

Photochemical Reactions of 6-Isobutyrylbenzocycloalken-5-ones with Oxygen. Photochemistry of Enolic 1,3-Diketones

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6-Isobutyrylbenzocycloalken-5-ones (**4**) exist in the enol form in solution. The seven- and eight-membered enolic 1,3-diketones (**4c**) and (**4d**) underwent photoketonization and subsequent type II reaction to generate biradicals which were trapped by oxygen to yield the furanones (**5**) and (**6**), and the peroxide (**7**) [only formed from (**4c**)] in various solvents in the presence of oxygen, whereas the six-membered enolic 1,3-diketone (**4a**) underwent oxidative dehydrogenation to yield the naphthol (**10**). Photoreaction of the six-membered enolic 1,3-diketone (**4b**) in the presence of oxygen gave the naphthalenone (**11**) and the epoxide (**12**).

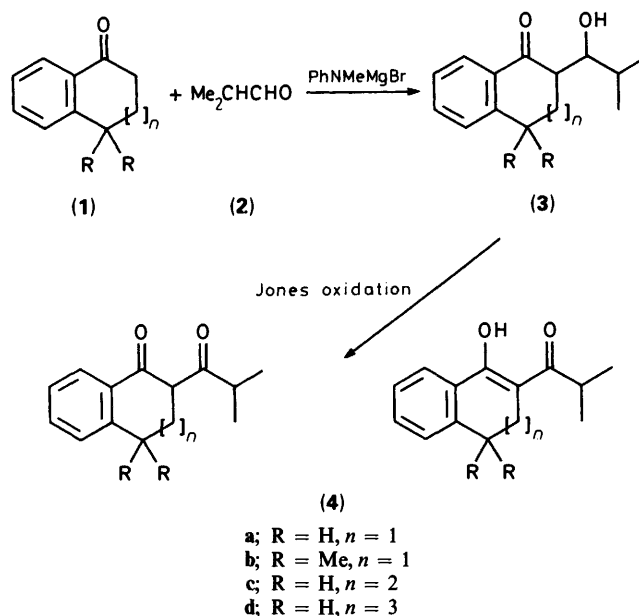
Enol tautomers of 1,3-diketones undergo [2 + 2] photocycloaddition with alkenes to form acyl cyclobutanols which readily undergo retro-aldol cleavage to yield 1,5-diketones.¹ However, irradiation of some 1,3-dicarbonyl compounds in the absence of alkenes gives no product, but results in a shift of their enol-keto equilibrium to the keto form, though cessation of the irradiation causes a gradual restoration of the enol form to the thermodynamic enol-keto equilibrium.²

We have previously reported that 1-aryl 1,3-diketones bearing a weak γ C-H bond underwent type II cyclization to give hydroxycyclobutanones.³ Recently, we have reported that biradicals generated in the type II reaction of some 1-aryl 1,3-diketones were trapped by molecular oxygen to yield oxygenated products.⁴ The isobutyrylbenzocycloalkenones (**4**) exist in the enol form in solution and may undergo photoketonization followed by a secondary photoreaction, the type II reaction, of the resulting keto form. We report here the photochemical reaction of (**4**) in the presence of oxygen.

Results and Discussion

The isobutyrylbenzocycloalkenones (**4a-d**) were prepared in 40–70% overall yields *via* condensation of the corresponding benzocycloalkenones (**1a-d**) with 2-methylpropanal (**2**) using *N*-methylanilinomagnesium bromide as the condensing agent,⁵ followed by oxidation of the ketols (**3a-d**) with Jones reagent. Compounds (**4a-d**) existed in the keto form just after preparation, but they isomerized to the enol form on passing through a silica gel column followed by distillation or recrystallization for purification; *e.g.*, crude (**4d**) showed two carbonyl IR absorptions at 1 740 and 1 680 cm^{-1} and two ¹³C NMR carbonyl peaks at δ 202.4 and 208.0, but purified (**4d**) showed IR peaks due to the enolic 1,3-diketone at 1 620 and 1 600 cm^{-1} , and only one ¹³C NMR carbonyl peak at δ 203.4. The UV spectra of (**4a-d**) in hexane showed maxima ascribable to the enol structure at 340 nm (ϵ 13 540) for (**4a**), 338 nm (ϵ 13 220) for (**4b**), 312 nm (ϵ 12 600) for (**4c**), and 306 nm (ϵ 12 860) for (**4d**). The ¹H and ¹³C NMR spectra of (**4a-d**) revealed that they existed in only one tautomeric form, the enol tautomer. Thus, (**4a-d**) existed completely in the enol form in solution.

