Photochemical Reaction of 3-Hydroxy-1-(*o*-methylaryl)alkan-1-ones: Formation of Cyclopropane-1,2-diols and Benzocyclobutenols through β- and γ-Hydrogen Abstractions

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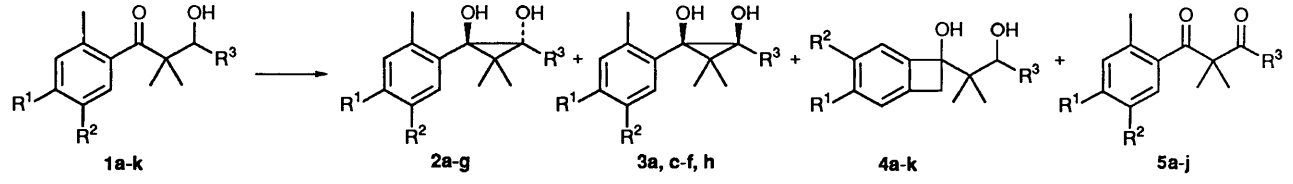
Irradiation of 3-hydroxy-2,2-dimethyl-1-(*o*-methylaryl)-alkan-1-ones **1a–h** having a bulky alkyl group or an aryl group on C-3 in methanol gave *trans*- and *cis*-cyclopropane-1,2-diols **2a–g** and **3a**, **c–f**, **h** and benzocyclobutenols **4a–h** through β- and γ-hydrogen abstractions. Irradiation of 3-hydroxy-2,2-dimethyl-1-(*o*-methylphenyl)-alkan-1-ones **1i–k** having ethyl, methyl or no substituent at C-3 gave benzocyclobutenols **4i–k** and 1,3-diketones **5i**, **j**, but no cyclopropane-1,2-diols. The cyclopropane-1,2-diols were sensitive to air and readily oxidized to the corresponding 1,3-diketones. Irradiation of 3-hydroxy-4,4-dimethyl-1-(*o*-methylaryl)pentan-1-ones **8a**, **b** having a methyl group or no substituent on C-2 gave benzocyclobutenols **9a**, **b**, the peroxide **10** and phthalides **11a**, **b**. 3-Hydroxy-2,2-dimethyl-1,3-diphenylpropan-1-one **12a** and 3-hydroxy-2,2,4-trimethylpentan-1-one **12b** also underwent photocyclization through β-hydrogen abstraction to give cyclopropane-1,2-diols **13a**, **b** and **14**.

The photochemistry of *o*-alkylphenyl ketones has been extensively studied and a number of comprehensive reviews have been published.[1] The triplet states of these ketones are transformed into diradicals *via* intramolecular hydrogen abstraction, which decay to short-lived *Z*- and long-lived *E*-enols. The *Z*-enol undergoes a rapid 1,5-hydrogen shift to regenerate the starting ketone, while the *E*-enol lives long enough to rearrange to a benzocyclobutenol by an intramolecular [2 + 2] cycloaddition.[2] The benzocyclobutenols from *o*-alkylphenyl ketones are thermally unstable and revert to the parent ketone *via* the enol at room temperature.[3] It has been reported that the formation of benzocyclobutenols is efficient from 2,6-dialkylphenyl ketones because the second alkyl group destabilizes the enols, but favours the benzocyclobutenol.[4] We have recently reported that 1-(*o*-methylaryl)-2,2-dimethyl 1,3-diketones underwent photocyclization to give benzocyclobutenols because the reverse transfer of hydrogen in the intermediate diradicals to reproduce the starting ketones was suppressed owing to intramolecular hydrogen bonding.[5] Because of our interest in the effect of β-functional groups on the photoreactivity of *o*-alkylaryl ketones, we have studied the photochemistry of 3-hydroxy ketones **1**, **8** and **12**. We report here that these ketones undergo photocylization through β- and γ-hydrogen abstractions to give cyclopropane-1,2-diols and benzocyclobutenols.

