

Photochemical Reaction of 1-(*o*-Methylphenyl)-2,2-dimethyl 1,3-Diketones

Michikazu Yoshioka,^{*,a} Kaori Nishizawa,^a Masayuki Arai^a and Tadashi Hasegawa^b

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

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

The photochemistry of 1-(*o*-methylphenyl)-2,2-dimethylpropane-1,3-diones **4** has been investigated. Compounds **4a–h** underwent photocyclization to give benzocyclobutenols **11a–h** and naphthalenones **12a–h** in hexane or methanol. Compound **4i** gave the naphthalenone **12i** in methanol. The product ratio **11**:**12** was greater in hexane than in methanol. This ratio increases with chain branching of the C-3 substituent R and with increasing size of R. Compounds **4a**, **b** and **d** gave isobutyrophenones **13a**, **b** and **d** along with products **11** and **12** in hexane.

The photochemistry of *o*-alkylphenyl ketones has been extensively studied and a number of comprehensive reviews have been published.¹ In these ketones, the carbonyl oxygen of the n,π^* triplet state² abstracts hydrogen from the α -carbon of the *ortho*-alkyl group to produce a triplet diradical (a triplet state of the enol^{1c}). The resulting diradical decays both to the enol and to the starting ketone ground state. The ground-state enol is normally a short lived species at ambient temperature and undergoes a rapid reketonization. In the case of highly hindered aromatic ketones such as 2,4,6-trialkylphenyl ketones, the formation of benzocyclobutenols has been reported to occur *via* a diradical process because the enol is more hindered than the benzocyclobutenols.³ The enol species from *o*-alkylphenyl ketones can be trapped with dienophiles and such reactions have been used as a method for demonstrating the existence of these species.⁴ The triplet diradicals and/or the ground-state enols from *o*-alkylphenyl 1,2-diketones,^{4b,5} *o*-alkylphenyl α,β -acetylenic ketones,⁶ or *o*-alkylphenyl α -chloro ketones⁷ transform to indanones by intramolecular addition to a carbonyl group or a triple bond, or by loss of hydrogen chloride. The inter- and intra-molecular hydrogen bonding in the Norrish Type II diradical suppresses the reverse transfer of hydrogen to reproduce the starting ketone.⁸ The intramolecular hydrogen bonding in the enol species also stabilizes these species.⁹

Recently, we have reported that some *o*-alkylaryl 1,3-diketones undergo photocyclization to give benzocyclobutenols in hexane.¹⁰ The diradical intermediates from these diketones are expected to be stabilized by intramolecular hydrogen bonding. On the other hand, Hornback reported that irradiation of some *o*-methylphenyl 1,3-diketones in methanol gave 3-hydroxy-3,4-dihydronaphthalen-1(*2H*)-ones.¹¹ We report here that *o*-methylphenyl 1,3-diketones **4** undergo photocyclization in hexane or methanol to give benzocyclobutenols **11**, naphthalenones **12** and/or isobutyrophenones **13** and that the ratio of products **11**:**12** depends on the solvent and the substituent R.

Results and Discussion

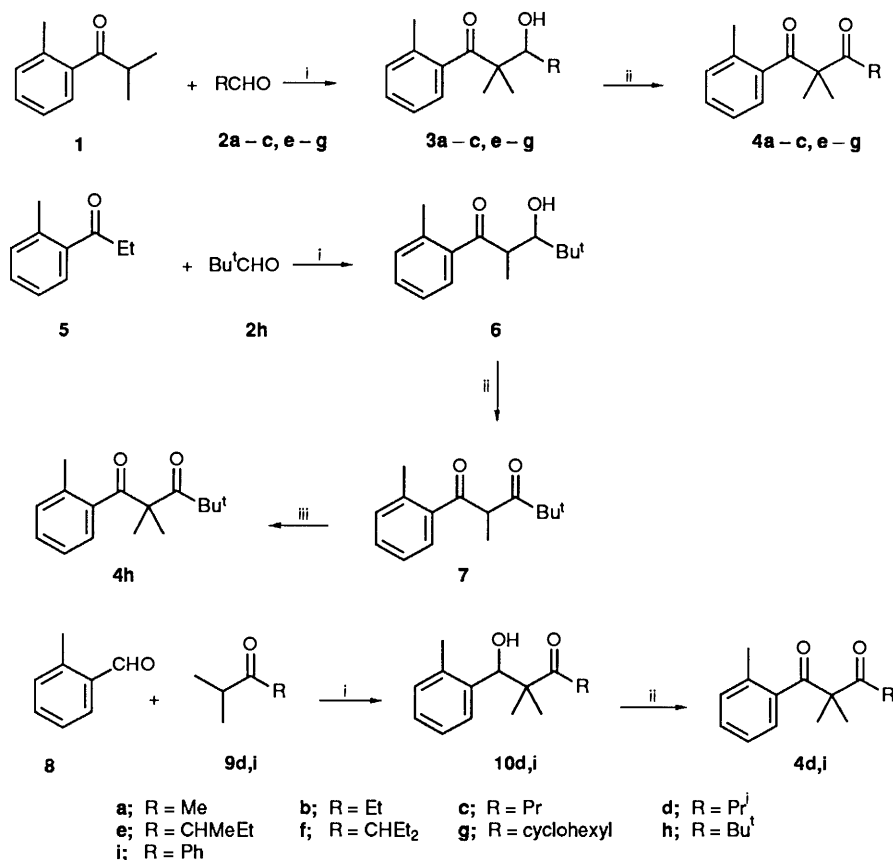
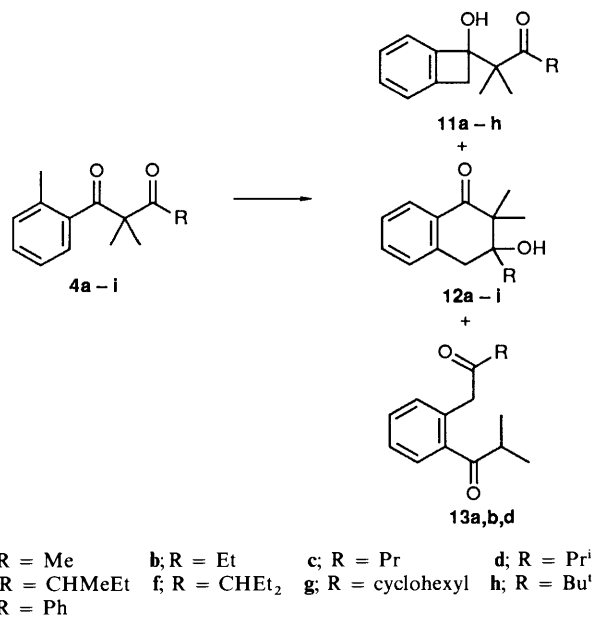
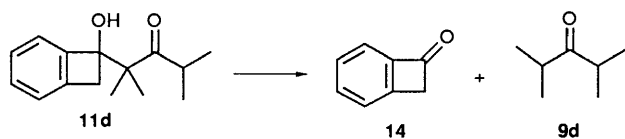
The *o*-methylphenyl 1,3-diketones **4a–c** and **4e–g** were prepared in 35–70% overall yield *via* the condensation of *o*-methylisobutyrophenone **1** with the corresponding aldehydes **2**, with *N*-methylanilinomagnesium bromide as the condensing agent,¹² followed by oxidation of the corresponding product ketols **3** with Jones' reagent. The condensation of ketone **1** with pivalaldehyde **2h** by the same procedure gave compound **3h** in very low yield. However, condensation of *o*-methylpropio-phenone **5** with pivalaldehyde **2h** gave the ketol **6** in excellent yield. The ketol **6** was oxidized to give dione **7**, and this was

methylated to give compound **4h**. The 1,3-diketones **4d** and **4i** were prepared by the condensation of *o*-tolualdehyde **8** with the corresponding isopropylketones **9d** and **9i**, followed by oxidation of the ketols **10d** and **10i** thus formed. The three routes to compounds **4a–i** are shown in Scheme 1.