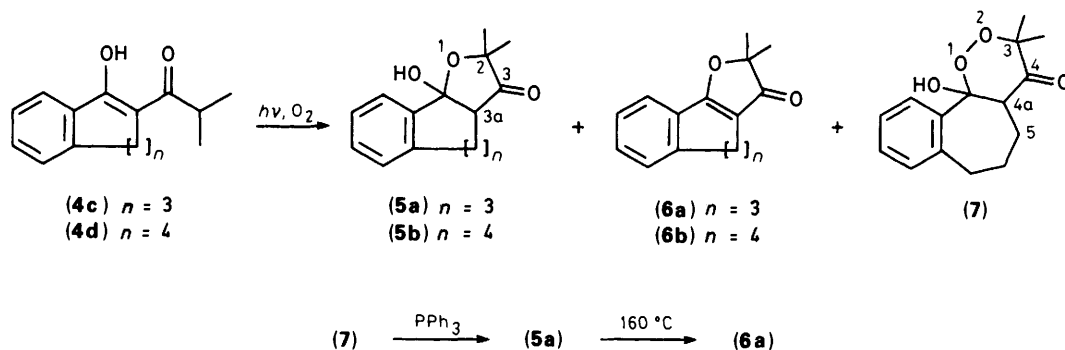
Irradiation of compound (**4c**) with a high-pressure mercury lamp through a Pyrex filter in hexane under nitrogen gave an intractable mixture, but when (**4c**) was irradiated in hexane under bubbling air, the furanones (**5a**) and (**6a**), and the peroxide (**7**) were obtained.⁶ Irradiation of (**4c**) in benzene or acetonitrile under the same conditions gave a similar result.



However, irradiation of (**4c**) in methanol in the presence or absence of oxygen resulted in no reaction.

The structures of the photoproducts were assigned on the basis of their analytical and spectral data and chemical evidence. The IR spectrum of (**5a**) showed five-membered carbonyl (1 765 cm^{-1}) and hydroxy (3 600 cm^{-1}) absorptions. The ¹H NMR spectrum of (**5a**) showed two singlets due to two methyl groups on C-2 at δ 1.32 and 1.47. Compound (**5a**) was dehydrated to give (**6a**) quantitatively on heating at 160 °C. The UV spectrum of (**6a**) showed maxima at 248, 300, and 313 nm (ϵ 6 400, 15 400, and 15 900). The spectrum resembled those of bullatenone [2,2-dimethyl-5-phenylfuran-3(2*H*)-one]⁷ and 2,2,4-trimethyl-5-phenylfuran-3(2*H*)-one,⁴ suggesting a conjugated structure for (**6a**) analogous to those of phenylfuranones. The ¹H NMR spectrum of (**6a**) showed a singlet due to two methyl groups at δ 1.42. Compound (**7**) showed hydroxy (3 600 cm^{-1}) and carbonyl (1 735 cm^{-1}) IR absorptions and two ¹H NMR singlets due to two methyl groups at δ 1.22 and 1.48. Deoxygenation of (**7**) using triphenylphosphine gave (**5a**) in 63% yield.

The isobutyrylbenzocyclo-octenone (**4d**) was irradiated under the same conditions as for (**4c**). In hexane, benzene, or acetonitrile, the furanones (**5b**) and (**6b**) were produced, but in

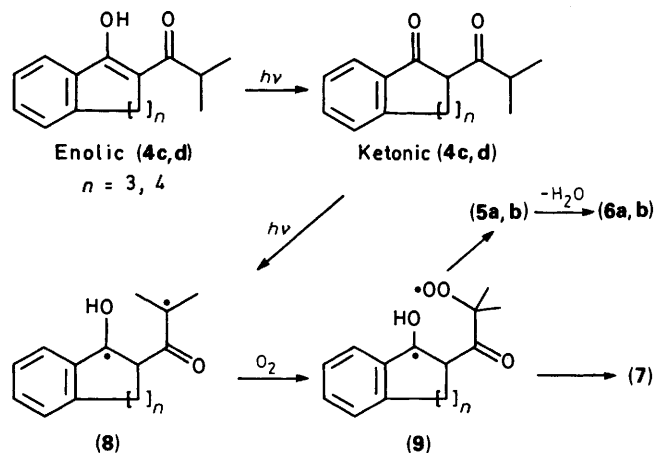
**Table 1.** Results of the photo-oxidation of (4c,d).