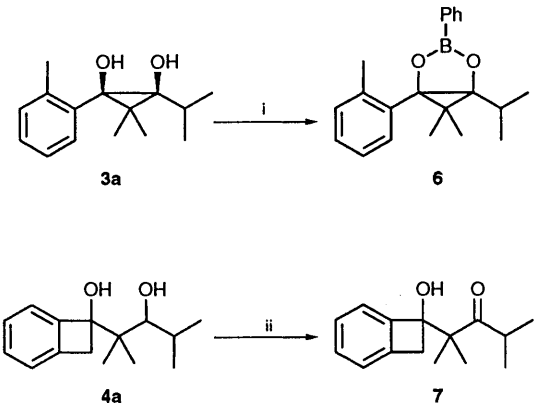
Results and Discussion

Irradiation of an ice-cooled methanol solution of the hydroxy ketone **1a** with Pyrex-filtered light gave two isomeric cyclopropane-1,2-diols **2a** and **3a**, the benzocyclobutenol **4a** and the 1,3-diketone **5a**,[5] in 31 and 12, 17 and 8% yield, respectively, at 66% conversion (Scheme 1).[6] The structures of **2a** and **3a** were assigned on the basis of their analytical and spectral data and chemical evidence. Their IR spectra showed hydroxy and no carbonyl absorptions. Their ^{1}H NMR spectra showed two hydroxy groups at δ 1.42 and 1.67 for **2a** and δ 2.48 and 2.53 for **3a**, and an arylmethyl group at δ 2.38 for **2a** and δ 2.39 for **3a**. Their ^{13}C NMR spectra showed two singlet peaks due to carbons bearing the hydroxy groups at δ 65–67. However, the configurations of these compounds could not be assigned on the basis of these data. Their configurations were established by cyclic esterification using phenylboronic acid. Compounds **3a** reacted with phenylboronic acid to give the ester **6**, while **2a** did not react (Scheme 2). It is known that solutions of cyclopropane-1,2-diols are readily oxidized to 1,3-diketones by oxygen in the air.[7] When carbon tetrachloride solutions of **2a** and **3a** were left at room temperature for several days, they were converted quantitatively into the diketone **5a**. Compound **4a** was a 4:1 mixture of two stereoisomers with respect to C-1′ and C-3. The ^{1}H NMR spectrum of the mixture showed peaks due to the two methylene protons of the four-membered ring as two AB quartets in the ratio of 4:1 at δ 2.92 and 3.56 and at δ 3.01 and 3.53. The chromic acid oxidation of **4a** gave the benzocyclobutenyl ketone **7**[5a] (Scheme 2). Irradiation of ketones having a branched alkyl group or an aryl group on C-3 **1b–h** under the same conditions also gave cyclopropane-1,2-diols **2** and **3**, along with the benzocyclobutenol **4** and the 1,3-diketone **5**, but that of ketones having ethyl, methyl or no substituent on C-3 **1i–k** did not give the



a $R^1 = R^2 = H$, $R^3 = Pr^j$ **b** $R^1 = Me$, $R^2 = H$, $R^3 = Pr^j$ **c** $R^1 = H$, $R^2 = Me$, $R^3 = Pr^j$ **d** $R^1 = R^2 = H$, $R^3 = CHEt_2$
e $R^1 = R^2 = H$, R^3 = cyclohexyl **f** $R^1 = R^2 = H$, $R^3 = Bu^t$ **g** $R^1 = R^2 = H$, $R^3 = Ph$ **h** $R^1 = R^2 = H$, $R^3 = o$-MeC_6H_4
i $R^1 = R^2 = H$, $R^3 = Et$ **j** $R^1 = R^2 = H$, $R^3 = Me$ **k** $R^1 = R^2 = R^3 = H$

Scheme 1 *Conditions: hv*



Scheme 2 *Reagents:* i, $PhB(OH)_2$; ii, CrO_3

Table 1 Yields of photoproducts **2**, **3**, **4** and **5**

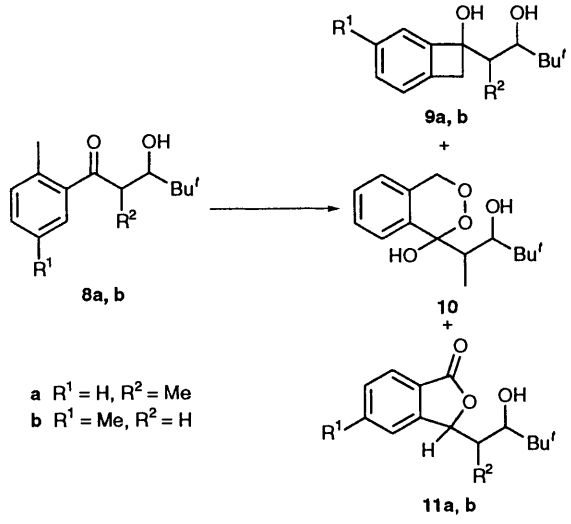
Ketone 1	Irradiation time (h)[a]	Conversion (%)[b]	Yield (%)[c] 2	3	4	5
a	2	66	31	12	17[d]	8
b	2	78	24	—	11[e]	6
c	3	66	27	10	21[f]	14
d	3	78	24	19	23[f]	17
e	3	81	24	11	23[d]	21
f	3	81	39	8	11[d]	8
g	2	83	30	—	40[d]	2
h	3	65	—	10	47[e]	3
i	4	74	—	—	47[d]	8
j	5	50	—	—	37[f]	30
k	3	58	—	—	89	—

[a] An ice-cooled solution of the ketone (600 mg) in methanol (160 cm^3) was irradiated with a 100 W high-pressure mercury lamp through a Pyrex filter. [b] Based on the amount of consumed starting material. [c] Based on converted starting material. [d] Mixture of two stereoisomers. [e] Only one stereoisomer was isolated. [f] Two stereoisomers were isolated in 11 and 10% from **1c**, 12 and 11% from **1d** and 22 and 15% yields from **1j**. Their configurations could not be assigned.