Irradiation of 2,2,4-trimethyl-1-(*o*-methylphenyl)pentane-1,3-dione **4d**, with a high-pressure mercury lamp, through a Pyrex filter, in hexane under nitrogen gave the benzocyclobutenol **11d**¹⁰ as the major product, along with the naphthalenone **12d** and the isobutyrophenone **13d** as minor products (see Scheme 2). The structure of the photoproducts was assigned on the basis of their analytical and spectral data and chemical evidence. The ¹H NMR spectrum of compound **11d** showed an AB-quartet (δ 3.04, 3.38, *J* 14 Hz) due to the two methylene protons of the four-membered ring. The IR spectrum showed hydroxy (3600 and 3500 cm^{-1}) and carbonyl (1700 cm^{-1}) absorptions. The carbonyl band appeared at rather lower wavenumber than that found for normal alkyl ketones because of intramolecular hydrogen bonding. The benzocyclobutenol **11d** readily underwent retro-aldol cleavage, probably through a six-membered cyclic mechanism.¹⁰ Hence, when compound **11d** was heated in a sealed glass tube at 150 °C for 3 h and the mixture was analysed by ¹H NMR spectroscopy, the quantitative formation of benzocyclobuten-1(*2H*)-one **14**¹³ and 2,4-dimethylpentan-3-one **9d** was observed (Scheme 3). The IR spectrum of compound **12d** showed the presence of hydroxy (3600 and 3500 cm^{-1}) and conjugated carbonyl (1690 cm^{-1}) groups. The ¹H NMR spectrum showed an AB-quartet (δ 2.96, 3.23, *J* 18 Hz) due to the two methylene protons. Compound **13d** showed two carbonyl IR absorptions at 1725 and 1690 cm^{-1} and two ¹³C NMR carbonyl peaks at δ_c 207.7 and 211.1.

In contrast to compound **4d**, irradiation of 2,2-dimethyl-1-(*o*-methylphenyl)butane-1,3-dione **4a** and 2,2-dimethyl-1-(*o*-methylphenyl)pentane-1,3-dione **4b** under the same conditions gave the corresponding naphthalenone **12a/12b** as the major product, along with the benzocyclobutenol **11a/11b**, and the isobutyrophenone **13a/13b** (see Scheme 2). Thus, *o*-methylphenyl 1,3-diketones **4** underwent photolysis to give benzocyclobutenols **11**, naphthalenones **12**, and isobutyrophenones **13**, but the product distribution was influenced by the C-3 substituent. Irradiation of *o*-methylphenyl 1,3-diketones **4c** and **4e–h** under the same conditions gave the corresponding benzocyclobutenols **11c** and **11e–h** and naphthalenones **12c** and **12e–h**. However, irradiation of compound **4i** under the same conditions gave a complex mixture of products.

The photochemical behaviour of species **4** in methanol is somewhat different from that in hexane. Irradiation of a methanolic solution of a dione **4a–h** with Pyrex-filtered light under nitrogen gave the corresponding benzocyclobutenol

Scheme 1 Reagents: i, PhNMeMgBr; ii, CrO₃; iii, MeIScheme 2 Conditions: *hν*

Scheme 3 Conditions: 150 °C

11a-h and naphthalenone **12a-h**. In all cases the naphthalenone was the major product. Irradiation of compound **4i** under the same conditions gave a complex mixture of products. However,

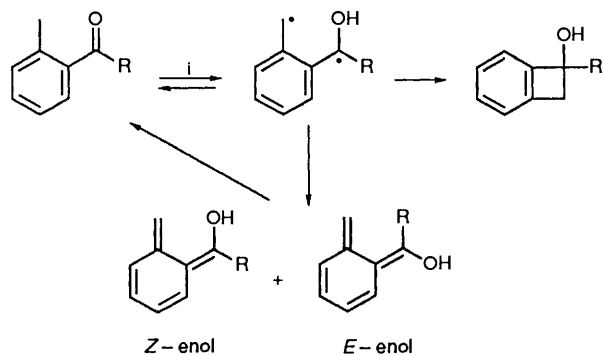
Table 1 Yields of photoproducts **11**, **12** and **13**

| Solvent | Diketone | Conversion (%) ^a | Yield (%) ^b | | |
|-------------------|-----------|-----------------------------|------------------------|----|----|
| | | | 11 | 12 | 13 |
| Hexane | 4a | 90 | 10 | 56 | 5 |
| MeOH | 4a | 67 | 2 | 88 | |
| Hexane | 4b | 93 | 8 | 45 | 6 |
| MeOH | 4b | 93 | trace | 66 | |
| Hexane | 4c | 57 | 28 | 32 | |
| MeOH | 4c | 77 | 3 | 85 | |
| Hexane | 4d | 75 | 45 | 3 | 2 |
| MeOH | 4d | 90 | 5 | 58 | |
| Hexane | 4e | 69 | 80 | 12 | |
| MeOH | 4e | 70 | 12 | 67 | |
| Hexane | 4f | 93 | 68 | 15 | |
| MeOH | 4f | 73 | 37 | 41 | |
| Hexane | 4g | 77 | 64 | | |
| MeOH | 4g | 90 | 4 | 52 | |
| Hexane | 4h | 68 | 34 | 23 | |
| MeOH | 4h | 86 | 3 | 36 | |
| MeOH ^c | 4i | 77 | | 51 | |

^a Based on the amount of consumed starting material. ^b Based on converted starting material. ^c Irradiation was carried out through a Pb(NO₃)₂ filter solution.

when dione **4i** was irradiated in methanol through a Pb(NO₃)₂ filter solution ($\lambda > 347$ nm) it gave the naphthalenone **12i** in 51% yield. Results of the photolysis of diones **4** are given in Table 1.

The triplet diradicals (enol triplets) from *o*-alkylphenyl ketones normally collapse to give back the parent ketones by direct hydrogen reversion or by a two-step process involving intermediate ground-state *Z*- and *E*-enols (Scheme 4).^{2d,14} In some cases, the diradicals cyclize to give benzocyclo-

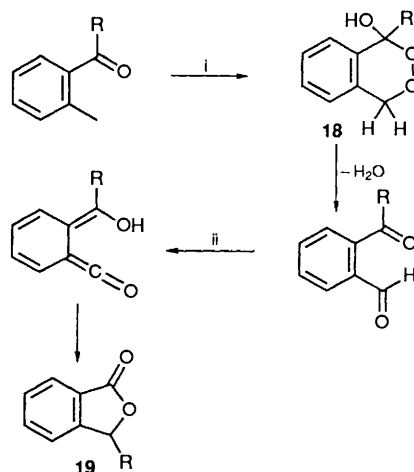
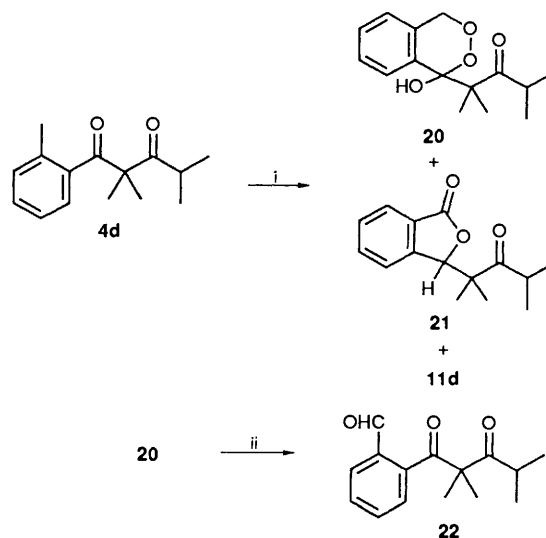
Scheme 4 Conditions: i, $h\nu$

butenols.^{3,4b} Benzocyclobutenols are formed from the diradical and not from the ground-state enol.¹⁵ The readily occurring formation of the benzocyclobutenol **11** from the dione **4** can be rationalized by intramolecular hydrogen bonding retarding the reketonization of the diradical **15** to the starting ketone **4**.

The formation of the naphthalenone **12** can be explained in terms of trapping of the arylmethyl radical site of the diradical **15** by the β -carbonyl group, followed by hydrogen shift or by cyclization of the enol *E*-**16** (see Scheme 5). It is known that the *Z*-enol from *o*-alkylphenyl ketones cannot be trapped by a variety of dienophiles, while the *E*-enol can be trapped.¹⁶ When compound **4d** was irradiated in hexane or methanol in the presence of diethyl maleate, ethyl crotonate, or dimethyl acetylenedicarboxylate there was no formation of trapping products. The photoproducts and their distribution were the same as those in the absence of dienophiles. Hornback reported that irradiation of dione **4a** in CD_3OD resulted in no deuterium incorporation into the aromatic methyl group.¹¹ The failure of trapping and the absence of deuterium incorporation seem to suggest that diones **4** do not form enols. The formation of compounds **12** seems to be rationalized by a mechanism in which the diradical **15** is trapped by the β -carbonyl group to produce the tetralin diradicals **17**, which would give products **12** by hydrogen shift, though the absence of deuterium incorporation does not necessarily rule out the existence of enols.^{4b,6b} The failure of trapping also does not rule out the existence of enols since rapid intramolecular trapping of the enol by the β -carbonyl group might predominate.

