

Preparation of Benzocyclobutenones *via* the Photochemical Cyclization of 1-(*ortho*-Alkylaryl)-2,2,4-trimethylpentane-1,3-diones

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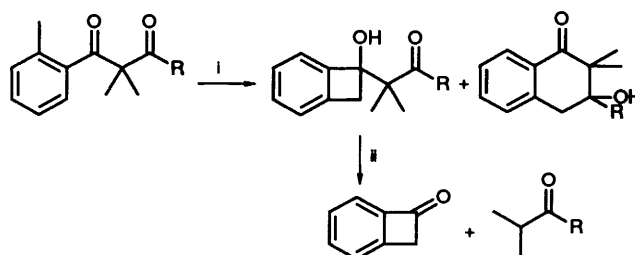
Irradiation of 1-(*ortho*-methylaryl)- and 1-(*ortho*-ethylaryl)-2,2,4-trimethylpentane-1,3-diones **4a–g** in hexane gave benzocyclobutenols **10a–g**. However, irradiation of 1-(*ortho*-isopropylaryl)-2,2,4-trimethylpentane-1,3-diones **4i** and **4j** resulted in no reaction. Irradiation of 1-mesityl-2,2,4-trimethylpentane-1,3-dione **4h** gave a complex mixture of products. Pyrolysis of benzocyclobutenols **10a, b, d–f** gave benzocyclobutenones **11a, b, d–f** and 2,4-dimethylpentan-3-one **2**, whereas that of the benzocyclobutenols **10c, g** gave the starting 1,3-diketones **4c, g** predominantly along with small amounts of benzocyclobutenones **11c, g** and the dimethylpentanone **2**.

The reactivity of benzocyclobutenone and its derivatives has been extensively studied¹ and a number of methods for the synthesis of these compounds have been developed. The [2 + 2]cycloaddition of benzynes to 1,1-dimethoxyethylene followed by hydrolysis,^{1e} the thermal elimination of hydrogen chloride from *o*-(trichloromethyl)methylbenzenes to afford 1,1-dichlorobenzocyclobutenes followed by hydrolysis,^{1b,2} the ring closure of *ortho*-alkylbenzoyl chlorides,³ *o*-trimethylsilylmethyl- and *o*-bis(trimethylsilyl)methyl-benzoyl chlorides⁴ with thermal loss of hydrogen chloride or trimethylsilyl chloride, and the ring closure of *ortho*-[(α -phenylthio)alkyl]benzoyltrimethylsilanes in the presence of a Group 6 metal carbonyl catalyst⁵ are major routes for the preparative synthesis of benzocyclobutenones. We have recently reported that 1-(*o*-methylphenyl)-2,2-dimethyl 1,3-diketones underwent photocyclization to give benzocyclobutenols and naphthalenones in hexane, and that the benzocyclobutenols thus formed underwent thermal retro-aldol cleavage to give benzocyclobutenone and isopropyl ketone (Scheme 1).^{6,7} The benzocyclobutenol:naphthalenone ratio was influenced by the substituent R. This ratio increased with chain branching of R and with increasing size of R. When R = Me or Et the naphthalenone was the main product, and when R = Prⁱ the benzocyclobutenol predominated. The photocyclization of 1-(*ortho*-alkylaryl)-3-isopropyl 1,3-diketones may be applicable to the synthesis of various substituted benzocyclobutenones. We report here the new method for the preparation of substituted benzocyclobutenones *via* the photochemical cyclization of 1-(*ortho*-alkylaryl)-2,2,4-trimethylpentane-1,3-diones **4** followed by thermal cleavage of the resulting benzocyclobutenols **10**.

Results and Discussion

The *ortho*-alkylaryl 1,3-diketones **4a–c** were prepared in 60–70% overall yield *via* the condensation of 2,4-dimethylpentan-3-one **2** with the corresponding *ortho*-alkylaryl aldehyde **1**, followed by oxidation of the corresponding product ketols **3** with Jones' reagent.⁷ The 1,3-diketones **4d–j** were prepared by the reaction of substituted isobutyrophenones **7d–j**, which were prepared by the Friedel–Crafts acylation of the corresponding alkylbenzenes **5**, with isobutyraldehyde **8**, followed by oxidation of the resulting ketols **9d–j** in 40–65% overall yield by the same method as above (Scheme 2).

Irradiation of a solution of 1-(*ortho*-methylaryl)-2,2,4-trimethylpentane-1,3-diones **4a, b, d–f** in hexane (0.6–15 g in 100–450 cm³) under nitrogen with a high-pressure mercury lamp through a Pyrex filter gave benzocyclobutenols **10a, b, d–f**, which