cyclopropane-1,2-diol. Irradiation of **1i**, **j** gave benzocyclobutenols **4i**, **j** and diketones **5i**, **j** and that of **1k** gave the benzocyclobutenol **4k**. Results of the photolysis of 3-hydroxy-2,2-dimethyl-1-(*o*-methylaryl)alkan-1-ones **1a–k** are given in Table 1. The configurations of cyclopropane-1,2-diols from **1b–h** were assigned by comparison of their ^1H NMR spectra with those of **2a** and **3a**, and by thin layer chromatographic behaviour on silica gel. In the ^1H NMR spectrum, the hydroxy protons appeared at higher field in the *trans*-isomer **2** than in the *cis*-isomer **3** (*trans*: δ 1.3–2.3; *cis*: δ 2.3–3.5). R_f Values on a silica gel thin layer plate were higher in the *trans*-isomer than in the *cis*-isomer. Although benzocyclobutenols **4a**, **e–g**, **i** were obtained as a mixture of two stereoisomers with respect to the two hydroxy groups, only one of the two possible stereoisomers of **4b**, **h** and both isomers of **4c**, **d**, **j** were isolated. However, their configurations could not be assigned.

Cyclopropane-1,2-diols were postulated as intermediates in the Clemmensen reduction of 1,3-diketones, and such species have been trapped as diacetates.[8] However, there are few reports on the preparation of free cyclopropane-1,2-diols; methods include electrochemical reduction of 1,3-diketones[9] and their reduction[7a] using alkali metal in liquid ammonia.

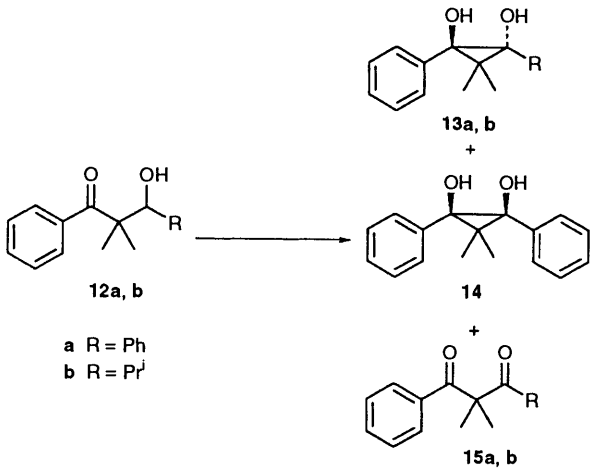
As already mentioned, cyclopropane-1,2-diols were produced from hydroxy ketones having a bulky alkyl group or an aryl group on C-3 **1a–h** on irradiation. The hydroxy ketones **1i j** gave the 1,3-diketones **5i**, **j** instead of cyclopropane-1,2-diols. Since the cyclopropane-1,2-diols are sensitive to air and are readily oxidized to the 1,3-diketones (*vide supra*), compounds **5i**, **j** may be produced by air oxidation of the initially formed cyclopropane-1,2-diol. Hydroxy ketone **1k** gave only the benzocyclobutenol **4k**. Thus, steric factors seem to be important for the formation of the cyclopropane-1,2-diol from the hydroxy ketone. Therefore, we studied the photochemistry of hydroxy ketones **8a**, **b** which have a *tert*-butyl group on C-3 and a methyl or no substituent on C-2. Irradiation of **8a** under the same conditions as **1** gave benzocyclobutenol **9a**, peroxide **10** and phthalide **11a** in 13, 18 and 25% yield, respectively, at 67% conversion (irradiation time: 5 h), and irradiation of **8b** gave **9b** and **11b** in 17 and 19% yield, respectively, at 94% conversion (irradiation time: 12 h) (Scheme 3). Neither cyclopropane-1,2-diols nor 1,3-diketones were produced. These results indicate that the presence of 2,2-dimethyl groups and a bulky alkyl or an aryl group on C-3 in the starting hydroxy ketones is important for the formation of cyclopropane-1,2-diols.



Scheme 3 *Conditions: hv*

Photolysis of ketones having hydrogens on both β- and γ-carbons leads preferentially to abstraction of the latter.[10] The formation of benzocyclobutenols **4** and **9** can be reasonably explained in terms of γ-hydrogen abstraction from the arylmethyl group by the carbonyl oxygen followed by cyclization of the resulting diradicals. The addition of oxygen remaining in the solvent to the diradical would given the peroxide **10**, which would undergo further reaction to give the phthalide **11**.[5a,11] Molecular oxygen is an efficient quencher of diradicals.[12]