Solvent ^a	Diketone	Conversion (%) ^b	Product distribution (%) ^c		
			(5)	(6)	(7)
Hexane	(4c)	75	23	14	14
Hexane	(4d)	73	8	12	
Benzene	(4c)	100	6	16	10
Benzene	(4d)	77		13	
MeCN	(4c)	95		17	2
MeCN	(4d)	93		17	

^a No reaction was observed on photolysis in methanol. ^b Based on the amount of unchanged starting material recovered after chromatography. ^c Based on converted starting material.

methanol, the starting (4d) was recovered unchanged even on prolonged irradiation.

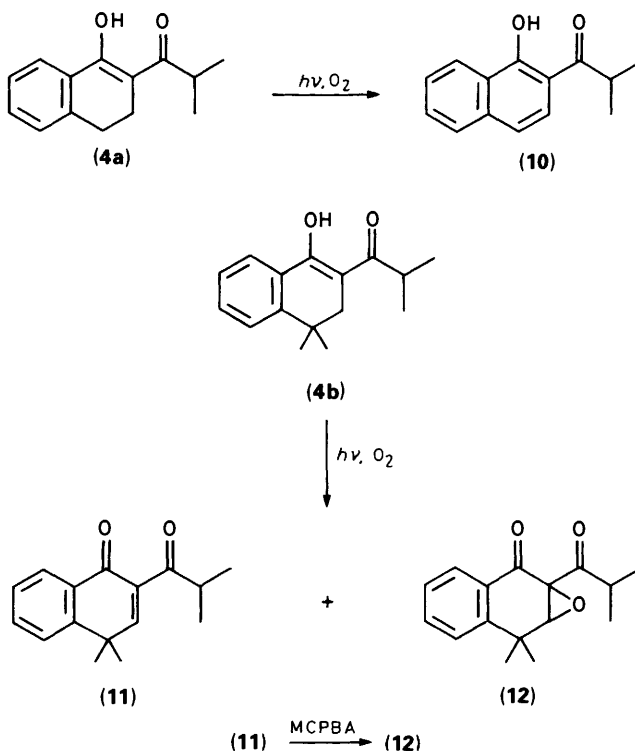
The formation of (5), (6), and (7) can be rationalized in terms of initial photoketonization and subsequent 1,5-hydrogen shift from the isobutyryl group to the ring carbonyl oxygen in the resulting keto isomer to give the biradical (8). The biradical (8) may interact with molecular oxygen to give the peroxy radical (9)⁸ which may be transformed into (5) with loss of oxygen or may undergo ring closure to form (7).⁹



The photochemical behaviour of the six-membered benzocycloalkenones (4a,b) was quite different from that of the seven- and eight-membered benzocycloalkenones (4c,d). Irradiation of (4a) in various solvents (hexane, acetonitrile, or methanol) under bubbling air gave 2-isobutyryl-1-naphthol (10) in 10–30% yield depending on the solvent used. Irradiation of (4b) in hexane or acetonitrile under the same conditions gave the naphthalenone (11) and the epoxy-naphthalenone (12). Thus, compounds (4a,b) underwent dehydrogenation more rapidly

than the photoketonization and subsequent type II reaction.

The ¹³C NMR spectrum of (11) showed two carbonyl peaks at δ 182.7 and 206.4 and eight peaks due to aromatic and olefinic sp^2 carbons. Its ¹H NMR spectrum showed a doublet at δ 1.15 and a septet at δ 3.60 due to the isobutyryl group. Epoxidation of (11) with *m*-chloroperoxybenzoic acid (MCPBA) gave (12) in 72% yield.

