-trisopropylbenzophenone.¹²

Compounds (**5**) were produced only in alcoholic solvents and their formation is of interest. It has been reported that photolysis of cyclobutanones in the presence of oxygen yields tetrahydrofuran-2-ones *via* type I cleavage followed by rearrangement to oxacarbene.¹³ Similar photo-oxygenation of 3-aryl-3-hydroxy-2,2,4-trimethylcyclobutanones which arise from the type II cyclization of (**1**) may explain the formation of compounds (**5**). However, irradiation of 3-hydroxy-2,2,4-

trimethyl-3-phenylcyclobutanone (**12**)^{9a} in propan-2-ol in the presence of oxygen gave compounds (**13**) and (**13'**), the adducts of propan-2-ol with the oxacarbene generated through C¹-C² bond fission. No trace of compound (**5a**) was detected. On the other hand, irradiation of compound (**12**) in acetonitrile in the presence of oxygen gave (**5a**), whereas that of (**1a**) under the same conditions did not give compound (**5a**) (Scheme 4).



Therefore, compound (**12**) should not be the intermediate for the formation of compounds (**5**). Since tetrahydrofuran-3-ones have been reported to undergo type I cleavage¹⁴ and since compound (**5a**) is a skeletal isomer of 5-hydroxy-2,2,4-trimethyl-5-phenyl-4,5-dihydrofuran-3(2*H*)-one (**6a**), the photochemical transformation of (**6a**) to (**5a**) was examined. However, irradiation of (**6a**) in propan-2-ol in the presence or absence of oxygen gave no trace of (**5a**). Although we have no confirmatory evidence, the formation of compounds (**5**) is tentatively explained as follows; the biradical-oxygen complex (**9**) and/or the hydroperoxide (**10**) may be transformed into the epoxy *O*-radical (**11**), which would give (**5**) by rearrangement with C-C bond fission of the epoxide ring followed by hydrogen capture from the solvent. Rearrangement of the similar epoxy *O*-radical with C-C bond fission has been reported in the photochemical transformation of 3,4-diphenyl-4,5-epoxycyclopent-2-en-1-one to 4,5-diphenyl-2-pyrone.¹⁵

Experimental

M.p.s and b.p.s are uncorrected. M.p.s were measured with a Mitamura 7-20 apparatus and b.p.s were measured with a Büchi Kugelrohr KR apparatus. U.v. spectra were recorded on a Hitachi 340 spectrometer and i.r. spectra on a Hitachi 270-50 spectrometer. ¹H N.m.r. spectra were obtained with a JEOL PMX-60, a JEOL FX-90Q, or a Bruker AM 400 spectrometer

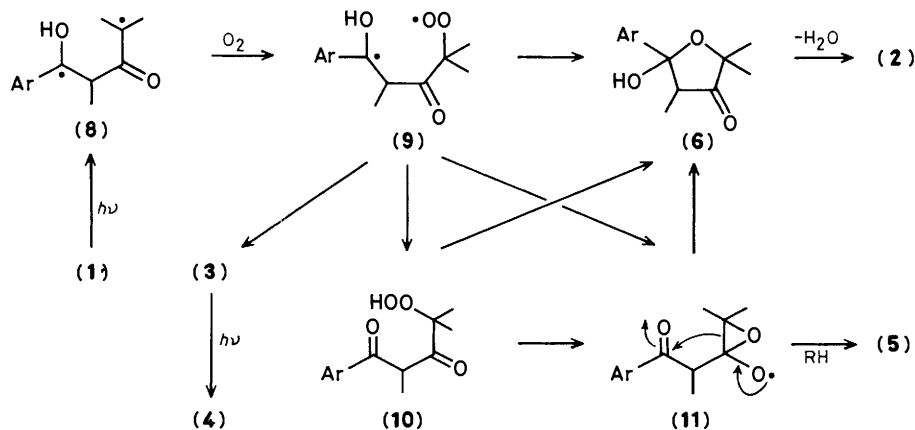


Table. Photolysis of (1) in various solvents

Solvent	Diketone	Con- version (%) ^a	Product distribution (%) ^b			
			(2)	(3) ^c	(4)	(5) ^c
MeCN	(1a)	73	34		15	
MeCN	(1b)	40	13		Trace	
MeCN	(1c)	57	28		7	
Pentane	(1a)	92	31	28	9	
Pentane	(1b)	69	10	6	28	
Pentane	(1c)	75	32	5	15	
Benzene	(1b)	60	22	9	15	
Benzene	(1c)	60	Trace	13	10	
Pr ⁱ OH	(1a)	85	3	15	10	13
Pr ⁱ OH	(1b)	42	6	2	20	9
Pr ⁱ OH	(1c)	38		4	12	7
MeOH	(1a)	75	15	10	12	7