The cyclopropane-1,2-diols **2** and **3** may be cyclization products involving unusual β-hydrogen abstraction. Cormier *et al.* reported that some α-methylene ketones underwent photocyclization *via* β-hydrogen abstraction to give cyclopropyl ketones.[13] When 3-hydroxy-2,2-dimethyl-1,3-diphenylpropan-1-one **12a** was irradiated under the same conditions as **1** and **8**, *trans*- and *cis*-cyclopropane-1,2-diols **13a** and **14** were obtained in 89 and 6% yield, respectively, along with trace amount of the 1,3-diketone **15a**. Irradiation of 3-hydroxy-2,2,4-trimethyl-1-phenylpentan-1-one **12b** under the same conditions also gave the *trans*-cyclopropane-1,2-diol **13b** and the 1,3-diketone **15b** in 31 and 18% yield, respectively (Scheme 4). The compounds **13a**, **b** and **14** were so sensitive to air that they were rapidly oxidized to give the 1,3-diketones **15a**, **b**. Even the ^1H NMR spectra of **13a**, **b** and **14** just after isolation showed peaks due to the 1,3-diketone as well as peaks due to the cyclopropane-1,2-diol. Therefore, the formation of the cyclopropane-1,2-diols can be rationalized in terms of the abstraction of hydrogen on C-3 which is activated by the hydroxy group, followed by cyclization of the resulting 1,3-diradicals. The higher yield of the *trans*-cyclopropane-1,2-diol



Scheme 4 *Conditions: hv*

than that of the *cis*-isomer (see Table 1) may be attributed to the repulsive interaction of the C-1 and C-3 substituents in the 1,3-diradical.

In conclusion, the 3-hydroxy-2,2-dimethyl-1- (*o*-methylaryl)-alkan-1-ones underwent photocyclization through β-and γ-hydrogen abstractions to give cyclopropane-1,2-diols and benzocyclobutenols. The hydroxy ketones having a bulky alkyl group on C-3 underwent the β-hydrogen abstraction more efficiently than the γ-hydrogen abstraction. The hydroxy ketones having only one methyl or no substituent on C-2 gave only products arising from the γ-hydrogen abstraction. The 3-hydroxy-2,2-dimethyl-1-phenylalkan-1-ones also gave cyclopropane-1,2-diols on irradiation. However, these diols were so sensitive to oxygen in the air that they were rapidly oxidized to give the 1,3-diketones.

Experimental

M.p.s are uncorrected. IR spectra were recorded on a Hitachi 270-50 spectrometer for solutions in CCl_4 unless otherwise stated. ^1H NMR spectra were obtained with a JEOL PMX-60 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. Column chromatography was performed with Merck Kieselgel 60. An Ushio 100 W high-pressure mercury lamp was used as the irradiation source. Starting compounds **1a–k**, **8a**, **b** and **12a**, **b** were prepared by the condensation of the aryl ketone with the aldehyde according to previously described methods.[5,12a,14]

General Procedure for the Photolysis of Hydroxy Ketones **1**, **8** *and* **12**.—A solution of the hydroxy ketone (*ca.* 600 mg) in methanol (160 cm^3) was cooled with ice and irradiated with a 100 W high-pressure mercury lamp through a Pyrex filter under nitrogen for 2–12 h. The solvent was removed under reduced pressure at room temperature. The photoproducts were isolated by silica gel column chromatography with hexane–ethyl acetate (1:1 to 6:1) or benzene–hexane–ethyl acetate (12:7:1) as eluent.

trans-1-*Isopropyl*-3,3-*dimethyl*-2-(o-*methylphenyl*)*cyclopropane*-1,2-*diol* **2a**. M.p. 102–103 °C (from hexane) (Found: C, 76.7; H, 9.4. $C_{15}H_{22}O_2$ requires C, 76.9; H, 9.5%); ν_{max}-($CHCl_3$)/cm^{-1} 3600 and 3450br (OH); δ_H(400 MHz) 0.92 (3 H, s) and 1.32 (3 H, s) (3-Me_2), 1.05 (3 H, d, *J* 7) and 1.22 (3 H, d, *J* 7) (CH*Me*$_2$), 1.42 (1 H, s, OH), 1.67 (1 H, s, OH), 2.28 (1 H, sept, *J* 7, C*H*Me_2), 2.38 (3 H, s, ArMe) and 7.1–7.4 (4 H, m, ArH); δ_C 15.5 (q), 17.6 (q), 17.8 (q), 18.9 (q) and 19.3 (q) (5 × Me), 26.6 (d, *C*HMe_2), 27.8 (s, C-3), 65.1 (s) and 66.6 (s) (C-1 and -2), 125.4 (d), 127.7 (d), 130.9 (d), 131.4 (d), 136.8 (s) and 139.2 (s) (ArC).

cis-1-*Isopropyl*-3,3-*dimethyl*-2-(o-*methylphenyl*)*cyclopropane*-1,2-*diol* **3a**. M.p. 117–119 °C (from hexane) (Found: C, 76.6; H, 9.4. $C_{15}H_{22}O_2$ requires C, 76.9; H, 9.5%); ν_{max}-($CHCl_3$)/cm^{-1} 3550 (OH); δ_H(400 MHz) 0.83 (3 H, s) and 1.23 (3 H, s) (3-Me_2), 1.08 (3 H, d, *J* 7) and 1.37 (3 H, d, *J* 7) (CH*Me*$_2$), 1.69 (1 H, sept, *J* 7, C*H*Me_2), 2.39 (3 H, s, ArMe), 2.48 (1 H, s, OH), 2.53 (1 H, s, OH) and 7.1–7.4 (4 H, m, ArH); δ_C 13.9 (q), 18.4 (q), 19.1 (q), 19.8 (q), 20.4 (q) (5 × Me), 25.9 (s, C-3), 29.7 (d, *C*HMe_2), 64.4 (s) and 64.8 (s) (C-1 and -2), 125.3 (d), 127.9 (d), 128.4 (d), 131.2 (d), 136.5 (s) and 140.0 (s) (ArC).