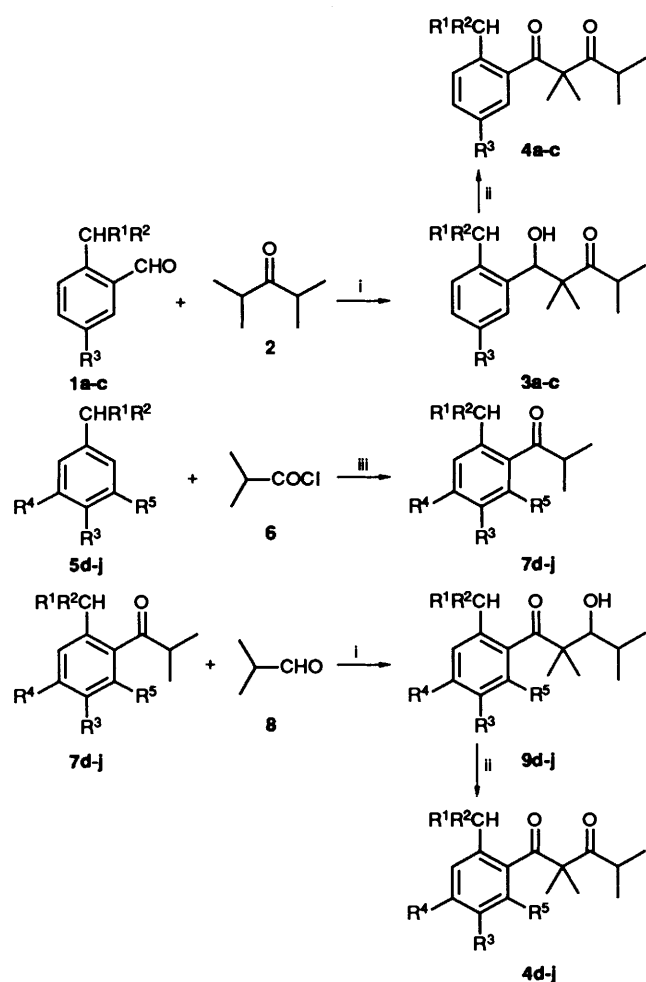
Scheme 1 Conditions: i, *hv*; ii, 150 °C

Table 1 Yield of benzocyclobutenols **10** obtained in the photolysis of 1-(*ortho*-alkylaryl)-2,2,4-trimethylpentane-1,3-diones **4** in hexane

Diketone	Irradiated solution (g/cm ³)	Hg lamp ^a (W)	Time (h)	Conversion (%) ^b	Yield of 10 (%) ^c
4a	15.0/400	450	22	98	72
4b	3.05/100	100	8	80	87
4c	0.60/100	100	20	73	60
4d	2.64/100	100	7	94	42
4e	0.60/120	100	5	58	44
4f	2.00/400	450	2	74	58
4g	2.50/400	450	6	42	50
4h^d	0.65/120	100	0.5		
4i^e	0.62/120	100	20		
4j^e	0.61/120	100	20		

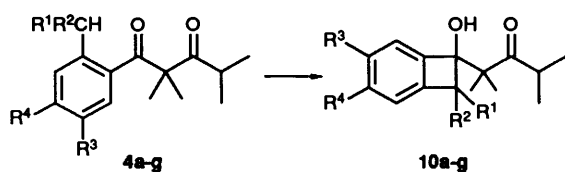
^a High-pressure mercury lamp with Pyrex filter was used. ^b Based on the amount of consumed starting material. ^c Based on converted starting material. ^d Reaction was very fast and gave a complex mixture of products. ^e No reaction.

were isolated by column chromatography (Scheme 3). The ¹H NMR spectra of compounds **10a, b, d–f** showed an AB-quartet at δ 2.98–3.05 and 3.35–3.40 (*J* 14 Hz) due to two methylene protons of the four-membered ring. The IR spectra showed hydroxy (3450–3550 cm⁻¹) and carbonyl (1680–1700 cm⁻¹) absorptions. In contrast to compounds **4a, b, d–f**, irradiation of 1-mesityl-2,2,4-trimethylpentane-1,3-dione **4h** gave a complex mixture of products, from which we could not isolate the corresponding benzocyclobutenol. Irradiation of *o*-ethylphenyl 1,3-diketones **4c** and **4g** under the same conditions gave the corresponding benzocyclobutenol **10c** and **10g** (Scheme 3), though the rate of reaction was about five times slower than that of *ortho*-methylaryl 1,3-diketones (see Table 1). The stereochemistry of compounds **10c** and **10g** is probably *cis* with respect to the C(1') hydroxy and C(2') methyl groups, because



- a; R¹ = R² = R³ = H
 b; R¹ = R² = H, R³ = Me
 c; R¹ = Me, R² = R³ = H
 d; R¹ = R² = R³ = R⁵ = H, R⁴ = Me
 e; R¹ = R² = R⁴ = R⁵ = H, R³ = Prⁱ
 f; R¹ = R² = R⁴ = R⁵ = H, R³ = Buⁱ
 g; R¹ = Me, R² = R⁴ = R⁵ = H, R³ = Et
 h; R¹ = R² = R³ = H, R⁴ = R⁵ = Me
 i; R¹ = R² = Me, R³ = Prⁱ, R⁴ = R⁵ = H
 j; R¹ = R² = Me, R³ = R⁵ = H, R⁴ = Prⁱ

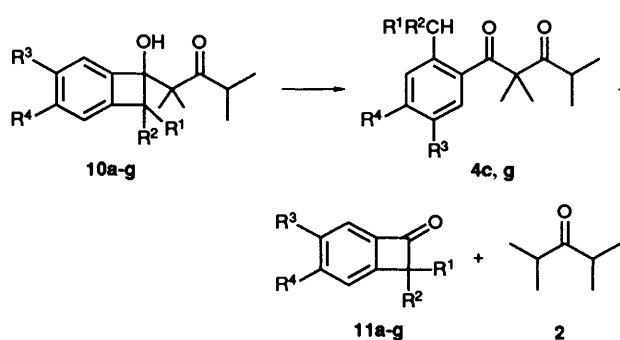
Scheme 2 Reagents: i, PhNMeMgBr; ii, CrO₃; iii, AlCl₃