^a Percentage of the unchanged starting material was determined by ¹H n.m.r. spectroscopy. ^b Yields are based on converted starting material, and were determined after chromatography on SiO₂ by ¹H n.m.r. spectroscopy of the fractions. ^c Only a single stereoisomer was isolated.

using tetramethylsilane as internal standard. ¹³C N.m.r. spectra were measured on a JEOL FX-90Q spectrometer with CDCl₃ as solvent. Mass spectra were obtained with a JEOL JMS-01SG-2 spectrometer. G.l.c. was carried out on a JEOL JGC-20K instrument (flame ionization detector) and the column used was 1 m × 4 mm of 10% SE-30 on Chromosorb W. Column chromatography was performed with Merck Kieselgel 60. An Ushio 100 W high-pressure mercury lamp was used as the irradiation source.

Starting Materials.—Phenyl 1,3-diketone (1a)¹⁶ was prepared from propiophenone and isobutyraldehyde according to the method reported in the literature, and *p*-tolyl 1,3-diketone (1b) was prepared from *p*-methylpropiophenone and isobutyraldehyde by the same procedure. *m*-Tolyl 1,3-diketone (1c) was prepared by the reaction of *m*-toluoyl chloride and 3-methylbutan-2-one in the presence of sodium amide,¹⁷ followed by methylation.

2,4-Dimethyl-1-phenylpentane-1,3-dione (1a). B.p. 105–107 °C at 0.7 mmHg; ν_{\max} (CHCl₃) 1 720 (saturated ketone) and 1 680 cm⁻¹ (phenyl ketone); δ_{H} (90 MHz; CDCl₃) 1.01 and 1.08 (6 H, 2 d, *J* 6.9 Hz, CHMe₂), 1.43 (3 H, d, *J* 7.2 Hz, CHMe), 2.75 (1 H, sep, *J* 6.9 Hz, CHMe₂), 4.60 (1 H, q, *J* 7.2 Hz, CHMe), 7.30–7.60 (3 H, m, Ph), and 7.80–8.00 (2 H, m, Ph).

2,4-Dimethyl-1-(*p*-tolyl)pentane-1,3-dione (1b). B.p. 117 °C at 0.7 mmHg; ν_{\max} (CCl₄) 1 730 (saturated ketone) and 1 680 cm⁻¹ (aryl ketone); δ_{H} (60 MHz; CCl₄) 0.90 and 1.02 (6 H, 2 d, *J* 7.0 Hz, CHMe₂), 1.33 (3 H, d, *J* 7.0 Hz, CHMe), 2.40 (3 H, s, ArMe), 2.67 (1 H, sep, *J* 7.0 Hz, CHMe₂), 4.35 (1 H, q, *J* 7.0 Hz, CHMe), 7.16 (2 H, d, *J* 8.0 Hz, ArH), and 7.76 (2 H, d, *J* 8.0 Hz, ArH).

2,4-Dimethyl-1-(*m*-tolyl)pentane-1,3-dione (1c). B.p. 115 °C at 0.5 mmHg; ν_{\max} (CCl₄) 1 730 (saturated ketone) and 1 680 cm⁻¹ (aryl ketone); δ_{H} (60 MHz; CCl₄) 0.95 and 1.02 (6 H, 2 d, *J* 6.8 Hz, CHMe₂), 1.38 (3 H, d, *J* 7.0 Hz, CHMe), 2.43 (3 H, s, ArMe), 2.67 (1 H, sep, *J* 6.8 Hz, CHMe₂), 4.40 (1 H, q, *J* 7.0 Hz, CHMe), 7.17–7.43 (2 H, m, ArH), and 7.50–7.83 (2 H, m, ArH).

General Procedure for Photo-oxygenation of Aryl 1,3-Diketones (1a–c).—A solution of the aryl 1,3-diketone (1) (1.2 g) in a variety of solvents (120 ml) was irradiated under bubbling air through a Pyrex filter for 4 h. The photoproducts were isolated

by column chromatography with hexane–ethyl acetate (4:1) or hexane–ether (3:1) as eluant. Yields are given in the Table.