2-(1′-*Hydroxy*-1′,2′-*dihydrobenzocyclobuten*-1′-*yl*)-2,4-*dimethylpentan*-3-*ol* **4a** (4:1 *mixture of two stereoisomers*). M.p. 96–97 °C (from hexane) (Found: C, 77.1; H, 9.3. $C_{15}H_{22}O_2$ requires C, 76.9; H, 9.5%); ν_{max}/cm^{-1} 3350br (OH); δ_H(400 MHz) 0.69 (0.6 H, s), 0.75 (2.4 H, s), 1.10 (2.4 H, s) and 1.24 (0.6 H, s) (1-H_3 and 2-Me), 0.97 (3.0 H, d, *J* 7), 1.04 (0.6 H, d, *J* 7) and 1.05 (2.4 H, d, *J* 7.0) (CH*Me*$_2$), 1.97 (1.0 H, m, C*H*Me_2), 2.92 (0.8 H) and 3.56 (0.8 H) (AB-system, *J* 15) and 3.01 (0.2 H) and 3.53 (0.2 H) (AB-system, *J* 15) (2′-H_2), 3.23 (0.2 H, br s), 3.32 (0.8 H, br s), 4.29 (0.8 H, br s) and 4.35 (0.2 H, br s, 2 × OH), 3.75 (0.2 H, d, *J* 2) and 3.86 (0.8 H, d, *J* 2) (3-H) and 7.1–7.3 (4 H, m, ArH).

trans-1-*Isopropyl*-3,3-*dimethyl*-2-(2′,4′-*dimethylphenyl*)*cyclopropane*-1,2-*diol* **2b**. M.p. 93–94 °C (from hexane) (Found: C, 77.5; H, 9.5. $C_{16}H_{24}O_2$ requires C, 77.4; H, 9.7%); ν_{max}/cm^{-1} 3610, 3550 and 3500br (OH); δ_H(400 MHz) 0.92 (3 H, s) and 1.31 (3 H, s) (3-Me_2), 1.05 (3 H, d, *J* 7) and 1.21 (3 H, d, *J* 7) (CH*Me*$_2$), 1.40 (1 H, s, OH), 1.57 (1 H, s, OH), 2.27 (1 H, sept, *J* 7, C*H*Me_2), 2.30 (3 H, s, ArMe), 2.35 (3 H, s, ArMe) and 6.97 (1 H, d, *J* 7), 7.06 (1 H, s) and 7.28 (1 H, d, *J* 7) (ArH); δ_C 15.5 (q), 17.7 (q), 17.9 (q), 18.9 (q), 19.2 (q), 21.0 (q) (6 × Me), 26.7 (d, *C*HMe_2), 27.7 (s, C-3), 64.9 (s) and 66.6 (s) (C-1 and -2), 126.2 (d), 131.3 (d), 131.8 (d), 133.9 (s), 137.6 (s) and 139.0 (s) (ArC).

2-(1′-*Hydroxy*-4′-*methyl*-1′,2′-*dihydrobenzocyclobuten*-1′-*yl*)-2,4-*dimethylpentan*-3-*ol* **4b**.* M.p. 96–97 °C (from hexane) (Found: C, 77.4; H, 9.6. $C_{16}H_{24}O_2$ requires C, 77.4; H, 9.7%); ν_{max}($CHCl_3$)/cm^{-1} 3600 and 3450br (OH); δ_H(400 MHz) 0.77 (3 H, s) and 1.11 (3 H, s) (1-H_3 and 2-Me), 0.98 (3 H, d, *J* 7) and 1.06 (3 H, d, *J* 7) (CH*Me*$_2$), 1.98 (1 H, sept × d, *J* 7 and 2, C*H*Me_2), 2.34 (3 H, s, ArMe), 2.90 (1 H) and 3.55 (1 H) (AB-system, *J* 15, 2′-H_2), 3.18 (1 H, br s, OH), 3.87 (1 H, br s, OH), 3.87 (1 H, d, *J* 2, 3-H) and 6.96 (1 H, s), 7.02 (1 H, d, *J* 7) and 7.08 (1 H, d, *J* 7) (ArH).