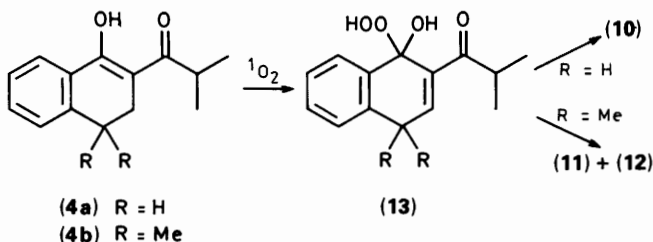


The photo-oxidation of (4a,b) to give (10), (11), and (12) may proceed *via* a singlet oxygen reaction. Irradiation of a methanolic solution of (4a) in the presence of Rose Bengal under bubbling air with a halogen lamp through a K_2CrO_4 filter solution gave (10) in 33% yield. Irradiation of a methanolic solution of (4b) under the same conditions gave (11) and (12) in 61 and 4% yield, respectively. It has been observed that epoxides are sometimes produced in the reaction of olefins with singlet oxygen.¹⁰ However, irradiation of (11) in the presence of Rose Bengal under oxygen resulted in no reaction. On the basis of these results, the photo-oxidation of (4a,b) can be explained in terms of an ene reaction with singlet oxygen to form hydroperoxides (13) which undergo thermal decomposition to form (10), (11), and (12). A similar reaction was observed by

Table 2. Results of the photo-oxidation of (4a,b).

Solvent	Diketone	Conversion (%) ^a	Yield (%) ^b		
			(10)	(11)	(12)
Hexane ^c	(4a)	39	29		
Hexane ^c	(4b)	29		29	7
MeCN ^c	(4a)	89	9		
MeCN ^c	(4b)	64		28	15
MeOH ^c	(4a)	23	11		
MeOH ^d	(4a)	75	33		
MeOH ^d	(4b)	86		61	4

^a Based on the amount of unchanged starting material recovered after chromatography. ^b Based on converted starting material. ^c Irradiation was carried out with Pyrex-filtered light. ^d Irradiation was carried out with a halogen lamp through a K₂CrO₄ filter solution in the presence of Rose Bengal.



Ensley in the reaction of β -alkoxyenones with singlet oxygen. He reported that the singlet oxygen oxidation of 1-acetyl-2-methoxycyclopentene gave 2-acetyl-2,3-epoxycyclopentanone and that the intermediate of this reaction was 1-acetyl-5-hydroperoxy-5-methoxycyclopentene.¹¹

In the photoreaction of (4) in the presence of oxygen, the transfer of excitation energy to molecular oxygen may compete with photoketoneization. The UV absorption maxima of (4a,b) appeared at longer wavelength than those of (4c,d) (*vide supra*). This result indicates that the π -orbital overlap between the enone moiety and the benzene ring is more effective in (4a,b) than in (4c,d). Therefore, the activation energy for ketoneization in (4a,b) must be higher than that in (4c,d). This seems to be the reason for the lack of the type II photoreaction of (4a,b).

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 with a Büchi Kugelrohr KR apparatus. UV spectra were recorded on a Hitachi 340 spectrometer and IR spectra on a Hitachi 270-50 spectrometer. ¹H NMR spectra were obtained with a JEOL PMX-60, a JEOL FX-90Q, or a Bruker AM 400 spectrometer using tetramethylsilane as an internal standard. ¹³C NMR spectra were measured on a JEOL FX-90Q or a Bruker AM 400 spectrometer with CDCl₃ as solvent. Column chromatography was performed with Merck Kieselgel 60 with hexane-ethyl acetate as eluant. An Ushio 100 W high-pressure mercury lamp and an Ushio 55 W tungsten-halogen lamp were used as irradiation sources.

Starting Materials.—Compounds (4a-d) were prepared by the condensation of the corresponding benzocycloalkenones (1) with 2-methylpropanal (2), followed by Jones oxidation. 7,8,9,10-Tetrahydrobenzocyclo-octen-5(6H)-one (1d)¹² and 4,4-dimethyl-3,4-dihydronaphthalen-1(2H)-one (1b)¹³ were prepared by the reported methods. By the same procedure as that reported by Nielsen,⁵ the ketols (3) were prepared in 60–85% yields. These ketols were oxidized by Jones reagent according to the general procedure to give the keto tautomers (4a-d) in 40–

80% yields. Compounds (4a-d) were purified by silica gel column chromatography and further distilled or recrystallized.