- a; R¹ = R² = R³ = R⁴ = H
 b; R¹ = R² = R⁴ = H, R³ = Me
 c; R¹ = Me, R² = R³ = R⁴ = H
 d; R¹ = R² = R³ = H, R⁴ = Me
 e; R¹ = R² = R⁴ = H, R³ = Prⁱ
 f; R¹ = R² = R⁴ = H, R³ = Buⁱ
 g; R¹ = Me, R² = R⁴ = H, R³ = Et

Scheme 3 Conditions: *hν*

in the benzocyclobutenol **10** intramolecular hydrogen bonding between the hydroxy and the carbonyl is expected⁷ and this hydrogen bonding causes the severe steric interaction between the C(1') 2,4-dimethyl-3-oxopentan-2-yl group and the C(2')



- a; R¹ = R² = R³ = R⁴ = H
 b; R¹ = R² = R⁴ = H, R³ = Me
 c; R¹ = Me, R² = R³ = R⁴ = H
 d; R¹ = R² = R³ = H, R⁴ = Me
 e; R¹ = R² = R⁴ = H, R³ = Prⁱ
 f; R¹ = R² = R⁴ = H, R³ = Buⁱ
 g; R¹ = Me, R² = R⁴ = H, R³ = Et

Scheme 4 Conditions: 150–180 °C

methyl group *trans* to the C(1') hydroxy group. *ortho*-Isopropylaryl 1,3-diketones **4i** and **4j** underwent no photoreaction under the same conditions. The benzocyclobutenols from **4i**, **j** have two methyl groups on C(2'), and the methyl group *trans* to the C(1') hydroxy group interacts severely with the 2,4-dimethyl-3-oxopentan-2-yl group of C(1'). This severe steric interaction would cause the reversion of the intermediate diradicals from **4i**, **j** to the starting ketones, rather than cyclization to give benzocyclobutenols.

The benzocyclobutenol **10a** (**8g**) was placed in a sealed glass tube under reduced pressure (0.5 mmHg) and heated at 180 °C for 3 h. The ¹H NMR analysis of the reaction mixture revealed the quantitative formation of benzocyclobuten-1(2*H*)-one **11a** and 2,4-dimethylpentane-3-one **2**. Compound **11a** was separated by distillation in a Kugelrohr apparatus in 72% isolated yield (Scheme 4). Pyrolysis of benzocyclobutenols **10b**, **d–f**, which have no substituent on C(2'), gave the corresponding benzocyclobutenones **11b**, **d–f** in good yield. In contrast to **10a**, **b**, **d–f**, pyrolysis of **10c**, **g** which have a methyl group on C(2') gave the starting ketones **4c**, **g** as the major product along with small amounts of the benzocyclobutenone **11c**, **g** and 2,4-dimethylpentan-3-one **2**. The product ratio **4**:**11** was *ca.* 9:1 on the basis of the ¹H NMR spectrum of the pyrolysis mixture. The conversion into diketones **4** in preference to the formation of cyclobutenones **11** may be ascribed to the methyl group stabilizing a radical or an enol arising from C(1')–C(2') bond fission. It is known that benzocyclobutenols revert to the starting ketones when heated.⁸ Direct injection of the benzocyclobutenol **10** onto the GLC column heated at 150–180 °C caused the decomposition of compounds **10** to the benzocyclobutenone **11**, the pentanone **2**, and the starting ketone **4**. The isolation of 2-methylbenzocyclobutenones **11c** and **11g** was achieved by preparative GLC with direct injection of the benzocyclobutenol **10** onto the column.

In conclusion, irradiation of 1-(*ortho*-methylaryl)- and 1-(*ortho*-ethylaryl)-2,2,4-trimethylpentane-1,3-diones in hexane gave benzocyclobutenols. The benzocyclobutenols thus formed underwent thermal reaction to give benzocyclobutenones, 2,4-dimethylpentan-3-one, and/or the starting 1,3-diketones. This reaction is useful for the synthesis of benzocyclobutenones having no substituent on C(2') because benzocyclobutenols having no substituent on C(2') undergo thermal retro-aldol cleavage in preference to the C(1')–C(2') bond fission, whereas benzocyclobutenols having a methyl group on C(2') undergo C(1')–C(2') bond fission predominantly.

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 for solutions in CCl_4 . ^1H NMR spectra were obtained with a JEOL PMX-60, a JEOL FX-90Q, or a Bruker AM-400 spectrometer with CDCl_3 as solvent unless otherwise stated. Tetramethylsilane was used as internal standard and J values are given in Hz. ^{13}C NMR spectra were measured on a Bruker AM-400 spectrometer with CDCl_3 as solvent. GLC was carried out on a Gasukuro Kogyo KOR-70 instrument using 5 m \times 6 mm aluminium column containing 10% SE-30 on Chromosorb W. Column chromatography was performed with Merck Kieselgel 60. An Ushio 100 W or 450 W high-pressure mercury lamp was used as the irradiation source.