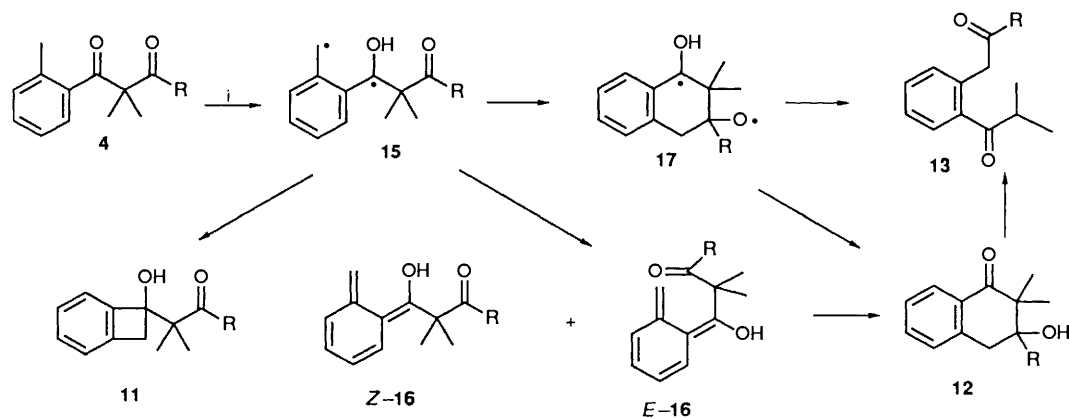
Molecular oxygen is an efficient quencher of diradicals.^{2b,2d,17} The photo-oxidation of *o*-methylphenyl ketones yields an unstable cyclic peroxide **18**, which undergoes further reaction to yield the phthalide **19**¹⁸ (Scheme 6).

Irradiation of compound **4d** in hexane bubbled with air gave the peroxide **20** and the phthalide **21** in 29 and 19% yield, respectively, along with a 16% yield of the benzocyclobutenol

Scheme 6 Conditions: i, $h\nu$, O_2 ; ii, $h\nu$ Scheme 7 Conditions: i, $h\nu$, O_2 ; ii, 80 °C

11d (Scheme 7). Irradiation in methanol under the same conditions gave compounds **20**, **21**, **11d** and **12d**, in 3, 4, 12 and 46% yield, respectively. The ^1H NMR spectrum of peroxide **20** showed an AB-quartet at δ 4.85 and 5.34 due to the two methylene protons. Compound **20** was dehydrated by heating at 80 °C to give the aldehyde **22**, which showed a ^1H NMR aldehyde peak at δ 9.97. The IR spectrum of the phthalide **21** showed a phthalide carbonyl peak at 1755 cm^{-1} . These results support the formation of cyclic ketones **12** via the diradicals **15**.

Compounds **13** may arise from the corresponding diradicals

Scheme 5 Conditions: i, $h\nu$

17 by radical cleavage or from cyclic ketones 12 by retro-aldol cleavage. However, since compounds 12 were stable on irradiation or on heating above their melting points, compounds 13 probably arise from diradicals 17. Compounds 13 were formed only in hexane solution. In methanolic solution, the radicals 17 abstract hydrogen from the solvent faster than C–C bond fission, such that products 13 do not arise.

The ratio of the benzocyclobutenol 11 to the naphthalenone 12 was greater in hexane than in methanol. In methanol, intramolecular hydrogen bonding in the diradical 15 has to compete with intermolecular hydrogen bonding with the solvent. The intermolecular hydrogen bonding causes an increase in population of the preferred conformation of diradical 15, leading to the cyclic diradical 17. The ratio of product 11 to product 12 was also affected by the C-3 substituent R. The ratio tends to increase with chain branching of R and with increasing size of R, both in hexane and in methanol. The strength of intramolecular hydrogen bonding in diradicals 15 is stronger with more highly branched R. The chemical shift of the hydroxy group in the ¹H NMR spectra of compounds 11 appeared at δ 3.82 in 11a, 3.89 in 11b, 3.92 in 11d and 4.19 in 11h. These values are related to the strength of intramolecular hydrogen bonding in the corresponding diradical 15. The hydroxy group appearing at lower field is hydrogen-bonded more strongly. Intramolecular trapping of species 15 by the β -carbonyl group seems to be difficult with a bulky R because of the sterically repulsive interaction. Thus, combination of the strength of the intramolecular hydrogen bonding in diradicals 15 and the size of C-3 substituent probably explains the observed ratio 11:12.

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. IR spectra were recorded 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 with CDCl₃ as solvent unless otherwise stated. Tetramethylsilane was used as internal standard and *J*-values are given in Hz. ¹³C NMR spectra were measured on a JEOL FX-90Q or a Bruker AM 400 spectrometer with CDCl₃ as solvent. Mass spectra were recorded with a Shimadzu GCMS-QP 1000 spectrometer. Column chromatography was performed with Merck Kieselgel 60. An Ushio 100 W high-pressure mercury lamp was used as the irradiation source.

Starting Materials.—Compounds 4a–c and 4e–g were prepared by the condensation of *o*-methylisobutyrophenone 1 with the corresponding aldehydes 2a–c and 2e–g with *N*-methylanilinomagnesium bromide as the condensing agent,¹² followed by Jones oxidation. Compounds 4d and 4i were prepared from *o*-tolualdehyde 8 and 2,4-dimethylpentan-3-one 9d or isobutyrophenone 9i by the same method. Compound 4h was prepared by the condensation of *o*-methylpropiophenone 5 with pivalaldehyde 2h, followed by Jones oxidation and methylation.

2,2-Dimethyl-1-(*o*-methylphenyl)butane-1,3-dione 4a had b.p. 75 °C at 0.5 mmHg; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1725 (alkyl ketone) and 1680 (aryl ketone); $\delta_{\text{H}}(60 \text{ MHz})$ 1.42 (6 H, s, CMe₂), 2.17 (3 H, s, COMe), 2.36 (3 H, s, ArMe) and 7.00–7.40 (4 H, m, ArH); $\delta_{\text{C}}(22.5 \text{ MHz})$ 20.1 (q, Me), 22.5 (q, CMe₂), 25.7 (q, Me), 62.2 (s, C-2), 124.8 (d), 125.5 (d), 129.9 (d), 131.3 (d), 136.4 (s) and 137.6 (s) (ArC) and 204.5 (s) and 206.6 (s) (2 × C=O).

2,2-Dimethyl-1-(*o*-methylphenyl)pentane-1,3-dione 4b had b.p. 91 °C at 0.4 mmHg; $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$ 1730 (alkyl ketone) and 1700 (aryl ketone); $\delta_{\text{H}}(90 \text{ MHz})$ 1.01 (3 H, t, *J* 7, CH₂Me), 1.39 (6 H, s, CMe₂), 2.36 (3 H, ArMe), 2.49 (2 H, q, *J* 7, CH₂Me)

and 7.00–7.30 (4 H, m, ArH); $\delta_{\text{C}}(22.5 \text{ MHz})$ 7.4 (q, Me), 19.6 (q, Me), 22.2 (q, CMe₂), 31.0 (t, CH₂), 61.6 (s, C-2), 124.5 (d), 125.3 (d), 129.5 (d), 131.0 (d), 136.1 (s) and 137.5 (s) (ArC) and 204.2 (s) and 209.0 (s) (2 × C=O).

2,2-Dimethyl-1-(*o*-methylphenyl)hexane-1,3-dione 4c had b.p. 90 °C at 0.4 mmHg; $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$ 1720 (alkyl ketone) and 1680 (aryl ketone); $\delta_{\text{H}}(90 \text{ MHz})$ 0.84 (3 H, t, *J* 7, CH₂CH₂Me), 1.41 (6 H, s, CMe₂), 1.55 (2 H, sext., *J* 7, CH₂CH₂Me), 2.37 (3 H, s, ArMe), 2.44 (2 H, t, *J* 7, CH₂CH₂Me) and 7.00–7.30 (4 H, m, ArH); $\delta_{\text{C}}(22.5 \text{ MHz})$ 13.0 (q, Me), 20.0 (q, Me), 22.5 (q, CMe₂), 16.9 (t) and 39.9 (t) (2 × CH₂), 61.9 (s, C-2), 124.7 (d), 125.8 (d), 129.8 (d), 131.3 (d), 136.5 (s) and 137.6 (s) (ArC) and 204.4 (s) and 208.7 (s) (2 × C=O).