trans-1-*Isopropyl*-3,3-*dimethyl*-2-(2′,5′-*dimethylphenyl*)*cyclopropane*-1,2-*diol* **2c**. M.p. 110–112 °C (from hexane) (Found: C, 77.2; H, 9.7. $C_{16}H_{24}O_2$ requires C, 77.4; H, 9.7%); ν_{max}/cm^{-1} 3610 and 3450br (OH); δ_H(400 MHz) 0.91 (3 H, s) and 1.30 (3 H, s) (3-Me_2), 1.03 (3 H, d, *J* 7) and 1.20 (3 H, d, *J* 7) (CH*Me*$_2$), 1.40 (1 H, s, OH), 1.73 (1 H, s, OH), 2.25 (1 H, sept, *J* 7, C*H*Me_2), 2.30 (3 H, s, ArMe), 2.32 (3 H, s, ArMe) and 7.00 (1 H, d, *J* 7), 7.11 (1 H, d, *J* 7) and 7.17 (1 H, s) (ArH); δ_C 15.5 (q), 17.7 (q), 17.9 (q), 18.8 (q), 18.9 (q), 21.0 (q) (6 × Me), 26.7 (d, *C*HMe_2), 27.7 (s, C-3), 65.2 (s) and 66.6 (s) C-1 and -2), 128.6 (d), 130.9 (d), 131.9 (d), 134.9 (s), 135.9 (s) and 136.6 (s) (ArC).

cis-1-*Isopropyl*-3,3-*dimethyl*-2-(2′,5′-*dimethylphenyl*)*cyclopropane*-1,2-*diol* **3c**. M.p. 114–115 °C (from hexane) (Found: C, 77.4; H, 9.6. $C_{16}H_{24}O_2$ requires C, 77.4; H, 9.7%); ν_{max}/cm^{-1} 3610, 3550 and 3450br (OH); δ_H(400 MHz) 0.84 (3 H, s) and 1.22 (3 H, s) (3-Me_2), 1.08 (3 H, d, *J* 7) and 1.37 (3 H, d, *J* 7) (CH*Me*$_2$), 1.89 (1 H, sept, *J* 7, C*H*Me_2), 2.28 (3 H, s, ArMe),

* The configurations of these compounds could not be assigned.

2.31 (1 H, br s, OH), 2.34 (3 H, s, ArMe), 2.49 (1 H, br s, OH) and 7.01 (1 H, d, *J* 7), 7.11 (1 H, d, *J* 7) and 7.20 (1 H, s) (ArH); δ_C 13.9 (q), 18.5 (q), 19.2 (q), 19.3 (q), 20.4 (q), 21.0 (q) (6 × Me), 25.8 (s, C-3), 29.7 (d, *C*HMe$_2$), 64.5 (s) and 64.8 (s), (C-1 and -2), 128.6 (d), 129.3 (d), 131.1 (d), 134.6 (s), 136.4 (s) and 136.6 (s) (ArC).

2-(1′-*Hydroxy*-5′-*methyl*-1′,2′-*dihydrobenzocyclobuten*-1′-*yl*)-2,4-*dimethylpentan*-3-*ol* **4c** (*two stereoisomers* **A*** *and* **B*** *were isolated*). **A**: M.p. 136 °C (from hexane) (Found: C, 77.4; H, 9.6. $C_{16}H_{24}O_2$ requires C, 77.4; H, 9.7%); ν_{max}/cm^{-1} 3400br (OH); δ_H(60 MHz, CCl_4) 0.72 (3 H, s) and 1.01 (3 H, s) (1-H$_3$ and 2-Me), 0.91 (3 H, d, *J* 7) and 1.02 (3 H, d, *J* 7) (CH*Me*$_2$), 1.90 (1 H, m, C*H*Me$_2$), 2.32 (3 H, s, ArMe), 2.74 (1 H) and 3.49 (1 H) (AB-system, *J* 14, 2′-H$_2$), 3.27 (2 H, br s, 2 × OH), 3.72 (1 H, d, *J* 2, 3-H) and 6.8–7.1 (3 H, m, ArH). **B**: M.p. 95 °C (from hexane) (Found: C, 77.2; H, 9.5. $C_{16}H_{24}O_2$ requires C, 77.4; H, 9.7%); ν_{max}/cm^{-1} 3350br (OH); δ_H(60 MHz, CCl_4) 0.64 (3 H, s) and 1.14 (3 H, s) (1-H$_3$ and 2-Me), 0.87 (3 H, d, *J* 7) and 0.92 (3 H, d, *J* 7) (CH*Me*$_2$), 1.81 (1 H, m, C*H*Me$_2$), 2.14 (3 H, s, ArMe), 2.83 (1 H) and 3.41 (1 H) (AB-system, *J* 14, 2′-H$_2$), 3.58 (1 H, d, *J* 2, 3-H), 4.03 (2 H, br s, 2 × OH) and 6.7–7.1 (3 H, m, ArH).

trans-1-(1-*Ethylpropyl*)-3,3-*dimethyl*-2-(o-*methylphenyl*)-*cyclopropane*-1,2-*diol* **2d**.† Oil; ν_{max}/cm^{-1} 3610 and 3450br (OH); δ_H(400 MHz) 0.88 (3 H, s) and 1.29 (3 H, s) (3-Me$_2$), 0.98 (3 H, t, *J* 7, CH$_2$*Me*), 1.06 (3 H, t, *J* 7, CH$_2$*Me*), 1.43 (1 H, m), 1.52 (1 H, m) and 1.68 (2 H, m) (2 × C*H*$_2$Me), 1.71 (1 H, m, C*H*Et$_2$), 1.73 (2 H, br s, 2 × OH), 2.37 (3 H, s, ArMe) and 7.1–7.5 (4 H, ArH); δ_C 12.7 (q), 12.8 (q), 16.7 (q), 17.4 (q) and 19.4 (q) (5 × Me), 23.8 (t) and 24.8 (t) (2 × *C*H$_2$Me), 28.0 (s, C-3), 40.0 (d, *C*HEt$_2$), 64.6 (s) and 66.5 (s) (C-1 and -2), 125.3 (d), 127.7 (d), 130.9 (d), 131.1 (d), 137.1 (s) and 139.5 (s) (ArC).