Starting Materials.—Compounds **4a–c** were prepared by the condensation of 2,4-dimethylpentan-3-one **2** with the corresponding aldehydes **1a–c** with *N*-methylanilinomagnesium bromide as the condensation agent,⁹ followed by Jones oxidation, where *o*-ethylbenzaldehyde **1c** was prepared by the reported method.¹⁰ Compounds **4d–j** were prepared by the same method from isobutyraldehyde **8** and isobutyrophenones **7d–j**, which were prepared by the Friedel–Crafts acylation of the corresponding alkylbenzenes **5d–j** with isobutyryl chloride **6**.

2,2,4-Trimethyl-1-(*o*-methylphenyl)pentane-1,3-dione **4a**⁷ had b.p. 115 °C at 0.7 mmHg (Found: C, 77.3; H, 8.5. Calc. for $\text{C}_{15}\text{H}_{20}\text{O}_2$: C, 77.6; H, 8.7%; $\nu_{\text{max}}/\text{cm}^{-1}$ 1720 (alkyl ketone) and 1690 (aryl ketone); δ_{H} (60 MHz; CCl_4) 0.95 (6 H, d, *J* 7, CHMe_2), 1.40 (6 H, s, CMe_2), 2.36 (3 H, s, *ArMe*), 2.93 (1 H, sept., *J* 7, CHMe_2) and 7.05–7.30 (4 H, m, *ArH*).

1-(2',5'-Dimethylphenyl)-2,2,4-trimethylpentane-1,3-dione **4b** had b.p. 95 °C at 0.3 mmHg (Found: C, 78.0; H, 9.1. $\text{C}_{16}\text{H}_{22}\text{O}_2$ requires C, 78.0; H, 9.0%; $\nu_{\text{max}}/\text{cm}^{-1}$ 1710 (alkyl ketone) and 1680 (aryl ketone); δ_{H} (90 MHz) 1.00 (6 H, d, *J* 7, CHMe_2), 1.44 (6 H, s, CMe_2), 2.30 (3 H, s) and 2.35 (3 H, s) ($2 \times \text{ArMe}$), 3.00 (1 H, sept., *J* 7, CHMe_2) and 7.00–7.20 (3 H, m, *ArH*).

1-(*o*-Ethylphenyl)-2,2,4-trimethylpentane-1,3-dione **4c** had b.p. 95 °C at 0.3 mmHg (Found: C, 78.0; H, 9.0. $\text{C}_{16}\text{H}_{22}\text{O}_2$ requires C, 78.0; H, 9.0%; $\nu_{\text{max}}/\text{cm}^{-1}$ 1720 (alkyl ketone) and 1690 (aryl ketone); δ_{H} (90 MHz) 1.00 (6 H, d, *J* 7, CHMe_2), 1.23 (3 H, t, *J* 7, CH_2Me), 1.45 (6 H, s, CMe_2), 2.69 (2 H, q, *J* 7, CH_2Me), 3.07 (1 H, sept., *J* 7, CHMe_2) and 7.10–7.40 (4 H, m, *ArH*).

(2',4'-Dimethylphenyl)-2,2,4-trimethylpentane-1,3-dione **4d** had b.p. 110 °C at 0.4 mmHg (Found: C, 78.0; H, 8.9. $\text{C}_{16}\text{H}_{22}\text{O}_2$ requires C, 78.0; H, 9.0%; $\nu_{\text{max}}/\text{cm}^{-1}$ 1720 (alkyl ketone) and 1680 (aryl ketone); δ_{H} (90 MHz) 0.96 (6 H, d, *J* 7, CHMe_2), 1.44 (6 H, s, CMe_2), 2.31 (3 H, s) and 2.39 (3 H, s) ($2 \times \text{ArMe}$), 2.94 (1 H, sept., *J* 7, CHMe_2) and 6.90–7.25 (3 H, m, *ArH*).

1-(5'-Isopropyl-2'-methylphenyl)-2,2,4-trimethylpentane-1,3-dione **4e** had b.p. 85 °C at 0.5 mmHg (Found: C, 78.5; H, 9.4. $\text{C}_{18}\text{H}_{26}\text{O}_2$ requires C, 78.8; H, 9.6%; $\nu_{\text{max}}/\text{cm}^{-1}$ 1705 (alkyl ketone) and 1680 (aryl ketone); δ_{H} (60 MHz; CCl_4) 0.93 (6 H, d, *J* 7) and 1.61 (6 H, d, *J* 7) ($2 \times \text{CHMe}_2$), 1.40 (6 H, s, CMe_2), 2.33 (3 H, s, *ArMe*), 2.56–3.17 (2 H, m, $2 \times \text{CHMe}_2$) and 7.03 (3 H, s, *ArH*).

1-(5'-tert-Butyl-2'-methylphenyl)-2,2,4-trimethylpentane-1,3-dione **4f** had b.p. 110 °C at 0.4 mmHg (Found: C, 79.1; H, 9.7. $\text{C}_{19}\text{H}_{28}\text{O}_2$ requires C, 79.1; H, 9.8%; $\nu_{\text{max}}/\text{cm}^{-1}$ 1710 (alkyl ketone) and 1680 (aryl ketone); δ_{H} (60 MHz; CCl_4) 0.93 (6 H, d, *J* 7, CHMe_2), 1.30 (9 H, s, *Bu*'), 1.37 (6 H, s, CMe_2), 2.38 (3 H, s, *ArMe*), 2.90 (1 H, sept., *J* 7, CHMe_2) and 7.13 (3 H, s, *ArH*).