2,2,4-Trimethyl-1-(*o*-methylphenyl)pentane-1,3-dione 4d had b.p. 115 °C at 0.7 mmHg; $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$ 1720 (alkyl ketone) and 1685 (aryl ketone); $\delta_{\text{H}}(60 \text{ MHz}; \text{CCl}_4)$ 0.95 (6 H, d, *J* 7, CHMe₂), 1.40 (6 H, s, CMe₂), 2.36 (3 H, s, ArMe), 2.93 (1 H, sept., *J* 7, CHMe₂) and 7.05–7.30 (4 H, m, ArH); $\delta_{\text{C}}(22.5 \text{ MHz})$ 19.8 (q, ArMe), 22.4 (q) and 22.6 (q) (CMe₂ and CHMe₂), 35.9 (d, C-4), 62.2 (s, C-2), 124.5 (d), 126.0 (d), 129.7 (d), 131.1 (d), 136.4 (s) and 137.7 (s) (ArC) and 204.0 (s) and 213.6 (s) (2 × C=O).

2,2,4-Trimethyl-1-(*o*-methylphenyl)hexane-1,3-dione 4e had b.p. 100 °C at 0.5 mmHg; $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$ 1720 (alkyl ketone) and 1685 (aryl ketone); $\delta_{\text{H}}(400 \text{ MHz})$ 0.84 (3 H, t, *J* 7, CH₂Me), 1.00 (3 H, d, *J* 7, CHMeEt), 1.37 (1 H, quint. of d, *J* 14 and 7) and 1.53 (1 H, quint. of d, *J* 14 and 7) (CH₂Me), 1.44 (3 H, s) and 1.46 (3 H, s) (CMe₂), 2.40 (3 H, s, ArMe), 2.86 (1 H, sext., *J* 7, CHMeEt) and 7.10–7.30 (4 H, m, ArH); $\delta_{\text{C}}(22.5 \text{ MHz})$ 11.1 (q), 17.2 (q), 19.9 (q), 22.6 (q) and 22.7 (q) (5 × Me), 26.7 (t, CH₂), 42.6 (d, C-4), 62.2 (s, C-2), 124.6 (d), 125.9 (d), 129.7 (d), 131.1 (d), 136.2 (s) and 138.1 (s) (ArC) and 204.5 (s) and 213.1 (s) (2 × C=O).

4-Ethyl-2,2-dimethyl-1-(*o*-methylphenyl)hexane-1,3-dione 4f had b.p. 100 °C at 0.5 mmHg; $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$ 1715 (alkyl ketone) and 1680 (aryl ketone); $\delta_{\text{H}}(400 \text{ MHz})$ 0.84 (6 H, t, *J* 7, 2 × CH₂Me), 1.46 (6 H, s, CMe₂), 1.44 (2 H, quint. of d, *J* 14 and 7) and 1.58 (2 H, quint. of d, *J* 14 and 7) (2 × CH₂Me), 2.34 (3 H, s, ArMe), 2.96 (1 H, quint., *J* 7, CHEt₂) and 7.13–7.33 (4 H, m, ArH); $\delta_{\text{C}}(22.5 \text{ MHz})$ 10.9 (q, ArMe), 19.6 (q) and 22.7 (q) [CMe₂ and CH(CH₂Me)₂], 23.8 (t, 2 × CH₂), 48.6 (d, C-4), 61.9 (s, C-2), 124.3 (d), 125.5 (d), 129.3 (d), 130.9 (d), 135.8 (s) and 138.4 (s) (ArC) and 204.6 (s) and 211.8 (s) (2 × C=O).

1-Cyclohexyl-2,2-dimethyl-3-(*o*-methylphenyl)propane-1,3-dione 4g had b.p. 110 °C at 0.3 mmHg; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1700 (cyclohexyl ketone) and 1670 (aryl ketone); $\delta_{\text{H}}(400 \text{ MHz})$ 1.05–1.80 (10 H, m, [CH₂]₅), 1.44 (6 H, s, CMe₂), 2.39 (3 H, s, ArMe), 2.73 (1 H, tt, *J* 12 and 4, CH) and 7.05–7.35 (4 H, m, ArH); $\delta_{\text{C}}(22.5 \text{ MHz})$ 20.0 (q, ArMe), 22.4 (q, CMe₂), 22.6 (t, 2.5 (t) and 29.8 (t) ([CH₂]₅), 46.6 (d, CH), 62.2 (s, C-2), 124.5 (d), 126.1 (d), 129.8 (d), 131.1 (d), 136.4 (s) and 137.8 (s) (ArC) and 204.0 (s) and 211.8 (s) (2 × C=O).

2,2,4,4-Tetramethyl-1-(*o*-methylphenyl)pentane-1,3-dione 4h had b.p. 95 °C at 0.3 mmHg; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1680 and 1665 (C=O); $\delta_{\text{H}}(60 \text{ MHz})$ 1.13 (9 H, s, Bu^t), 1.48 (6 H, s, CMe₂), 2.49 (3 H, s, ArMe) and 7.00–7.50 (4 H, m, ArH); $\delta_{\text{C}}(22.5 \text{ MHz})$ 21.5 (q, ArMe), 24.7 (q, CMe₂), 28.4 (q, Bu^t), 45.5 (s, C-4), 62.2 (C-2), 124.8 (d), 127.8 (d), 130.9 (d), 132.2 (d), 136.1 (s) and 139.1 (s) (ArC) and 201.4 (s) and 214.5 (s) (2 × C=O).

2,2-Dimethyl-1-(*o*-methylphenyl)-3-phenylpropane-1,3-dione 4i had b.p. 120 °C at 0.3 mmHg; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1680 (C=O); $\delta_{\text{H}}(90 \text{ MHz})$ 1.57 (6 H, s, CMe₂), 2.45 (3 H, s, ArMe) and 6.80–7.55 (7 H, m) and 7.75–7.95 (2 H, m) (ArH); $\delta_{\text{C}}(22.5 \text{ MHz})$ 20.9 (q, ArMe), 24.6 (q, CMe₂), 61.0 (s, C-2), 124.9 (d), 126.6 (d), 128.1 (d), 128.7 (d), 130.5 (d), 131.7 (d), 132.4 (d), 135.8 (s), 136.6 (s) and 138.2 (s) (ArC) and 198.6 (s) and 203.2 (s) (2 × C=O).

General Procedure for the Photolysis of Diones 4.—A solution

of a compound **4a-h** (ca. 600 mg) in hexane or methanol (120 cm³) was irradiated with a 100 W high-pressure mercury lamp through a Pyrex filter under nitrogen for 2–4 h. Photolysis of dione **4i** was carried out through an aqueous solution of Pb(NO₃)₂ (9 g dm⁻³) and KBr (750 g dm⁻³). The photo-products were isolated by silica gel column chromatography with hexane–ethyl acetate (6:1) as eluent.

3-(1'-Hydroxy-1',2'-dihydrobenzocyclobuten-1'-yl)-3-methylbutan-2-one **11a*** $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3500br (OH) and 1695 (C=O); $\delta_{\text{H}}(90 \text{ MHz})$ 1.22 (3 H, s) and 1.24 (3 H, s) (CMe₂), 2.24 (3 H, s, COMe), 3.08 (1 H) and 3.44 (1 H) (AB-system, *J* 15, 2'-H₂), 3.82 (1 H, s, OH) and 7.00–7.35 (4 H, m, ArH); $\delta_{\text{C}}(100 \text{ MHz})$ 20.9 (q), 21.3 (q) and 26.6 (q) (3 × Me), 42.6 (t, C-2'), 52.5 (s, CMe₂), 84.5 (s, C-1'), 122.0 (d), 123.5 (d), 127.2 (d), 129.3 (d), 142.2 (s) and 147.4 (s) (ArC) and 216.1 (s, C=O); *m/z* 118 (benzocyclobutenone, 100%).

2-(1'-Hydroxy-1',2'-dihydrobenzocyclobuten-1'-yl)-2-methylpentan-3-one **11b*** $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$ 3600 and 3500br (OH) and 1700 (C=O); $\delta_{\text{H}}(90 \text{ MHz})$ 1.04 (3 H, t, *J* 7, CH₂Me), 1.17 (3 H, s) and 1.20 (3 H, s) (CMe₂), 2.57 (2 H, q, *J* 7, CH₂Me), 3.00 (1 H) and 3.41 (1 H) (AB-system, *J* 15, 2'-H₂), 3.89 (1 H, s, OH) and 6.95–7.35 (4 H, m, ArH); $\delta_{\text{C}}(100 \text{ MHz})$ 7.9 (q), 20.9 (q) and 21.3 (q) (3 × Me), 31.4 (t, CH₂Me), 42.6 (t, C-2'), 52.2 (s, CMe₂), 84.7 (s, C-1'), 122.0 (d), 123.4 (d), 127.2 (d), 129.3 (d), 142.2 (s) and 147.5 (s) (ArC) and 218.6 (s, C=O); *m/z* 118 (benzocyclobutenone, 60%).