2-Isobutyryl-3,4-dihydronaphthalen-1(2H)-one (4a) had b.p. 110 °C at 0.3 mmHg (Found: C, 77.7; H, 7.5. C₁₄H₁₆O₂ requires C, 77.7; H, 7.5%); λ_{max} (hexane) 340 (ϵ 13 540 dm³ mol⁻¹ cm⁻¹); ν_{max} (CCl₄) 1 620 (C=O) and 1 600 cm⁻¹ (C=C); δ_{H} (90 MHz; CDCl₃) 1.16 (6 H, d, *J* 7.0 Hz, 2 \times Me), 2.50–3.15 (5 H, m, 2 \times CH₂ and CH), 7.05–7.45 (3 H, m, ArH), 7.80–8.00 (1 H, m, ArH), and 16.56 (1 H, s, OH); δ_{C} (CDCl₃) 18.5 (q, 2 \times Me), 21.9 (t, CH₂), 28.1 (t, CH₂), 32.9 (d, CH), 104.3 (s, C-2), 125.5 (d), 126.5 (d), 127.2 (s), 131.1 (d), 131.4 (d), and 140.5 (s) (ArC), 176.7 (s, ring C=O), and 200.9 (s, side chain C=O).

2-Isobutyryl-4,4-dimethyl-3,4-dihydronaphthalen-1(2H)-one (4b) had b.p. 120 °C at 0.4 mmHg (Found: C, 78.6; H, 8.4. C₁₆H₂₀O₂ requires C, 78.7; H, 8.3%); λ_{max} (hexane) 338 nm (ϵ 13 220 dm³ mol⁻¹ cm⁻¹); ν_{max} (CCl₄) 1 625 (C=O) and 1 600 cm⁻¹ (C=C); δ_{H} (60 MHz; CCl₄) 1.15 (6 H, d, *J* 7.0 Hz, 2 \times Me), 1.33 (6 H, s, 2 \times Me), 2.53 (2 H, s, CH₂), 2.95 (1 H, sept., *J* 7.0 Hz, CH), 7.20–7.60 (3 H, m, ArH), 7.85–8.10 (1 H, m, ArH), and 16.56 (1 H, s, OH); δ_{C} 18.7 (q, 2 \times Me), 28.6 (q, 2 \times Me), 32.9 (d, CH), 34.0 (s, C-4), 37.2 (t, C-3), 103.2 (s, C-2), 123.9 (d), 126.1 (d), 126.4 (d), 129.9 (s), 132.3 (d), and 149.0 (s) (ArC), 176.8 (s, ring C=O), and 201.0 (s, side chain C=O).

6-Isobutyryl-6,7,8,9-tetrahydrobenzocyclohepten-5-one (4c) had m.p. 54 °C (from pentane) (Found: C, 78.2; H, 7.9. C₁₅H₁₈O₂ requires C, 78.2; H, 7.9%); λ_{max} (hexane) 312 (ϵ 12 600 dm³ mol⁻¹ cm⁻¹); ν_{max} (CCl₄) 1 620 (C=O) and 1 600 cm⁻¹ (C=C); δ_{H} (90 MHz; CDCl₃) 1.19 (6 H, d, *J* 7.0 Hz, 2 \times Me), 1.84–2.24 (4 H, m, 7-H₂ and 8-H₂), 2.66 (2 H, t, *J* 7.0 Hz, 9-H₂), 2.97 (1 H, sept., *J* 7.0 Hz, CH), 7.04–7.37 (3 H, m, ArH), 7.48–7.63 (1 H, m, ArH), and 16.64 (1 H, s, OH); δ_{C} (CDCl₃) 19.5 (q, 2 \times Me), 22.9, 31.2, and 31.7 (3 \times t, 3 \times CH₂), 32.6 (d, CH), 107.9 (s, C-6), 126.5 (d), 127.5 (d), 128.6 (d), 130.8 (d), 137.7 (s), 139.7 (s) (ArC), 188.3 (s, ring C=O), and 197.6 (s, side chain C=O).