1-(2',5'-Diethylphenyl)-2,2,4-trimethylpentane-1,3-dione **4g** had b.p. 105 °C at 0.6 mmHg (Found: C, 78.8; H, 9.6. $\text{C}_{18}\text{H}_{26}\text{O}_2$ requires C, 78.8; H, 9.6%; $\nu_{\text{max}}/\text{cm}^{-1}$ 1720 (alkyl ketone) and 1680 (aryl ketone); δ_{H} (60 MHz, CCl_4) 0.96 (6 H, d, *J* 7, CHMe_2),

1.20 (6 H, t, *J* 7, $2 \times \text{CH}_2\text{Me}$), 1.40 (6 H, s, CMe_2), 2.57 (2 H, q, *J* 7) and 2.64 (2 H, q, *J* 7) ($2 \times \text{CH}_2\text{Me}$), 2.96 (1 H, sept., *J* 7, CHMe_2) and 6.85–7.16 (3 H, m, *ArH*).

2,2,4-Trimethyl-1-(2',4',6'-trimethylphenyl)pentane-1,3-dione **4h** had b.p. 105 °C at 0.4 mmHg (Found: C, 78.2; H, 9.3. $\text{C}_{17}\text{H}_{24}\text{O}_2$ requires C, 78.4; H, 9.3%; $\nu_{\text{max}}/\text{cm}^{-1}$ 1715 (alkyl ketone) and 1690 (aryl ketone); δ_{H} (60 MHz; CCl_4) 1.00 (6 H, d, *J* 7, CHMe_2), 1.36 (6 H, s, CMe_2), 2.03 (6 H, s, 2'- and 6'-Me), 2.23 (3 H, s, 4'-Me), 3.50 (1 H, sept., *J* 7, CHMe_2) and 6.67 (2 H, s, *ArH*).

1-(2',5'-Diisopropylphenyl)-2,2,4-trimethylpentane-1,3-dione **4i** had b.p. 115 °C at 0.5 mmHg (Found: C, 79.5; H, 9.9. $\text{C}_{20}\text{H}_{30}\text{O}_2$ requires C, 79.4; H, 10.0%; $\nu_{\text{max}}/\text{cm}^{-1}$ 1720 (alkyl ketone) and 1680 (aryl ketone); δ_{H} (60 MHz, CCl_4) 0.96 (6 H, d, *J* 7), 1.23 (6 H, d, *J* 7) and 1.35 (6 H, d, *J* 7) ($3 \times \text{CHMe}_2$), 1.40 (6 H, s, CMe_2), 2.60–3.33 (3 H, m, $3 \times \text{CHMe}_2$), 6.95 (2 H, m) and 7.15 (1 H, s) (*ArH*).

1-(2',4'-Diisopropylphenyl)-2,2,4-trimethylpentane-1,3-dione **4j** had b.p. 120 °C at 0.4 mmHg (Found: C, 79.6; H, 10.0. $\text{C}_{20}\text{H}_{30}\text{O}_2$ requires C, 79.4; H, 10.0%; $\nu_{\text{max}}/\text{cm}^{-1}$ 1710 (alkyl ketone) and 1680 (aryl ketone); δ_{H} (400 MHz) 1.00 (6 H, d, *J* 7), 1.23 (6 H, d, *J* 7) and 1.24 (6 H, d, *J* 7) ($3 \times \text{CHMe}_2$), 1.45 (6 H, s, CMe_2), 2.89 (1 H, sept., *J* 7) and 3.05 (2 H, sept., *J* 7) ($3 \times \text{CHMe}_2$), 6.99 (1 H, d, *J* 8), 7.05 (1 H, d, *J* 8) and 7.23 (1 H, s) (*ArH*).

General Procedure for the Preparative Photolysis of Diketones 4.—A solution of the diketone **4** in hexane was irradiated under nitrogen with light from a high-pressure mercury lamp through a Pyrex filter. The concentration, the lamp used, and the irradiation time are given in Table 1. The benzocyclobutenols **10** were isolated by silica gel column chromatography with benzene–ethyl acetate (20:1) for **10a, b, d**, hexane–ethyl acetate (6:1) for **10c, e**, or hexane–ethyl acetate (9:1) as eluent for **10f, g**. Irradiation of compound **4h** gave a complex mixture of products. Compounds **4i, j** underwent no photoreaction.

2-(1'-Hydroxy-1',2'-dihydrobenzocyclobuten-1'-yl)-2,4-dimethylpentan-3-one **10a**⁷ had m.p. 37 °C (from pentane) (Found: C, 77.4; H, 8.7. Calc. for $\text{C}_{15}\text{H}_{20}\text{O}_2$: C, 77.6; H, 8.7%; $\nu_{\text{max}}/\text{cm}^{-1}$ 3600 and 3500br (OH) and 1700 (C=O); δ_{H} (90 MHz) 1.08 (6 H, d, *J* 7, CHMe_2), 1.21 (3 H, s) and 1.24 (3 H, s) (CMe_2), 3.12 (1 H, sept., *J* 7, CHMe_2), 3.04 (1 H) and 3.38 (1 H) (AB-system, *J* 14, 2'- H_2), 3.92 (1 H, s, OH) and 7.00–7.30 (4 H, m, *ArH*); δ_{C} (22.5 MHz) 19.5 (q), 19.6 (q), 19.8 (q) and 20.3 (q) ($4 \times \text{Me}$), 34.9 (d, CHMe_2), 42.1 (t, C-2'), 52.7 (s, CMe_2), 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).