2,2,4-Trimethyl-5-phenylfuran-3(2H)-one (2a). M.p. 59–60 °C (from pentane) (Found: C, 77.2; H, 7.1. C₁₃H₁₄O₂ requires C, 77.20; H, 6.98%); λ_{\max} (EtOH) 242 (ϵ 11 400 dm³ mol⁻¹ cm⁻¹) and 304 nm (18 700); ν_{\max} (CCl₄) 1 700 (C=O) and 1 625 cm⁻¹ (C=C); δ_{H} (90 MHz; CDCl₃) 1.43 (6 H, s, 2 × Me), 1.97 (3 H, s, Me), 7.35–7.50 (3 H, m, Ph), and 7.68–7.88 (2 H, m, Ph); δ_{C} (CDCl₃) 7.2 (q, Me), 23.1 (q, Me), 85.6 (s, C-2), 108.0 and 177.3 (2 s, C-4 and -5), 127.7 (d), 128.5 (d), 130.8 (s), and 131.1 (d) (ArC), and 207.6 (s, C=O); *m/z* 202 (*M*⁺) and 116 (100%).

2,2,4-Trimethyl-5-(*p*-tolyl)furan-3(2H)-one (2b). B.p. 100 °C at 0.5 mmHg (Found: C, 77.45; H, 7.4. C₁₄H₁₆O₂ requires C, 77.75; H, 7.46%); ν_{\max} (CCl₄) 1 700 (C=O) and 1 620 cm⁻¹ (C=C); δ_{H} (60 MHz; CCl₄) 1.40 (6 H, s, 2 × Me), 1.92 (3 H, s, 4-Me), 2.41 (3 H, s, ArMe), 7.20 (2 H, d, *J* 8.0 Hz, ArH), and 7.65 (2 H, d, *J* 8.0 Hz, ArH); δ_{C} (CDCl₃) 7.3 (q, Me), 21.5 (q, Me), 23.2 (q, Me), 85.7 (s, C-2), 107.4 and 177.9 (2 s, C-4 and -5), 127.8 (d + s), 129.3 (d), and 141.9 (s) (ArC), and 208.0 (s, C=O).

2,2,4-Trimethyl-5-(*m*-tolyl)furan-3(2H)-one (2c). M.p. 55 °C (Found: C, 77.4; H, 7.5%); ν_{\max} (CCl₄) 1 705 (C=O) and 1 630 cm⁻¹ (C=C); δ_{H} (60 MHz; CCl₄) 1.40 (6 H, s, 2 × Me), 1.95 (3 H, s, 4-Me), 2.47 (3 H, s, ArMe), 7.18–7.37 (2 H, m, ArH), and 7.40–7.73 (2 H, m, ArH); δ_{C} (CDCl₃) 7.3 (q, Me), 21.3 (q, Me), 23.1 (q, Me), 85.6 (s, C-2), 107.8 and 177.8 (2 s, C-4 and -5), 125.0 (d), 128.0 (d), 128.4 (d), 130.5 (s), 132.0 (d), and 138.3 (s) (ArC), and 207.9 (s, C=O).

6-Hydroxy-3,3,5-trimethyl-6-phenyl-1,2-dioxan-4-one (3a). M.p. 95–96 °C (from hexane–benzene) (Found: C, 66.1; H, 6.8. C₁₃H₁₆O₄ requires C, 66.09; H, 6.83%); ν_{\max} (CHCl₃) 3 580 (OH) and 1 735 cm⁻¹ (C=O); δ_{H} (90 MHz; CDCl₃) 0.68 (3 H, d, *J* 7.0 Hz, 5-Me), 1.32 and 1.70 (6 H, 2 s, 2 × Me), 3.56 (1 H, q, *J* 7.0 Hz, 5-H), 3.64 (1 H, s, OH), and 7.10–7.40 (5 H, m, Ph); δ_{C} (CDCl₃) 9.0, 21.4, and 21.8 (3 q, 3 × Me), 47.8 (d, C-5), 89.9 and 108.3 (2 s, C-3 and -6), 126.5 (d), 128.3 (d), 129.3 (d), and 136.6 (s, ArC), and 212.5 (s, C=O); *m/z* 236 (*M*⁺), 204 (*M*⁺ – 32), and 134 (*M*⁺ – 102, 100%).