6-Isobutyryl-7,8,9,10-tetrahydrobenzocyclo-octen-5(6H)-one (4d) had b.p. 120 °C at 0.5 mmHg (Found: C, 78.5; H, 8.4. C₁₆H₂₀O₂ requires C, 78.7; H, 8.3%); λ_{max} 306 (ϵ 12 860 dm³ mol⁻¹ cm⁻¹); ν_{max} (CCl₄) 1 620 (C=O) and 1 600 cm⁻¹ (C=C); δ_{H} (90 MHz; CDCl₃) 1.16 (3 H, d, *J* 7.0 Hz, Me), 1.24 (3 H, d, *J* 7.0 Hz, Me), 1.32–3.16 (9 H, m, 4 \times CH₂ and CH), 7.08–7.44 (4 H, m, ArH), and 16.84 (1 H, s, OH); δ_{C} (CDCl₃) 18.5 and 19.5 (2 \times q, 2 \times Me), 24.3, 28.1, 28.4, and 32.5 (4 \times t, 4 \times CH₂), 33.0 (d, CH), 110.7 (s, C-6), 125.5 (d), 126.9 (d), 129.3 (d), 129.9 (d), 135.5 (s), 140.9 (s) (ArC), 183.3 (s, ring C=O), and 203.4 (s, side chain C=O).

General Procedure for the Photolysis of (4a-d).—A solution of compounds (4a-d) (*ca.* 550 mg) in various solvents (hexane, benzene, methanol, or acetonitrile) (110 ml) was irradiated with a high-pressure mercury lamp through a Pyrex filter under bubbling air for 5–10 h. The photoproducts were isolated by column chromatography.

10b-Hydroxy-2,2-dimethyl-4,5,6,10b-tetrahydro-3aH-benzocyclohepta[1,2-b]furan-3(2H)-one (5a) had m.p. 107–108 °C (from pentane) (Found: C, 73.2; H, 7.4. C₁₅H₁₈O₃ requires C, 73.1; H, 7.4%); ν_{max} (CCl₄) 3 600 (OH) and 1 765 cm⁻¹ (C=O); δ_{H} (90 MHz; CDCl₃) 1.32 (3 H, s, Me), 1.47 (3 H, s, Me), 1.76–2.28 (4 H, m), 2.40–2.86 (2 H, m), and 3.12–3.48 (1 H, m) (3 \times CH₂ and CH), 2.48 (1 H, s, OH), 7.00–7.24 (3 H, m, ArH), 7.68–7.86 (1 H, m, ArH); δ_{C} (CDCl₃) 25.9 and 26.2 (2 \times q, 2 \times Me), 24.3, 27.0, and 35.5 (3 \times t, 3 \times CH₂), 54.6 (d, C-3a), 80.8 and 101.8 (2 \times s, C-2 and C-10b), 124.0 (d), 125.8 (d), 128.5 (d), 130.8 (d), 141.0 (s), and 141.5 (s) (ArC), and 216.6 (s, C=O).

11b-Hydroxy-2,2-dimethyl-3a,4,5,6,7,11b-hexahydrobenzocyclo-octa[1,2-b]furan-3(2H)-one (5b) had m.p. 159–160 °C (from hexane-benzene) (Found: C, 74.0; H, 7.8. C₁₆H₂₀O₃ requires C, 73.8; H, 7.7%); ν_{max} (CHCl₃) 3 580 (OH) and 1 760

cm^{-1} (C=O); δ_{H} (90 MHz; CDCl_3) 1.39 (3 H, s, Me), 1.50 (3 H, s, Me), 1.22–2.70 (10 H, m, $4 \times \text{CH}_2$, CH, and OH), 7.00–7.36 (3 H, m, ArH), and 7.70–7.86 (1 H, m, ArH); δ_{C} (CDCl_3) 25.9 and 26.5 ($2 \times \text{q}$, $2 \times \text{Me}$), 19.2, 24.3, 29.3, and 31.2 ($4 \times \text{t}$, $4 \times \text{CH}_2$), 61.3 (d, C-3a), 80.3 and 103.0 ($2 \times \text{s}$, C-2 and C-11b), 125.2 (d), 125.9 (d), 128.9 (d), 131.6 (d), and 140.6 (s, $2 \times \text{C}$) (ArC), and 215.8 (s, C=O).