2-(1'-Hydroxy-1',2'-dihydrobenzocyclobuten-1'-yl)-2-methylhexan-3-one **11c*** $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$ 3500br (OH) and 1700 (C=O); $\delta_{\text{H}}(90 \text{ MHz})$ 0.91 (3 H, t, *J* 7, CH₂CH₂Me), 1.19 (3 H, s) and 1.21 (3 H, s) (CMe₂), 1.61 (2 H, sext., *J* 7, CH₂CH₂Me), 2.51 (2 H, t, *J* 7, CH₂CH₂Me), 3.01 (1 H) and 3.40 (1 H) (AB-system, *J* 15, 2'-H₂), 3.91 (1 H, s, OH) and 7.00–7.40 (4 H, m, ArH); $\delta_{\text{C}}(22.5 \text{ MHz})$ 13.6 (q), 20.7 (q) and 21.0 (q) (3 × Me), 17.1 (t), 40.1 (t) and 42.6 (t) (3 × CH₂), 52.3 (s, CMe₂), 84.3 (s, C-1'), 122.2 (d), 123.4 (d), 127.1 (d), 129.2 (d), 142.2 (s) and 147.6 (s) (ArC) and 217.6 (s, C=O); *m/z* 118 (benzocyclobutenone, 100%).

2-(1'-Hydroxy-1',2'-dihydrobenzocyclobuten-1'-yl)-2,4-dimethylpentan-3-one **11d**.¹⁰ M.p. 37 °C (from pentane) (Found: C, 77.4; H, 8.7. Calc. for C₁₅H₂₀O₂: C, 77.6; H, 8.7%); $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$ 3600 and 3500br (OH) and 1700 (C=O); $\delta_{\text{H}}(90 \text{ MHz})$ 1.08 (6 H, d, *J* 7, CHMe₂), 1.21 (3 H, s) and 1.24 (3 H, s) (CMe₂), 3.12 (1 H, sept., *J* 7, CHMe₂), 3.04 (1 H) and 3.38 (1 H) (AB-system, *J* 14, 2'-H₂), 3.92 (1 H, s, OH) and 7.00–7.30 (4 H, m, ArH); $\delta_{\text{C}}(22.5 \text{ MHz})$ 19.5 (q), 19.6 (q), 19.8 (q) and 20.3 (q) (4 × Me), 34.9 (d, CHMe₂), 42.1 (t, C-2'), 52.7 (s, CMe₂), 84.2 (s, C-1'), 121.7 (d), 122.9 (d), 126.7 (d), 128.8 (d), 141.8 (s) and 147.6 (s) (ArC) and 221.3 (s, C=O); *m/z* 118 (benzocyclobutenone, 100%).

2-(1'-Hydroxy-1',2'-dihydrobenzocyclobuten-1'-yl)-2,4-dimethylhexan-3-one **11e*** (1:1 mixture of two stereoisomers). $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$ 3550br (OH) and 1700 (C=O); $\delta_{\text{H}}(400 \text{ MHz})$ 0.86 (1.5 H, t, *J* 7) and 0.89 (1.5 H, t, *J* 7) (CH₂Me), 1.07 (1.5 H, d, *J* 7) and 1.08 (1.5 H, d, *J* 7) (CHMeEt), 1.21 (1.5 H, s), 1.23 (1.5 H, s), 1.24 (1.5 H, s) and 1.25 (1.5 H, s) (CMe₂), 1.38 (1 H, quint. of d, *J* 14 and 7) and 1.68 (1 H, quint. of d, *J* 14 and 7) (CH₂Me), 2.93 (1 H, sext., *J* 7, CHMeEt), 3.09 (1 H, A of AB, *J* 14), 3.38 (0.5 H, B of AB, *J* 14) and 3.40 (0.5 H, B of AB, *J* 14) (2'-H₂), 4.03 (0.5 H, s) and 4.10 (0.5 H, s) (OH) and 7.10–7.30 (4 H, m, ArH); $\delta_{\text{C}}(100 \text{ MHz})$ 12.0 (q), 17.8 (q), 17.9 (q), 20.0 (q), 20.2 (q), 20.4 (q), 20.7 (q) and 20.8 (q) (4 × Me), 27.1 (t) and 27.2 (t) (CH₂Me), 42.1 (d, CHMeEt), 42.2 (t, C-2'), 52.9 (s, CMe₂),

84.4 (s, C-1'), 121.9 (d), 122.0 (d), 123.3 (d), 127.0 (d), 129.0 (d), 129.1 (d), 142.0 (s), 142.1 (s), 147.5 (s) and 147.6 (s) (ArC) and 221.9 (s) and 222.1 (s) (C=O); *m/z* 118 (benzocyclobutenone, 41%).

4-Ethyl-2-(1'-hydroxy-1',2'-dihydrobenzocyclobuten-1'-yl)-2-methylhexan-3-one **11f*** $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$ 3500br (OH) and 1685 (C=O); $\delta_{\text{H}}(400 \text{ MHz})$ 0.86 (3 H, t, *J* 7) and 0.90 (3 H, t, *J* 7) (2 × CH₂Me), 1.21 (3 H, s) and 1.22 (3 H, s) (CMe₂), 1.40–1.52 (2 H, m) and 1.58–1.70 (2 H, m) (2 × CH₂Me), 2.79 (1 H, quint., *J* 7, CHEt₂), 3.09 (1 H) and 3.38 (1 H) (AB-system, *J* 15, 2'-H₂), 4.15 (1 H, s, OH) and 7.10–7.30 (4 H, m, ArH); $\delta_{\text{C}}(100 \text{ MHz})$ 11.9 (q), 12.0 (q), 20.2 (q) and 20.7 (q) (4 × Me), 24.8 (t, 2 × CH₂Me), 42.2 (t, C-2'), 49.1 (d, CHEt₂), 52.7 (s, CMe₂), 84.5 (s, C-1'), 121.9 (d), 123.2 (d), 127.0 (d), 129.0 (d), 142.1 (s) and 147.6 (s) (ArC) and 221.2 (s, C=O); *m/z* 118 (benzocyclobutenone, 41%).

1-Cyclohexyl-2-(1'-hydroxy-1',2'-dihydrobenzocyclobuten-1'-yl)-2-methylpropan-1-one **11g*** $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3500br (OH) and 1685 (C=O); $\delta_{\text{H}}(400 \text{ MHz})$ 1.22 (3 H, s) and 1.24 (3 H, s) (CMe₂), 1.15–1.85 (10 H, [CH₂]₅), 2.85 (1 H, tt, *J* 12 and 4, CHC₅H₁₀), 3.08 (1 H) and 3.38 (1 H) (AB-system, *J* 15, 2'-H₂), 4.01 (1 H, s, OH) and 7.10–7.30 (4 H, m, ArH); $\delta_{\text{C}}(22.5 \text{ MHz})$ 20.0 (q) and 20.4 (q) (CMe₂), 25.4 (t, 3 × CH₂), 29.5 (t, 2 × CH₂), 42.2 (t, C-2'), 45.9 (d, CH), 52.7 (s, CMe₂), 84.3 (s, C-1'), 121.8 (d), 123.0 (d), 126.8 (d), 128.8 (d), 142.0 (s) and 147.6 (s) (ArC) and 220.2 (s, C=O); *m/z* 118 (benzocyclobutenone, 33%).

2-(1'-Hydroxy-1',2'-dihydrobenzocyclobuten-1'-yl)-2,4,4-trimethylpentan-3-one **11h*** $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$ 3500br (OH) and 1670 (C=O); $\delta_{\text{H}}(90 \text{ MHz})$ 1.29 (9 H, s, Bu[†]), 1.32 (3 H, s) and 1.35 (3 H, s) (CMe₂), 3.03 (1 H) and 3.37 (1 H) (AB-system, *J* 15, 2'-H₂), 4.19 (1 H, s, OH) and 7.00–7.40 (4 H, m, ArH); $\delta_{\text{C}}(100 \text{ MHz})$ 21.1 (q) and 21.7 (q) (CMe₂), 28.4 (q, CMe₃), 42.7 (t, C-2'), 46.4 (s, CMe₃), 53.9 (s, CMe₂), 86.5 (s, C-1'), 122.2 (d), 123.3 (d), 127.1 (d), 129.1 (d), 142.5 (s) and 147.7 (s) (ArC) and 221.9 (s, C=O).