6-Hydroxy-3,3,5-trimethyl-6-(*p*-tolyl)-1,2-dioxan-4-one (3b). * ν_{\max} (CHCl₃) 3 600 and 3 450br (OH), and 1 750 cm⁻¹ (C=O); δ_{H} (60 MHz; CDCl₃) 0.67 (3 H, d, *J* 7.0 Hz, 5-Me), 1.30, 1.65, and 2.30 (9 H, 3 s, 3 × Me), 3.55 (1 H, q, *J* 7.0 Hz, 5-H), 3.80 (1 H, s, OH), 7.13 (2 H, d, *J* 9 Hz, ArH), and 7.40 (2 H, d, *J* 9 Hz, ArH); δ_{C} (CDCl₃) 9.2, 21.2, 21.4, and 21.8 (4 q, 4 × Me), 47.6 (d, C-5), 89.8 and 108.4 (2 s, C-3 and -6), 126.4 (d), 129.1 (d), 133.7 (s), and 139.4 (s) (ArC), and 212.7 (s, C=O).

6-Hydroxy-3,3,5-trimethyl-6-(*m*-tolyl)-1,2-dioxan-4-one (3c). M.p. 97–98 °C (from hexane–benzene) (Found: C, 67.25; H, 7.2. C₁₄H₁₈O₄ requires C, 67.18; H, 7.25%); ν_{\max} (CHCl₃) 3 600 and 3 450br (OH), and 1 750 cm⁻¹ (C=O); δ_{H} (90 MHz; CDCl₃) 0.68 (3 H, d, *J* 7.0 Hz, 5-Me), 1.30, 1.68, and 2.30 (9 H, 3 s, 3 × Me), 3.52 (1 H, q, *J* 7.0 Hz, 5-H), 3.83 (1 H, s, OH), and 6.88–7.24 (4 H, m, ArH); δ_{C} (CDCl₃) 9.2, 21.4, 21.5, and 21.8 (4 q, 4 × Me), 47.6 (d, C-5), 90.0 and 108.3 (2 s, C-3 and -6), 123.6 (d), 127.0 (d), 128.3 (d), 130.1 (d), 136.5 (s), and 138.2 (s) (ArC), and 212.7 (s, C=O).

4-Hydroxy-3,5,5-trimethyl-4-phenyl-4,5-dihydrofuran-2(3H)-one (5a). M.p. 140–141 °C (from hexane–benzene) (Found: C, 70.9; H, 7.3. C₁₃H₁₆O₃ requires C, 70.89; H, 7.32%); ν_{\max} (CHCl₃) 3 600 and 3 450br (OH), and 1 770 cm⁻¹ (γ -lactone); δ_{H} (90 MHz; CDCl₃) 1.02 and 1.53 (6 H, 2 s, 2 × Me), 1.20 (3 H, d, *J* 7.2 Hz, 3-Me), 2.14 (1 H, s, OH), 3.58 (1 H, q, *J* 7.2 Hz, 3-H), and 7.26–7.52 (5 H, m, Ph); δ_{C} (CDCl₃) 7.2, 20.0, and 25.0 (3 q, 3 × Me), 42.1 (d, C-3), 83.0 and 88.4 (2 s, C-4 and -5), 126.2 (d), 128.3 (d), 128.6 (d), and 138.3 (s) (ArC), and 176.8 (s, C=O); *m/z* 220 (*M*⁺) and 134 (*M*⁺ – 86, 100%).

4-Hydroxy-3,5,5-trimethyl-4-(*p*-tolyl)-4,5-dihydrofuran-2(3H)-one (5b). M.p. 150–151 °C (from hexane–benzene) (Found: C, 71.5; H, 7.65. C₁₄H₁₈O₃ requires C, 71.77; H, 7.74%);

* Compound (3b) could not be obtained crystalline and its complete purification could not be achieved.