2-(1'-Hydroxy-1',2'-dihydro-5'-methylbenzocyclobuten-1'-yl)-2,4-dimethylpentan-3-one **10b*** $\nu_{\text{max}}/\text{cm}^{-1}$ 3500 (OH) and 1690 (C=O); δ_{H} (90 MHz) 1.09 (6 H, d, *J* 7, CHMe_2), 1.24 (3 H, s) and 1.25 (3 H, s) (CMe_2), 2.32 (3 H, s, *ArMe*), 3.16 (1 H, sept., *J* 7, CHMe_2), 2.98 (1 H) and 3.35 (1 H) (AB-system, *J* 14, 2'- H_2), 3.90 (1 H, s, OH) and 6.95–7.10 (3 H, m, *ArH*); δ_{C} (100 MHz) 19.9 (q), 20.0 (q), 20.1 (q), 20.7 (q) and 21.9 (q) ($5 \times \text{Me}$), 35.0 (d, CHMe_2), 41.7 (t, C-2'), 53.1 (s, CMe_2), 84.2 (s, C-1'), 122.5 (d), 123.1 (d), 130.0 (d), 136.8 (s), 138.8 (s) and 147.5 (s) (*ArC*) and 222.4 (s, C=O).

2-(1'-Hydroxy-1',2'-dihydro-2'-methylbenzocyclobuten-1'-yl)-2,4-dimethylpentan-3-one **10c*** $\nu_{\text{max}}/\text{cm}^{-1}$ 3500 (OH) and 1685 (C=O); δ_{H} (90 MHz) 1.11 (3 H, d, *J* 7) and 1.13 (3 H, d, *J* 7) (CHMe_2), 1.17 (3 H, s) and 1.44 (3 H, s) (CMe_2), 1.36 (3 H, d, *J* 7,

* Compounds **10b–g** were obtained as oils of high purity as determined on the basis of their ^1H NMR spectra. However, their complete purification by distillation for microanalysis could not be achieved because they gradually decomposed to the corresponding benzocyclobutenones, 2,4-dimethylpentan-3-one, and/or the starting ketones.

Table 2 Yield of benzocyclobutenones **11** obtained in the pyrolysis of benzocyclobutenols **10**

Benzocyclobutenol	Temperature and pressure (°C/mmHg) ^a	Time (h)	Yield of 11 (%)
10a	180/0.5	1	72 ^b
10b	150/0.7	3	87 ^b
10c	180/0.5	3	~10 ^c
10d	150/760	3	75 ^b
10e	150/0.5	3	58 ^b
10f	150/0.5	3	67 ^b
10g	150/0.5	3	~10 ^c

^a Pyrolysis was carried out in a glass tube sealed under reduced pressure.

^b Isolated yield. ^c Pyrolysis of substrates **10c** and **10g** gave mainly the starting ketone **4c/4g** along with small amounts of the benzocyclobutenone **11c/11g**. Compounds **11c** and **11g** were isolated by direct pyrolysis of **10c/10g** on a GLC column.

2'-Me), 3.17 (1 H, sept., *J* 7, *CHMe*₂), 3.73 (1 H, q, *J* 7, 2'-H), 4.44 (1 H, s, OH) and 7.05–7.40 (4 H, m, ArH); δ_c (100 MHz) 15.4 (q), 19.9 (q), 20.3 (q), 21.3 (q) and 23.5 (q) (5 × Me), 35.2 (d, *CHMe*₂), 52.3 (s, *CMe*₂), 54.2 (d, C-2'), 86.8 (s, C-1'), 121.7 (d), 121.8 (d), 127.2 (d), 129.3 (d), 145.1 (s) and 147.3 (s) ArC and 223.3 (s, C=O).

2-(1'-Hydroxy-1',2'-dihydro-4'-methylbenzocyclobuten-1'-yl)-2,4-dimethylpentan-3-one **10d**.* $\nu_{\max}/\text{cm}^{-1}$ 3450 (OH) and 1680 (C=O); δ_H (90 MHz) 1.07 (6 H, d, *J* 7, *CHMe*₂), 1.23 (6 H, s, *CMe*₂), 2.33 (3 H, s, ArMe), 3.16 (1 H, sept., *J* 7, *CHMe*₂), 3.04 (1 H) and 3.40 (1 H) (AB-system, *J* 14, 2'-H₂), 3.87 (1 H, s, OH) and 6.92–7.08 (3 H, m, ArH); δ_c (100 MHz) 19.9 (q), 20.0 (q), 20.1 (q), 20.6 (q) and 22.1 (q) (5 × Me), 35.0 (d, *CHMe*₂), 42.0 (t, C-2'), 53.1 (s, *CMe*₂), 84.0 (s, C-1'), 121.7 (d), 124.0 (d), 127.9 (d), 139.0 (s), 142.1 (s) and 144.4 (s) (ArC) and 222.3 (s, C=O).