2,2-Dimethyl-5,6-dihydro-4H-benzo[6,7]cyclohepta[1,2-b]-furan-3(2H)-one (6a) had m.p. 99 °C (from hexane–benzene) (Found: C, 78.9; H, 7.2. $\text{C}_{15}\text{H}_{16}\text{O}_2$ requires C, 78.9; H, 7.1%); λ_{max} (EtOH) 248 (ϵ 6 400 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$), 300sh (15 400), and 313 nm (15 900); ν_{max} (CHCl_3) 1 680 (C=O) and 1 610 cm^{-1} (C=C); δ_{H} (90 MHz; CDCl_3) 1.42 (6 H, s, $2 \times \text{Me}$), 1.80–2.10 (2 H, m), 2.50 (2 H, m), and 2.80–3.00 (2 H, m) ($3 \times \text{CH}_2$), 7.04–7.38 (3 H, m, ArH), and 7.84–8.00 (1 H, m, ArH); δ_{C} (CDCl_3) 23.3 (q, $2 \times \text{Me}$), 23.5, 24.4, and 36.1 ($3 \times \text{t}$, $3 \times \text{CH}_2$), 84.6 and 113.4 ($2 \times \text{s}$, C-2 and C-3a), 126.3 (d), 127.5 (d), 129.2 (s), 129.8 (d), 131.5 (d), and 144.1 (s) (ArC), 175.6 (s, C-10b), and 208.3 (s, C=O).

2,2-Dimethyl-4,5,6,7-tetrahydrobenzo[7,8]cyclo-octa[1,2-b]-furan-3(2H)-one (6b) had m.p. 98–99 °C (from hexane) (Found: C, 79.0; H, 7.5. $\text{C}_{16}\text{H}_{18}\text{O}_2$ requires C, 79.3; H, 7.5%); ν_{max} (CHCl_3) 1 690 (C=O) and 1 615 cm^{-1} (C=C); δ_{H} (90 MHz; CDCl_3) 1.42 (6 H, s, $2 \times \text{Me}$), 1.50–1.92 (4 H, m), 2.20–2.40 (2 H, m), and 2.64–2.88 (2 H, m) ($4 \times \text{CH}_2$), and 7.10–7.62 (4 H, m, ArH); δ_{C} (CDCl_3) 23.2 (q, $2 \times \text{Me}$), 21.1, 21.9, 30.1, and 32.7 ($4 \times \text{t}$, $4 \times \text{CH}_2$), 85.4 and 114.9 ($2 \times \text{s}$, C-2 and C-3a), 126.0 (d), 127.3 (d), 129.7 (d), 131.3 (d + s), and 141.0 (s) (ArC), 177.4 (s, C-11b), and 207.8 (s, C=O).

11b-Hydroxy-3,3-dimethyl-5,6,7,11b-tetrahydro-4aH-benzo[6,7]cyclohepta[1,2-c][1,2]dioxin-4(3H)-one (7) had m.p. 77–79 °C (from hexane) (Found: C, 68.4; H, 7.0. $\text{C}_{15}\text{H}_{18}\text{O}_4$ requires C, 68.7; H, 6.9%); ν_{max} (CHCl_3) 3 600 (OH) and 1 735 cm^{-1} (C=O); δ_{H} (90 MHz; CDCl_3) 1.22 (3 H, s, Me), 1.48 (3 H, s, Me), 1.90–3.44 (8 H, m, $3 \times \text{CH}_2$, CH, and OH), and 7.04–7.32 (3 H, m, ArH), and 7.55–7.72 (1 H, m, ArH); δ_{C} (CDCl_3) 20.4 and 21.5 ($2 \times \text{q}$, $2 \times \text{Me}$), 23.9, 27.2, and 35.1 ($3 \times \text{t}$, $3 \times \text{CH}_2$), 50.9 (d, C-4a), 88.7 and 106.5 ($2 \times \text{s}$, C-3 and C-11b), 124.3 (d), 126.0 (d), 128.8 (d), 130.9 (d), 140.5 (s), and 140.9 (s) (ArC), and 210.8 (s, C=O).

2-Isobutyryl-1-naphthol (10)¹⁴ had m.p. 87–88 °C (from pentane); λ_{max} (EtOH) 367 nm (ϵ 7 600 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$); ν_{max} (CHCl_3) 1 620 cm^{-1} (C=O); δ_{H} (90 MHz; CDCl_3) 1.24 (6 H, d, J 6.8 Hz, $2 \times \text{Me}$), 3.60 (1 H, sept., J 6.8 Hz, CHMe_2), 7.10–7.25 (1 H, m, ArH), 7.25–7.76 (4 H, m, ArH), 8.27–8.47 (1 H, m, ArH), and 14.20 (1 H, s, OH).