$\nu_{\max}(\text{CHCl}_3)$ 3 620 and 3 450br (OH), and 1 780 cm^{-1} (γ -lactone); $\delta_{\text{H}}(90 \text{ MHz}; \text{CDCl}_3)$ 1.00, 1.52, and 2.35 (9 H, 3 s, 3 \times Me), 1.20 (3 H, d, J 7.0 Hz, 3-Me), 2.08 (1 H, s, OH), 3.54 (1 H, q, J 7.0 Hz, 3-H), 7.23 (2 H, d, J 8.0 Hz, ArH), and 7.34 (2 H, d, J 8.0 Hz, ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ 7.4, 20.0, 21.1, and 25.2 (4 q, 4 \times Me), 42.2 (d, C-3), 83.1 and 88.4 (2 s, C-4 and -5), 126.1 (d), 129.6 (d), 135.3 (s), and 138.6 (s) (ArC), and 176.7 (s, C=O).

4-Hydroxy-3,5,5-trimethyl-4-(m-tolyl)-4,5-dihydrofuran-2(3H)-one (5c). M.p. 147 °C (from hexane-benzene) (Found: C, 71.7; H, 7.6%); $\nu_{\max}(\text{CHCl}_3)$ 3 620 and 3 500br (OH), and 1 780 cm^{-1} (γ -lactone); $\delta_{\text{H}}(90 \text{ MHz}; \text{CDCl}_3)$ 1.03, 1.55, and 2.40 (9 H, 3 s, 3 \times Me), 1.22 (3 H, d, J 7.0 Hz, 3-Me), 2.06 (1 H, s, OH), 3.57 (1 H, q, J 7.0 Hz, 3-H), and 7.12–7.32 (4 H, m, ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ 7.4, 20.0, 21.6, and 25.2 (4 q, 4 \times Me), 42.2 (d, C-3), 83.1 and 88.3 (2 s, C-4 and -5), 123.2 (d), 126.8 (d), 128.7 (d), 129.4 (d), 138.2 (s), and 138.6 (s) (ArC), and 176.6 (s, C=O).

Deoxygenation of the Peroxide (3a).—A solution of the peroxide (3a) (107 mg, 0.45 mmol) and triphenylphosphine (120 mg, 0.46 mmol) in benzene (4 ml) was stirred at room temperature for 3 h. The solvent was removed under reduced pressure, and chromatography [hexane-ethyl acetate (2:1)] of the residue yielded compounds (6a) (57 mg, 57%) and (2a) (19 mg, 20%). Compound (6a) was dehydrated by heating at 100 °C or by treatment with PTSA in benzene at room temperature to form compound (2a).

5-Hydroxy-2,2,4-trimethyl-5-phenyl-4,5-dihydrofuran-3(2H)-one (6a). M.p. 67 °C (from hexane) (Found: C, 70.9; H, 7.4. $\text{C}_{13}\text{H}_{16}\text{O}_3$ requires C, 70.89; H, 7.32%); $\nu_{\max}(\text{CCl}_4)$ 3 600 and 3 450br (OH), and 1 775 cm^{-1} (γ -lactone); $\delta_{\text{H}}(90 \text{ MHz}; \text{CDCl}_3)$ 1.10 (3 H, d, J 7.2 Hz, 4-Me), 1.42 and 1.45 (6 H, 2 s, 2 \times Me), 2.56 (1 H, qd, J 7.2 and 2.0 Hz, 4-H), 2.80 (1 H, d, J 2.0 Hz, OH), 7.24–7.40 (3 H, m, Ph), and 7.40–7.60 (2 H, m, Ph); $\delta_{\text{C}}(\text{CDCl}_3)$ 6.9 (q, Me), 26.0 (q, Me), 52.6 (d, C-4), 80.9 and 103.1 (2 s, C-2 and -5), 125.4 (d), 128.4 (d), 128.6 (d), and 142.8 (s) (ArC), and 217.1 (s, C=O).