2-(1'-Hydroxy-1',2'-dihydro-5'-isopropylbenzocyclobuten-1'-yl)-2,4-dimethylpentan-3-one **10e**.* $\nu_{\max}/\text{cm}^{-1}$ 3600 and 3550br (OH) and 1695 (C=O); δ_H (400 MHz) 1.08 (3 H, d, *J* 7) and 1.09 (3 H, d, *J* 7) (*COCHMe*₂), 1.21 (3 H, d, *J* 7) and 1.22 (3 H, d, *J* 7) (*ArCHMe*₂), 1.25 (6 H, s, *CMe*₂), 2.87 (1 H, sept., *J* 7, *ArCHMe*₂), 3.16 (1 H, sept., *J* 7, *COCHMe*₂), 3.04 (1 H) and 3.35 (1 H) (AB-system, *J* 14, 2'-H₂), 3.94 (1 H, s, OH) and 7.01–7.14 (3 H, m, ArH); δ_c (100 MHz) 19.8 (q), 20.0 (q), 20.2 (q), 20.7 (q), 24.2 (q) and 24.3 (q) (6 × Me), 34.6 (d) and 35.0 (d) (2 × *CHMe*₂), 41.9 (t, C-2'), 53.1 (s, *CMe*₂), 84.1 (s, C-1'), 119.8 (d), 123.1 (d), 127.5 (d), 139.2 (s), 147.4 (s), 148.2 (s) (ArC) and 222.4 (s, C=O).

2-(5'-tert-Butyl-1'-hydroxy-1',2'-dihydrobenzocyclobuten-1'-yl)-2,4-dimethylpentan-3-one **10f**.* $\nu_{\max}/\text{cm}^{-1}$ 3600 and 3550br (OH) and 1700 (C=O); δ_H (400 MHz) 1.08 (3 H, d, *J* 7) and 1.09 (3 H, d, *J* 7) (*CHMe*₂), 1.24 (3 H, s) and 1.26 (3 H, s) (*CMe*₂), 1.30 (9 H, s, Bu^t), 3.05 (1 H) and 3.24 (1 H) (AB-system, *J* 14, 2'-H₂), 3.16 (1 H, sept., *J* 7, *CHMe*₂), 3.84 (1 H, s, OH), 7.05 (1 H, d, *J* 8), 7.17 (1 H, s) and 7.24 (1 H, d, *J* 8) (ArH); δ_c (100 MHz) 19.7 (q), 19.9 (q), 20.0 (q), 20.5 (q) and 31.4 (q) (7 × Me), 34.9 (s + d, *CMe*₃ and *CHMe*₂), 42.0 (t, C-2'), 53.0 (s, *CMe*₂), 83.9 (s, C-1'), 120.1 (d), 121.4 (d), 124.1 (d), 141.5 (s), 144.4 (s) and 152.2 (s) (ArC) and 221.9 (s, C=O).

2-(5'-Ethyl-1'-hydroxy-1',2'-dihydro-2'-methylbenzocyclobuten-1'-yl)-2,4-dimethylpentan-3-one **10g**.* $\nu_{\max}/\text{cm}^{-1}$ 3550br (OH) and 1690 (C=O); δ_H (400 MHz) 1.11 (3 H, d, *J* 7) and 1.13 (3 H, d, *J* 7) (*CHMe*₂), 1.18 (3 H, s) and 1.45 (3 H, s) (*CMe*₂), 1.21 (3 H, t, *J* 7, *CH*₂*Me*), 1.34 (3 H, d, *J* 7, 2'-Me), 2.62 (2 H, q, *CH*₂*Me*), 3.16 (1 H, sept., *J* 7, *CHMe*₂), 3.67 (1 H, q, *J* 7,

2'-H), 4.40 (1 H, s, OH) and 7.03–7.26 (3 H, m, ArH); δ_c (100 MHz) 15.3 (q), 15.9 (q), 19.6 (q), 20.0 (q), 21.1 (q) and 23.3 (q) (6 × Me), 29.2 (t, *CH*₂*Me*), 34.9 (d, *CHMe*₂), 52.0 (s, *CMe*₂), 53.5 (d, C-2'), 86.3 (s, C-1'), 120.7 (d), 121.3 (d), 128.6 (d), 143.1 (s), 144.1 (s) and 144.9 (s) (ArC) and 222.9 (s, C=O).

Pyrolysis of Benzocyclobutenols 10a–g.—Benzocyclobutenols **10a, b, d–f** (0.2–8 g) were placed in a sealed glass tube under reduced or at ordinary pressure and heated at 150–180 °C for 1–3 h. The pyrolysis mixture was distilled (Kugelrohr) below 50 °C at 25 mmHg to remove 2,4-dimethylpentan-3-one and then the benzocyclobutenone **11** was collected at 100–120 °C at 25 mmHg. Similar pyrolyses of compounds **10c** and **10g** gave mainly the starting ketone **4c/4g** along with small amounts of the benzocyclobutenone **11c/11g**. Isolation of compounds **11c** and **11g** was carried out by preparative GLC through direct pyrolysis of the benzocyclobutenol **10c/10g** on a column. Reaction conditions and yields of products **11** are given in Table 2.

Benzocyclobuten-1(2*H*)-one **11a**^{1a} had b.p. 100 °C at 25 mmHg (Found: C, 81.2; H, 5.1. Calc. for C₈H₆O: C, 81.3; H, 5.1%); $\nu_{\max}/\text{cm}^{-1}$ 1800 and 1780 (C=O); δ_H (60 MHz; CCl₄) 3.9 (2 H, s, CH₂) and 7.20–7.70 (4 H, m, ArH); δ_c (100 MHz) 52.0 (t, CH₂), 120.1 (d), 123.4 (d), 128.3 (d), 134.5 (d), 147.5 (s) and 150.9 (s) (ArC) and 188.3 (s, C=O).