2-Isobutyryl-4,4-dimethylnaphthalen-1(4H)-one (11) had m.p. 77–78 °C (from hexane) (Found: C, 79.2; H, 7.7. $\text{C}_{16}\text{H}_{18}\text{O}_2$ requires C, 79.3; H, 7.5%); ν_{max} (CHCl_3) 1 700 and 1 670 (C=O), and 1 600 cm^{-1} (C=C); δ_{H} (400 MHz; CDCl_3) 1.15 (6 H, d, J 7.0 Hz, $2 \times \text{Me}$), 1.54 (6 H, s, $2 \times \text{Me}$), 3.60 (1 H, sept., J 7.0 Hz, CHMe_2), 7.39 (1 H, s, 3-H), 7.43 (1 H, t, J 8.0 Hz, ArH), 7.55 (1 H, d, J 8.0 Hz, ArH), 7.62 (1 H, t, J 8.0 Hz, ArH), and 8.22 (1 H, d, J 8.0 Hz, ArH); δ_{C} (CDCl_3) 18.2 (q, $2 \times \text{Me}$), 29.4 (q, $2 \times \text{Me}$), 37.6 (s, C-4), 39.5 (d, CH), 126.1 (d), 127.1 (d), 127.2 (d), 130.6 (s), 133.0 (d), 136.3 (s), 148.8 (s), and 160.5 (d) (ArC, C-2 and -3), 182.7 (s, C=O), and 206.4 (s, C=O).

2,3-Epoxy-2-isobutyryl-4,4-dimethyl-3,4-dihydronaphthalen-1(2H)-one (12) had m.p. 93 °C (from hexane) (Found: C, 74.4; H, 7.3. $\text{C}_{16}\text{H}_{18}\text{O}_3$ requires C, 74.4; H, 7.0%); ν_{max} (CHCl_3) 1 725 and 1 685 cm^{-1} (C=O); δ_{H} (60 MHz; CDCl_3) 1.18 (3 H, d, J 7.0 Hz, Me), 1.20 (3 H, d, J 7.0 Hz, Me), 1.37 (3 H, s, Me), 1.67 (3 H, s, Me), 3.08 (1 H, sept., J 7.0 Hz, CHMe_2), 3.45 (1 H, s, 3-H),

7.13–7.77 (3 H, m, ArH), 7.83–8.10 (1 H, m, ArH); δ_{C} (CDCl_3) 16.7, 18.2, 25.3, and 30.2 ($4 \times \text{q}$, $4 \times \text{Me}$), 35.7 (s, C-4), 38.1 (d, CHMe_2), 63.8 (s, C-2), 67.5 (d, C-3), 126.2 (d), 127.2 (d), 128.0 (d), 128.1 (s), 134.7 (d), and 146.7 (s) (ArC), 191.00 (s, C=O), and 205.45 (s, C=O).

General Procedure for the Reaction of (4a,b) with Singlet Oxygen.—A solution of (4a,b) (ca. 500 mg) in methanol (100 ml) in the presence of Rose Bengal (ca. 2 mg) was irradiated with a halogen lamp through an aqueous solution of K_2CrO_4 (0.54 g dm^{-3}) and Na_2CO_3 (2 g dm^{-3}) under bubbling air for 2.5 h for (4a) and 8 h for (4b). After removal of the solvent, the residue was chromatographed to afford the naphthol (10) from (4a), and the naphthalenone (11) and the epoxy-naphthalenone (12) from (4b).

Deoxygenation of the Peroxide (7).—A solution of the peroxide (7) (138 mg, 0.53 mmol) and triphenylphosphine (143 mg, 0.53 mmol) in benzene (4 ml) was stirred at room temperature for 3 h. The residue after removal of the solvent was chromatographed to give (5c) (81 mg, 63%).

Epoxidation of the Naphthalenone (11).—To the naphthalenone (11) (35 mg, 0.15 mmol) in CH_2Cl_2 (3 ml) and 1M NaHCO_3 (1.5 ml) was added *m*-chloroperoxybenzoic acid (42 mg, 0.19 mmol) with vigorous stirring at 0 °C. The mixture was stirred at room temperature for 3 h. The organic phase was separated and washed with aqueous sodium hydrogen carbonate and water. Chromatography after removal of the solvent gave the epoxide (12) (10 mg) with 60% recovery of unchanged (11).

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