cis-1-(1-*Ethylpropyl*)-3,3-*dimethyl*-2-(o-*methylphenyl*)*cyclopropane*-1,2-*diol* **3d**. M.p. 84–85 °C (from hexane) (Found: C, 77.8; H, 9.9. $C_{17}H_{26}O_2$ requires C, 77.8; H, 10.0%); ν_{max}/cm^{-1} 3600, 3550 and 3400 (OH); δ_H(400 MHz) 0.79 (3 H, s) and 1.20 (3 H, s) (3-Me$_2$), 0.97 (3 H, t, *J* 7, CH$_2$*Me*), 1.12 (3 H, t, *J* 7, CH$_2$*Me*), 1.43 (1 H, m, C*H*Et$_2$), 1.60 (2 H, m), 1.80 (1 H, m) and 1.96 (1 H, m) (2 × C*H*$_2$Me), 2.38 (3 H, s, ArMe), 2.56 (1 H, s, OH), 2.63 (1 H, s, OH) and 7.1–7.3 (4 H, m, ArH); δ_C 12.6 (q), 12.9 (q), 13.8 (q), 19.1 (q) and 19.7 (q) (5 × Me), 24.9 (t) and 26.3 (t) (2 × *C*H$_2$Me), 26.0 (s, C-3), 42.4 (d, *C*HEt$_2$), 64.2 (s) and 66.2 (s) (C-1 and -2), 125.3 (d), 127.9 (d), 128.4 (d), 131.2 (d), 136.6 (s) and 140.1 (s) (ArC).

4-*Ethyl*-2-(1′-*hydroxy*-1′,2′-*dihydrobenzocyclobuten*-1′-*yl*)-2-*methylhexan*-3-*ol* **4d**. Two stereoisomers **A*** and **B*** were isolated. **A**: M.p. 116–117 °C (from hexane) (Found: C, 77.7; H, 10.0. $C_{17}H_{26}O_2$ required C, 77.8; H, 10.0%); ν_{max}(CHCl$_3$)/cm^{-1} 3610 and 3450br (OH); δ_H(400 MHz) 0.79 (3 H, s) and 1.07 (3 H, s) (1-H$_3$ and 2-Me), 0.92 (3 H, t, *J* 7, CH$_2$*Me*), 0.95 (3 H, t, *J* 7, CH$_2$*Me*), 1.18 (1 H, m, 4-H), 1.37 (2 H, m), 1.49 (1 H, m) and 1.68 (1 H, m) (2 × C*H*$_2$Me), 2.94 (1 H) and 3.58 (1 H) (AB-system, *J* 15, 2′-H$_2$), 3.00 (1 H, br s, OH), 3.99 (1 H, s, 3-H), 4.38 (1 H, br s, OH) and 7.1–7.3 (4 H, m, ArH). **B**:† Oil; ν_{max}(CHCl$_3$)/cm^{-1} 3610 and 3450br (OH); δ_H(60 MHz) 0.67 (3 H, s) and 1.21 (3 H, s) (1-H$_3$ and 2-Me), 0.8–2.1 [11 H, m, C*H*(C*H*$_2$*Me*)$_2$], 2.40 (1 H, s, OH), 3.01 (1 H) and 3.58 (1 H) (AB-system, *J* 14, 2′-H$_2$), 3.93 (2 H, m, OH and 3-H) and 6.9–7.6 (4 H, m, ArH).

trans-1-*Cyclohexyl*-3,3-*dimethyl*-2-(o-*methylphenyl*)*cyclopropane*-1,2-*diol* **2e**. M.p. 84–86 °C (from hexane) (Found: C, 78.8; H, 9.5. $C_{18}H_{26}O_2$ requires C, 78.8; H, 9.6%); ν_{max}/cm^{-1} 3600 and 3450br (OH); δ_H(400 MHz) 0.89 (3 H, s) and 1.30 (3 H, s) (3-Me$_2$), 1.3–1.9 (13 H, m, cyclohexyl and 2 × OH), 2.36 (3 H, s, ArMe) and 7.1–7.4 (4 H, m, ArH); δ_C 15.6 (q), 17.9 (q), 19.3 (q) (3 × Me), 26.3 (t), 26.5 (t), 26.6 (t), 28.0 (t), 29.1 (t) (5 × CH$_2$), 27.6 (s, C-3), 36.9 (d, CH), 65.0 (s) and 66.1 (s) (C-1 and -2), 125.4 (d), 127.8 (d), 130.9 (d), 131.5 (d), 136.9 (s) and 139.2 (s) (ArC).