5-Methylbenzocyclobuten-1(2*H*)-one **11b**³ had m.p. 46 °C (from pentane) (Found: C, 81.5; H, 6.1. Calc. for C₉H₈O: C, 81.8; H, 6.1%); $\nu_{\max}/\text{cm}^{-1}$ 1765 (C=O); δ_H (90 MHz) 2.39 (3 H, s, Me), 3.91 (2 H, s, CH₂) and 7.12–7.20 (1 H, br s) and 7.28–7.53 (2 H, m) (ArH); δ_c (100 MHz) 21.6 (q, Me), 51.5 (t, CH₂), 120.4 (d), 123.2 (d), 136.2 (d), 138.7 (s), 148.2 (s) and 148.4 (s) (ArC) and 188.7 (s, C=O).

2-Methylbenzocyclobuten-1(2*H*)-one **11c**. Isolated by GLC as an oil (Found: C, 81.6; H, 6.2. C₉H₈O requires C, 81.8; H, 6.1%); $\nu_{\max}/\text{cm}^{-1}$ 1820 and 1775 (C=O); δ_H (90 MHz) 1.46 (3 H, d, *J* 7, Me), 4.28 (1 H, q, *J* 7, *CHMe*) and 7.27–7.60 (4 H, m, ArH); δ_c (100 MHz) 15.1 (q, Me), 59.5 (d, *CHMe*), 120.9 (d), 122.7 (d), 129.0 (d), 135.1 (d), 146.1 (s) and 157.5 (s) (ArC) and 193.1 (s, C=O).

4-Methylbenzocyclobuten-1(2*H*)-one **11d** had m.p. 51 °C (from pentane) (Found: C, 81.7; H, 6.1. C₉H₈O requires C, 81.8; H, 6.1%); $\nu_{\max}/\text{cm}^{-1}$ 1825 and 1760 (C=O); δ_H (90 MHz) 2.44 (3 H, s, Me), 3.90 (2 H, s, CH₂) and 7.18–7.28 (2 H, br s) and 7.30–7.40 (1 H, br s) (ArH); δ_c (100 MHz) 22.6 (q, Me), 51.6 (t, CH₂), 120.3 (d), 124.1 (d), 129.9 (d), 145.2 (s), 146.6 (s) and 151.4 (s) (ArC) and 188.0 (s, C=O).

5-Isopropylbenzocyclobuten-1(2*H*)-one **11e** had b.p. 112 °C at 25 mmHg (Found: C, 82.2; H, 7.6. C₁₁H₁₂O requires C, 82.5; H, 7.6%); $\nu_{\max}/\text{cm}^{-1}$ 1775 (C=O); δ_H (400 MHz) 1.25 (6 H, d, *J* 7, *CHMe*₂), 2.95 (1 H, sept., *J* 7, *CHMe*₂), 3.90 (2 H, s, CH₂), 7.20 (1 H, s), 7.40 (1 H, d, *J* 7) and 7.45 (1 H, d, *J* 7) (ArH); δ_c (100 MHz) 23.8 (q, *CHMe*₂), 34.2 (d, *CHMe*₂), 51.4 (t, CH₂), 117.7 (d), 123.3 (d), 134.1 (d), 148.1 (s), 148.8 (s) and 149.9 (s) (ArC) and 188.5 (s, C=O).

5-tert-Butylbenzocyclobuten-1(2*H*)-one **11f** had m.p. 87–89 °C (from pentane) (Found: C, 82.4; H, 8.2. C₁₂H₁₄O requires C, 82.7; H, 8.1%); $\nu_{\max}/\text{cm}^{-1}$ 1770 (C=O); δ_H (60 MHz; CCl₄) 1.37 (9 H, s, Bu^t), 3.86 (2 H, s, CH₂) and 7.05–7.55 (3 H, m, ArH); δ_c (100 MHz) 31.3 (q, *CMe*₃), 36.0 (s, *CMe*₃), 51.8 (t, CH₂), 120.3 (d), 120.4 (d), 126.5 (d), 145.2 (s), 151.3 (s) and 159.8 (s) and 188.2 (s, C=O).

5-Ethyl-2-methylbenzocyclobuten-1(2*H*)-one **11g**.† $\nu_{\max}/\text{cm}^{-1}$ 1775 (C=O); δ_H (400 MHz) 1.24 (3 H, t, *J* 7, *CH*₂*Me*), 1.43 (3 H, d, *J* 7, *CHMe*), 2.69 (2 H, q, *J* 7, *CH*₂*Me*), 4.21 (1 H, q, *J* 7, *CHMe*), 7.19 (1 H, s), 7.37 (1 H, d, *J* 7) and 7.43 (1 H, d, *J* 7) (ArH); δ_c (100 MHz) 15.2 (q) and 15.7 (q) (2 × Me), 29.0 (t, *CH*₂*Me*), 58.7 (d, *CHMe*), 119.7 (d), 122.5 (d), 135.5 (d), 145.6 (s), 146.5 (s) and 155.1 (s) (ArC) and 193.3 (s, C=O).

* See footnote on preceding page.

† Compound **11g** was isolated by GLC as an oil in 90% purity on the basis of its ¹H NMR spectrum.

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