Dehydration of the Tetrahydrofuran-2-one (5a).—A solution of the tetrahydrofuran-2-one (5a) (57 mg, 0.26 mmol) and PTSA (17 mg) in dry benzene (3 ml) was heated under reflux for 40 h. The mixture was washed with water and worked up. Chromatography of the mixture with hexane-ethyl acetate (4:1) as eluant gave 3,5,5-trimethyl-4-phenylfuran-2(5H)-one (7) (36 mg, 70%), m.p. 99–100 °C (from hexane-ether) (Found: C, 77.2; H, 6.9. $\text{C}_{13}\text{H}_{14}\text{O}_2$ requires C, 77.20; H, 6.98%); $\lambda_{\max}(\text{EtOH})$ 244 nm (ϵ 8 300 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$); $\nu_{\max}(\text{CCl}_4)$ 1 765 cm^{-1} (C=O); $\delta_{\text{H}}(90 \text{ MHz}; \text{CDCl}_3)$ 1.50 (6 H, s, 2 \times Me), 1.78 (3 H, s, 3-Me), 7.10–7.30 (2 H, m, Ph), and 7.35–7.50 (3 H, m, Ph); $\delta_{\text{C}}(\text{CDCl}_3)$ 9.3 (q, Me), 25.2 (q, Me), 86.2 (s, C-5), 124.2 and 165.6 (2 s, C-3 and -4), 127.5 (d), 128.8 (d), 129.0 (d), and 132.3 (s) (ArC), and 173.0 (s, C=O).

Photolysis of 3-Hydroxy-2,2,4-trimethyl-3-phenylcyclobutanone (12).—(a) A solution of the cyclobutanone (12) (168 mg) in propan-2-ol (80 ml) was irradiated under bubbling air through a Pyrex filter. Chromatography of the irradiation mixture with hexane-ethyl acetate (9:1) as eluant gave two isomeric solvent adducts (13) (49 mg, 23%) and (13') (73 mg, 34%). Since the starting cyclobutanone (12) is a single stereoisomer,^{9a} isomers (13) and (13') seem to be epimers with respect to C-5.

(b) A solution of compound (12) (5 mg) in acetonitrile (1.5 ml) was placed in a Pyrex tube. Oxygen was bubbled through the solution for 10 min. The tube was irradiated with a high-pressure mercury lamp. G.l.c. analysis of the irradiation mixture revealed the formation of the tetrahydrofuran-2-one (5a).

3-Hydroxy-5-isopropoxy-2,2,4-trimethyl-3-phenyltetrahydrofuran (13). M.p. 86–87 °C (from hexane) (Found: C, 72.5; H, 9.05. $\text{C}_{16}\text{H}_{24}\text{O}_3$ requires C, 72.69; H, 9.15%); $\nu_{\max}(\text{CCl}_4)$ 3 600 and 3 500br cm^{-1} (OH); $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 1.03 and 1.29 (6 H, 2 s, 2 \times Me), 1.07 (3 H, d, J 7.0 Hz, 4-Me), 1.17 and 1.26 (6 H, 2 d, J 6.2 Hz, CHMe_2), 1.95 (1 H, s, OH), 3.10 (1 H, quin, J 7.0 Hz, 4-H), 3.95 (1 H, sep, J 6.2 Hz, CHMe_2), 4.98 (1 H, d, J 7.0 Hz, 5-H), and 7.26–7.37 (3 H, m, Ph), and 7.48–7.50 (2 H, m, Ph); $\delta_{\text{C}}(\text{CDCl}_3)$ 9.4, 21.0, 21.7, 21.8, and 26.6 (5 q, 5 \times Me), 46.2, 70.2, and 106.4 (3 d, 3 \times CH), 85.3 and 86.5 (2 s, C-2 and -3), 126.5 (d), 127.6 (d), 128.2 (d), and 139.5 (s) (ArC).

3-Hydroxy-5-isopropoxy-2,2,4-trimethyl-3-phenyltetrahydrofuran (13'). B.p. 85 °C at 0.3 mmHg; $\nu_{\max}(\text{CCl}_4)$ 3 500br cm^{-1} (OH); $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 0.76 and 1.40 (6 H, 2 s, 2 \times Me), 1.03 (3 H, d, J 7.0 Hz, 4-Me), 1.15 and 1.27 (6 H, 2 d, J 6.2 Hz, CHMe_2), 3.02 (1 H, dq, J 7.0 and 5.0 Hz, 4-H), 4.00 (1 H, sep, J 7.2 Hz, CHMe_2), 4.08 (1 H, s, OH), 5.16 (1 H, d, J 5.0 Hz, 5-H), and 7.25–7.48 (5 H, m, Ph); $\delta_{\text{C}}(\text{CDCl}_3)$ 7.1, 21.4, 23.4, 23.8, and 28.4 (5 q, 5 \times Me), 42.6, 69.4, and 102.0 (3 d, 3 \times CH), 83.7 and 88.6 (2 s, C-2 and -3), 126.1 (d), 127.1 (d), 128.0 (d), and 140.0 (s) (ArC).

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