3-Hydroxy-2,2,3-trimethyl-3,4-dihydronaphthalen-1(2H)-one **12a**¹¹ had m.p. 67–69 °C (from hexane) (Found: C, 76.3; H, 7.7. Calc. for C₁₃H₁₆O₂: C, 76.4; H, 7.9%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3600 and 3450br (OH) and 1680 (C=O); $\delta_{\text{H}}(90 \text{ MHz})$ 1.16 (3 H, s), 1.26 (3 H, s) and 1.30 (3 H, s) (3 × Me), 1.83 (1 H, s, OH), 3.00 (1 H) and 3.21 (1 H) (AB-system, *J* 16, 4-H₂) and 7.00–7.60 (3 H, m) and 7.85–8.05 (1 H, m) (ArH); $\delta_{\text{C}}(100 \text{ MHz})$ 16.0 (q), 20.7 (q) and 24.5 (q) (3 × Me), 40.9 (t, C-4), 50.9 (s, C-2), 75.5 (s, C-3), 126.8 (d), 127.7 (d), 129.1 (d), 130.6 (s), 133.4 (d) and 139 (s) (ArC) and 202.3 (s, C=O); *m/z* 204 (M⁺, 15%) and 161 (100).

3-Ethyl-3-hydroxy-2,2-dimethyl-3,4-dihydronaphthalen-1(2H)-one **12b** had m.p. 116–118 °C (from hexane) (Found: C, 77.2; H, 8.3. C₁₄H₁₈O₂ requires C, 77.0; H, 8.3%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3600 and 3500br (OH) and 1680 (C=O); $\delta_{\text{H}}(90 \text{ MHz})$ 0.95 (3 H, t, *J* 7, CH₂Me), 1.16 (3 H, s) and 1.26 (3 H, s) (CMe₂), 1.35–1.85 (3 H, m, CH₂Me and OH), 3.10 (2 H, s, 4-H₂)[†] and 7.15–7.62 (3 H, m) and 7.95–8.12 (1 H, m) (ArH); $\delta_{\text{C}}(22.5 \text{ MHz})$ 7.2 (q, CH₂Me), 18.3 (q) and 19.7 (q) (CMe₂), 27.7 (t, CH₂Me), 35.6 (t, C-4), 51.5 (s, C-2), 76.7 (s, C-3), 126.6 (d), 127.4 (d), 129.0 (d), 130.7 (s), 133.2 (d) and 138.9 (s) (ArC) and 202.6 (s, C=O); *m/z* 218 (M⁺, 17%) and 175 (100).

3-Hydroxy-2,2-dimethyl-3-propyl-3,4-dihydronaphthalen-1(2H)-one **12c** had m.p. 76–77 °C (from hexane) (Found: C, 77.4; H, 8.5. C₁₅H₂₀O₂ requires C, 77.6; H, 8.7%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3600 and 3500br (OH) and 1680 (C=O); $\delta_{\text{H}}(400 \text{ MHz})$ 0.93 (3 H, t, *J* 7, CH₂CH₂Me), 1.18 (3 H, s) and 1.27 (3 H, s) (CMe₂), 1.35–1.60 (4 H, m, CH₂CH₂Me), 1.59 (1 H, s, OH), 3.13 (2 H, s, 4-H₂)[†] and 7.23 (1 H, d, *J* 8), 7.33 (1 H, t, *J* 8), 7.49 (1 H, t, *J* 8) and 8.03 (1 H, d, *J* 8) (ArH); $\delta_{\text{C}}(100 \text{ MHz})$ 14.6 (q), 18.3 (q) and 20.0 (q) (3 × Me), 16.3 (t), 36.6 (t) and 37.9 (t) (3 × CH₂), 51.6 (s, C-2), 77.0 (s, C-3), 126.6 (d), 127.7 (d), 129.1 (d), 130.9 (s), 133.4 (d) and 138.9 (s) (ArC) and 202.4 (s, C=O).

* Compounds **11a-c** and **11e-h** were obtained as thermally labile oils, and their complete purification by distillation could not be achieved.

† The 4-H₂ protons of compounds **12** appeared as an AB-system except for **12b** and **12c**.

3-Hydroxy-3-isopropyl-2,2-dimethyl-3,4-dihydronaphthalen-1(2H)-one 12d had m.p. 85 °C (from pentane) (Found: C, 77.5; H, 8.7. $C_{15}H_{20}O_2$ requires C, 77.6; H, 8.7%); $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$ 3600 and 3500br (OH) and 1690 (C=O); $\delta_{\text{H}}(90 \text{ MHz})$ 0.70 (3 H, d, *J* 7) and 1.04 (3 H, d, *J* 7) (CHMe_2), 1.24 (3 H, s) and 1.27 (3 H, s) (CMe_2), 1.68 (1 H, s, OH), 2.05 (1 H, sept., *J* 7, CHMe_2), 2.96 (1 H) and 3.23 (1 H) (AB-system, *J* 18, 4- H_2), 7.05–7.50 (4 H, m, ArH); $\delta_{\text{C}}(22.5 \text{ MHz})$ 17.8 (q, 2-Me), 19.2 (q, CHMe_2), 20.3 (q, 2-Me), 33.0 (t, C-4), 35.2 (d, CHMe_2), 51.4 (s, C-2), 78.4 (s, C-3), 126.2 (d), 127.0 (d), 128.4 (d), 131.2 (s), 132.9 (d) and 139.4 (s) (ArC) and 202.6 (s, C=O); *m/z* 232 (M^+ , 17%) and 189 ($\text{M} - \text{Pr}^+$, 100).

3-s-Butyl-3-hydroxy-2,2-dimethyl-3,4-dihydronaphthalen-1(2H)-one 12e had m.p. 111–112 °C (from hexane) (Found: C, 77.9; H, 8.7. $C_{16}H_{22}O_2$ requires C, 78.0; H, 9.0%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3600 and 3450br (OH) and 1680 (C=O); $\delta_{\text{H}}(400 \text{ MHz})$ 0.69 (3 H, d, *J* 7, CHMe), 0.94 (3 H, t, *J* 7, CH_2Me), 1.00–1.15 (1 H, m) and 1.85–1.97 (1 H, m) (CH_2Me), 1.27 (3 H, s) and 1.29 (3 H, s) (CMe_2), 1.54 (1 H, s, OH), 1.57–1.68 (1 H, m, CHMeEt), 3.03 (1 H) and 3.25 (1 H) (AB-system, *J* 18, 4- H_2) and 7.21 (1 H, d, *J* 8), 7.30 (1 H, t, *J* 8), 7.45 (1 H, t, *J* 8) and 8.00 (1 H, d, *J* 8) (ArH); $\delta_{\text{C}}(100 \text{ MHz})$ 12.9 (q), 15.5 (q), 19.4 (q) and 20.4 (q) (4 × Me), 24.2 (t, CH_2Me), 33.8 (t, C-4), 43.6 (d, CHMeEt), 51.6 (s, C-2), 79.1 (s, C-3), 126.7 (d), 127.4 (d), 128.6 (d), 131.5 (s), 133.2 (d) and 139.3 (s) (ArC) and 202.6 (s, C=O); *m/z* 246 (M^+ , 10%) and 203 (100).

3-(1-Ethylpropyl)-3-hydroxy-2,2-dimethyl-3,4-dihydronaphthalen-1(2H)-one 12f had m.p. 85–88 °C (from hexane) (Found: C, 78.2; H, 9.1. $C_{17}H_{24}O_2$ requires C, 78.4; H, 9.3%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3600 and 3500br (OH) and 1680 (C=O); $\delta_{\text{H}}(400 \text{ MHz})$ 0.81 (3 H, m at ordinary temperature, but t at 60 °C, CH_2Me), 1.01 (3 H, t, *J* 7, CH_2Me), 1.25 (3 H, s) and 1.29 (3 H, s) (CMe_2), 1.24–1.41 (3 H, m) and 1.76–1.87 (1 H, m) (2 × CH_2Me), 1.48–1.57 (2 H, m, OH and CHEt_2), 3.06 (1 H) and 3.28 (1 H) (AB-system, *J* 18, 4- H_2) and 7.20 (1 H, d, *J* 8), 7.30 (1 H, t, *J* 8), 7.46 (1 H, t, *J* 8) and 8.00 (1 H, d, *J* 8) (ArH); $\delta_{\text{C}}(100 \text{ MHz})$ 12.9 (q), 14.9 (q), 19.6 (q) and 20.8 (q) (4 × Me), 22.3 (t) and 24.4 (t) (2 × CH_2Me), 34.7 (t, C-4), 49.5 (d, CHEt_2), 51.8 (s, C-2), 79.7 (s, C-3), 126.6 (d), 127.4 (d), 128.7 (d), 131.3 (s), 133.2 (d) and 139.4 (s) (ArC) and 202.6 (s, C=O); *m/z* 260 (M^+ , 14%) and 71 (100).

3-Cyclohexyl-3-hydroxy-2,2-dimethyl-3,4-dihydronaphthalen-1(2H)-one 12g had m.p. 112–113 °C (from hexane) (Found: C, 79.5; H, 8.7. $C_{18}H_{24}O_2$ requires C, 79.4; H, 8.9%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3600 and 3450 (OH) and 1675 (C=O); $\delta_{\text{H}}(90 \text{ MHz})$ 1.24 (6 H, s, CMe_2), 1.79 (1 H, s, OH), 0.85–2.20 (11 H, m, C_6H_{11}), 3.00 (1 H) and 3.25 (1 H) (AB-system, *J* 18, 4- H_2) and 7.05–7.60 (3 H, m) and 7.85–8.05 (1 H, m) (ArH); $\delta_{\text{C}}(100 \text{ MHz})$ 26.8 (q) and 27.2 (q) (CMe_2), 26.3 (t), 27.6 (t) and 29.9 (t) (5 × CH_2), 34.4 (t, C-4), 46.8 (d, CH), 51.4 (s, C-2), 78.4 (s, C-3), 126.7 (d), 127.4 (d), 128.5 (d), 131.5 (s), 133.3 (d) and 139.5 (s) (ArC) and 202.7 (s, C=O).

3-t-Butyl-3-hydroxy-2,2-dimethyl-3,4-dihydronaphthalen-1(2H)-one 12h had m.p. 102–103 °C (from pentane) (Found: C, 78.1; H, 8.8. $C_{16}H_{22}O_2$ requires C, 78.0; H, 9.0%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3600 and 3500br (OH) and 1680 (C=O); $\delta_{\text{H}}(90 \text{ MHz})$ 1.04 (9 H, s, CMe_3), 1.24 (3 H, s) and 1.34 (3 H, s) (CMe_2), 2.32 (1 H, s, OH), 3.08 (1 H) and 3.38 (1 H) (AB-system, *J* 18, 4- H_2) and 7.10–7.55 (3 H, m) and 7.85–8.00 (1 H, m) (ArH); $\delta_{\text{C}}(22.5 \text{ MHz})$ 21.9 (q) and 22.9 (q) (CMe_2), 28.2 (q, CMe_3), 36.5 (t, C-4), 40.4 (s, CMe_3), 53.2 (s, C-2), 80.3 (s, C-3), 126.2 (d), 126.9 (d), 128.6 (d), 131.2 (s), 132.7 (d) and 139.5 (s) (ArC) and 202.2 (s, C=O).

3-Hydroxy-2,2-dimethyl-3-phenyl-3,4-dihydronaphthalen-1(2H)-one 12i had m.p. 149–150 °C (from hexane–benzene) (Found: C, 81.3; H, 6.9. $C_{18}H_{18}O_2$ requires C, 81.2; H, 6.8%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3600 and 3450 (OH) and 1685 (C=O); $\delta_{\text{H}}(60 \text{ MHz})$ 1.10 (6 H, s, CMe_2), 1.82 (1 H, s, OH), 3.04 (1 H) and 4.10 (1 H) (AB-system, *J* 18, 4- H_2) and 7.10–7.70 (8 H, m) and 7.95–

8.20 (1 H, m) (ArH); $\delta_{\text{C}}(100 \text{ MHz})$ 17.9 (q) and 22.3 (q) (CMe_2), 39.7 (t, C-4), 51.0 (s, C-2), 79.7 (s, C-4), 126.4 (d), 126.8 (d), 127.5 (d), 127.7 (d), 127.8 (d), 129.2 (d), 133.3 (d), 130.9 (s), 138.6 (s) and 143.0 (s) (ArC) and 201.6 (s, C=O).

o-Acetylisobutyrophenone 13a had b.p. 80 °C at 0.4 mmHg (Found: C, 76.2; H, 7.9. $C_{13}H_{16}O_2$ requires C, 76.4; H, 7.9%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1700 (alkyl ketone) and 1675 (aryl ketone); $\delta_{\text{H}}(90 \text{ MHz})$ 1.17 (6 H, d, *J* 7, CHMe_2), 2.25 (3 H, s, COMe), 3.49 (1 H, sept., *J* 7, CHMe_2), 3.93 (2 H, s, CH_2) and 7.10–7.55 (3 H, m) and 7.70–7.90 (1 H, m) (ArH); $\delta_{\text{C}}(100 \text{ MHz})$ 18.9 (q, CHMe_2), 29.9 (q, COMe), 37.3 (d, CHMe_2), 49.2 (t, CH_2), 127.1 (d), 128.9 (d), 131.7 (d), 133.0 (d), 135.4 (s) and 136.5 (s) (ArC) and 205.8 (s) and 207.5 (s) (2 × C=O).

o-(2-Oxobutyl)isobutyrophenone 13b had b.p. 125 °C at 0.5 mmHg (Found: C, 76.8; H, 8.3. $C_{14}H_{18}O_2$ requires C, 77.0; H, 8.3%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1720 (alkyl ketone) and 1680 (aryl ketone); $\delta_{\text{H}}(90 \text{ MHz})$ 1.05 (3 H, t, *J* 7, CH_2Me), 1.13 (6 H, d, *J* 7, CHMe_2), 2.57 (2 H, q, *J* 7, CH_2Me), 3.45 (1 H, sept., *J* 7, CHMe_2), 3.91 (2 H, s, CH_2) and 7.10–7.55 (3 H, m) and 7.70–7.85 (1 H, m) (ArH); $\delta_{\text{C}}(22.5 \text{ MHz})$ 7.6 (q, CH_2Me), 18.7 (q, CHMe_2), 35.4 (t, CH_2Me), 37.3 (d, CHMe_2), 47.8 (t, ArCH_2), 126.7 (d), 128.4 (d), 131.2 (d), 132.7 (d), 135.1 (s) and 136.8 (s) (ArC) and 207.5 (s) and 207.8 (s) (2 × C=O).

o-(3-Methyl-2-oxobutyl)isobutyrophenone 13d had b.p. 100 °C at 0.3 mmHg (Found: C, 77.3; H, 8.6. $C_{15}H_{20}O_2$ requires C, 77.6; H, 8.7%); $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$ 1725 (alkyl ketone) and 1690 (aryl ketone); $\delta_{\text{H}}(90 \text{ MHz})$ 1.14 (12 H, d, *J* 7, 2 × CHMe_2), 2.78 (1 H, sept., *J* 7, CHMe_2), 3.41 (1 H, sept., *J* 7, CHMe_2), 4.08 (2 H, s, CH_2) and 7.04–7.48 (3 H, m) and 7.55–7.75 (1 H, m) (ArH); $\delta_{\text{C}}(22.5 \text{ MHz})$ 18.2 (q, CHMe_2), 18.9 (q, CHMe_2), 37.6 (d, CHMe_2), 40.5 (d, CHMe_2), 46.0 (t, CH_2), 126.7 (d), 128.4 (d), 131.2 (d), 132.8 (d), 135.3 (s) and 137.2 (s) (ArC) and 207.7 (s) and 211.1 (s) (2 × C=O).

Pyrolysis of Compound 11d.—Compound 11d was placed in a sealed glass tube and heated at 150 °C for 3 h. ^1H NMR analysis of the mixture revealed the quantitative formation of benzocyclobuten-1(2H)-one 14¹³ and 2,4-dimethylpentan-3-one 9d. The benzocyclobutenone 14 was separated by GC and identified by its spectral data.

Photo-oxygenation of Compound 4d.—A solution of dione 4d (600 mg) in air-bubbled hexane (120 cm³) was irradiated with a 100 W high-pressure mercury lamp through a Pyrex filter for 45 min. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel, and eluted with hexane–ethyl acetate (6:1), to give the peroxide 20 (52 mg, 29% based on converted starting material), the phthalide 21 (35 mg, 19%) and the benzocyclobutenol 11d (29 mg, 16%), with recovery of 420 mg of unchanged substrate 4d.

Irradiation of dione 4d (602 mg) in methanol (120 cm³) under the same conditions for 13 h gave peroxide 20 (15 mg, 3%), the phthalide 21 (16 mg, 4%), the alcohol 11d (54 mg, 12%) and ketone 12d (203 mg, 46%) with recovery of 16 mg of unchanged substrate 4d. The peroxide 20 (64 mg) in CDCl_3 (0.5 cm³) was placed in an NMR tube and heated at 40 °C for 1 h. The ^1H NMR spectrum showed the appearance of an aldehyde peak at δ 9.97. The tube was heated at 80 °C for further 5 min. After removal of the solvent, the residue was chromatographed on silica gel with hexane–ethyl acetate (2:1) as eluent to give the aldehyde 22 (21 mg, 33%).

2-(1-Hydroxy-1,4-dihydrobenzo[*d*][1,2]dioxin-1-yl)-2,4-dimethylpentan-3-one 20 had m.p. 40 °C (decomp.) (from hexane–diethyl ether); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3400br (OH) and 1680 (C=O); $\delta_{\text{H}}(400 \text{ MHz})$ 1.09 (3 H, d, *J* 7) and 1.15 (3 H, d, *J* 7) (CHMe_2), 1.10 (3 H, s) and 1.46 (3 H, s) (CMe_2), 3.18 (1 H, sept., *J* 7, CHMe_2), 4.85 (1 H) and 5.34 (1 H) (AB-system, *J* 15, CH_2), 6.24 (1 H, s, OH) and 7.10–7.60 (4 H, m, ArH); $\delta_{\text{C}}(100 \text{ MHz})$ 19.0 (q),

19.8 (q), 20.7 (q) and 23.5 (q) ($4 \times \text{Me}$), 36.2 (d, CHMe_2), 53.5 (s, CMe_2), 71.7 (t, C-4), 105.5 (s, C-1), 124.5 (d), 126.7 (d), 127.1 (d), 128.0 (d), 132.2 (s) and 134.4 (s) (ArC) and 222.7 (s, C=O).

3-(1,1,3-Trimethyl-2-oxobutyl)phthalide **21** had m.p. 91.5 °C (from pentane) (Found: C, 73.2; H, 7.4. $\text{C}_{15}\text{H}_{18}\text{O}_3$ requires C, 73.2; H, 7.4%); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1760 (phthalide) and 1700 (side-chain C=O); $\delta_{\text{H}}(90 \text{ MHz})$ 0.97 (3 H, s) and 1.33 (3 H, s) (CMe_2), 1.06 (3 H, d, J 7) and 1.16 (3 H, d, J 7) (CHMe_2), 3.09 (1 H, sept., J 7, CHMe_2), 5.87 (1 H, s, 3-H) and 7.15–7.95 (4 H, m, ArH); $\delta_{\text{C}}(22.5 \text{ MHz})$ 17.8 (q), 19.5 (q), 19.7 (q) and 21.8 (q) ($4 \times \text{Me}$), 34.9 (d, CHMe_2), 52.0 (s, CMe_2), 84.3 (d, C-3), 123.6 (d), 125.4 (d), 126.9 (s), 129.0 (d), 133.8 (d) and 147.6 (s) (ArC), 170.0 (s, ring C=O) and 217.3 (s, side-chain C=O).

o-(2,2,4-Trimethyl-1,3-dioxopentyl)benzaldehyde **22** had $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 1705 and 1692 (C=O); $\delta_{\text{H}}(400 \text{ MHz})$ 1.08 (6 H, d, J 7, CHMe_2), 1.51 (6 H, s, CMe_2), 3.29 (1 H, sept., J 7, CHMe_2), 7.30–7.90 (4 H, m, ArH) and 9.97 (1 H, s, CHO); $\delta_{\text{C}}(100 \text{ MHz})$ 20.5 (q, $2 \times \text{Me}$), 22.5 (q, $2 \times \text{Me}$), 35.6 (d, CHMe_2), 62.9 (s, CMe_2), 126.5 (d), 130.2 (d), 131.8 (d), 133.4 (d), 135.0 (s) and 140.9 (s) (ArC), 191.4 (d, CHO) and 205.6 (s) and 214.8 (s) ($2 \times \text{C=O}$).

References

- (a) P. G. Sammes, *Tetrahedron*, 1976, **32**, 405; (b) P. J. Wagner, *Rearrangement in Ground and Excited States*, ed. P. de Mayo, Academic, New York, 1980, vol. 3, p. 381; (c) J. C. Scaiano, *Acc. Chem. Res.*, 1982, **15**, 252.
- (a) E. F. Zwicker, L. I. Grossweiner and N. C. Yang, *J. Am. Chem. Soc.*, 1963, **85**, 2671; (b) G. Porter and M. F. Tchir, *J. Chem. Soc. A*, 1971, 3772; (c) P. J. Wagner and C.-P. Chen, *J. Am. Chem. Soc.*, 1976, **98**, 239; (d) R. Haag and J. Wirz, *Helv. Chim. Acta*, 1977, **60**, 2595.
- T. Matsuura and Y. Kitaura, *Tetrahedron*, 1969, **25**, 4487; Y. Ito, Y. Umehara, T. Hijiya, Y. Yamada and T. Matsuura, *J. Am. Chem. Soc.*, 1980, **102**, 5917; Y. Ito, H. Nishimura, Y. Umehara, Y. Yamada, M. Tone and T. Matsuura, *J. Am. Chem. Soc.*, 1983, **105**, 1590.
- (a) N. C. Yang and C. Rivas, *J. Am. Chem. Soc.*, 1961, **83**, 2213; (b) B. J. Arnold, S. M. Mellows, P. G. Sammes and T. W. Wallace, *J. Chem. Soc., Perkin Trans. 1*, 1974, 401; (c) M. Pfau, S. Combrisson, J. E. Rowe, Jr. and N. D. Heindel, *Tetrahedron*, 1978, **34**, 3459; (d) M. Pfau, J. E. Rowe, Jr. and N. D. Heindel, *Tetrahedron*, 1978, **34**, 3469.
- T. L. Burkoth and E. F. Ullman, *Tetrahedron Lett.*, 1970, 145; R. Bishop and N. K. Hamer, *J. Chem. Soc. C*, 1970, 1193; Y. Ogata and K. Takagi, *J. Org. Chem.*, 1974, **39**, 1385; N. K. Hamer, *J. Chem. Soc., Perkin Trans. 1*, 1979, 508.
- (a) V. B. Rao, S. Wolff and W. C. Agosta, *J. Am. Chem. Soc.*, 1985, **107**, 521; (b) W. C. Agosta, R. A. Caldwell, J. Jay, L. J. Johnston, B. R. Venepalli, J. C. Scaiano, M. Singh and S. Wolff, *J. Am. Chem. Soc.*, 1987, **109**, 3050.
- W. R. Bergmark, C. Barnes, J. Clark, S. Paparian and S. Marynowski, *J. Org. Chem.*, 1985, **50**, 5612.
- P. J. Wagner, *J. Am. Chem. Soc.*, 1967, **89**, 5898; T. Hasegawa, Y. Arata, M. Endoh and M. Yoshioka, *Tetrahedron*, 1985, **41**, 1667.
- W. A. Henderson, Jr. and E. F. Ullman, *J. Am. Chem. Soc.*, 1965, **87**, 5424.
- M. Yoshioka, M. Arai, K. Nishizawa and T. Hasegawa, *J. Chem. Soc., Chem. Commun.*, 1990, 374.
- J. M. Hornback, M. L. Poundstone, B. Vadlamani, S. M. Graham, J. Gabay and S. T. Patton, *J. Org. Chem.*, 1988, **53**, 5597.
- A. T. Nielsen, C. Gibbons and C. A. Zimmerman, *J. Am. Chem. Soc.*, 1951, **73**, 4696.
- M. P. Cava and K. Muth, *J. Am. Chem. Soc.*, 1960, **82**, 652.
- P. K. Das, M. V. Encinas, R. D. Small, Jr. and J. C. Scaiano, *J. Am. Chem. Soc.*, 1979, **101**, 6965.
- M.-C. Carré, M.-L. Viriot-Villaume and P. Caubère, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2542.
- F. Nerdel and W. Brodowski, *Chem. Ber.*, 1968, **101**, 1398; E. Block and R. Stevenson, *J. Chem. Soc., Perkin Trans. 1*, 1973, 308.
- D. M. Findlay and M. F. Tchir, *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 1096; Y. Ito, H. Nishimura, H. Shimizu and T. Matsuura, *J. Chem. Soc. Chem. Commun.*, 1983, 1110.
- P. Yates, A. C. Mackay and F. X. Garneau, *Tetrahedron Lett.*, 1968, 5389; M. Julliard and M. Pfau, *J. Chem. Soc., Chem. Commun.*, 1976, 184.

Paper 0/04029K

Received 5th September 1990

Accepted 23rd October 1990