cis-1-*Cyclohexyl*-3,3-*dimethyl*-2-(o-*methylphenyl*)*cyclopropane*-1,2-*diol* **3e**. M.p. 118–120 °C (from hexane) (Found: C, 78.6; H, 9.4. $C_{18}H_{26}O_2$ requires C, 78.8; H, 9.6%); ν_{max}(CHCl$_3$)/cm^{-1} 3600 and 3550 (OH); δ_H(400 MHz) 0.81 (3 H, s) and 1.21 (3 H, s) (3-Me$_2$), 1.1–2.2 (11 H, m, cyclohexyl), 2.39 (3 H, s, ArMe), 2.52 (1 H, s, OH), 2.61 (1 H, s, OH) and 7.1–7.4 (4 H, m, ArH); δ_C 14.0 (q), 18.5 (q), 19.8 (q) (3 × Me), 25.7 (s, C-3), 26.5 (t), 26.5 (t), 26.7 (t), 29.6 (t), and 31.0 (t) (5 × CH$_2$), 40.6 (d, CH), 64.3 (s) and 64.5 (s) (C-1 and -2), 125.4 (d), 127.9 (d), 128.2 (d), 131.2 (d), 136.6 (s) and 140.1 (s) (ArC).

1-*Cyclohexyl*-2-(1′-*hydroxy*-1′,2′-*dihydrobenzocyclobuten*-1′-*yl*)-2-*methylpropan*-1-*ol* **4e**.† Obtained as a mixture of two stereoisomers. Oil; ν_{max}/cm^{-1} 3400br (OH); δ_H(60 MHz) 0.64 (1.5 H, s), 0.70 (1.5 H, s), 1.01 (1.5 H, s) and 1.15 (1.5 H, s) (2-Me and 3-H$_3$), 0.9–1.9 (11 H, m, cyclohexyl), 2.78 (0.5 H) and 3.50 (0.5 H) (AB-system, *J* 14) and 2.89 (0.5 H) and 3.45 (0.5 H) (AB-system, *J* 14) (2′-H$_2$), 3.51 (0.5 H, s) and 3.62 (0.5 H, s) (1-H), 3.62 (2 H, br s, 2 × OH) and 6.9–7.4 (4 H, m, ArH).

trans-1-tert-*Butyl*-3,3-*dimethyl*-2-(o-*methylphenyl*)*cyclopropane*-1,2-*diol* **2f**. M.p. 107 °C (from hexane) (Found: C, 77.2; H, 9.7. $C_{16}H_{24}O_2$ requires C, 77.4; H, 9.7%); ν_{max}/cm^{-1} 3610 and 3450br (OH); δ_H(400 MHz) 0.97 (3 H, s) and 1.50 (3 H, s) (3-Me$_2$), 1.29 (9 H, s, Bu^t), 1.52 (1 H, s, OH), 1.72 (1 H, s, OH), 2.34 (3 H, s, ArMe) and 7.1–7.4 (4 H, m, ArH); δ_C 17.0 (q), 19.2 (q) and 20.4 (q) (3 × Me), 29.3 (q, C*Me*$_3$), 29.6 (s) and 37.6 (s) (C-3 and *C*Me$_3$), 66.6 (s) and 67.7 (s) (C-1 and -2), 125.4 (d), 127.7 (d), 131.1 (d), 131.4 (d), 137.5 (s) and 138.6 (s) (ArC).

cis-1-tert-*Butyl*-3,3-*dimethyl*-2-(o-*methylphenyl*)*cyclopropane*-1,2-*diol* **3f**. M.p. 129–132 °C (from hexane) (Found: C, 77.3; H, 9.7. $C_{16}H_{24}O_2$ requires C, 77.4; H, 9.7%); ν_{max}/cm^{-1} 3610, 3550 and 3400br (OH); δ_H(400 MHz) 0.97 (3 H, s), 1.10 (3 H, s), 1.19 (6 H, br s) and 1.24 (3 H, s) (5 × Me), 1.59 (1 H, s, OH), 2.38 (3 H, s, ArMe), 2.46 (1 H, s, OH) and 7.1–7.6 (4 H, m, ArH); δ_C 15.8 (q), 19.6 (q), 20.3 (q), 28.8 (q), 28.9 (q) and 29.4 (q) (6 × Me), 26.8 (s) and 36.7 (s) (C-3 and *C*Me$_3$), 65.5 (s) and 66.2 (s) (C-1 and -2), 124.9 (d), 128.3 (d), 131.0 (d), 132.4 (d), 136.7 (s) and 139.5 (s) (ArC).

2-(1′-*Hydroxy*-1′,2′-*dihydrobenzocyclobuten*-1′-*yl*)-2,4,4-*trimethylpentan*-3-*ol* **4f**.† Obtained as 2:1 mixture of two stereoisomers. Oil; ν_{max}/cm^{-1} 3350br (OH); δ_H(60 MHz, CCl_4) 0.84 (1.0 H, s), 0.92 (2.0 H, s), 1.09 (2.0 H, s) and 1.22 (1.0 H, s) (1-H$_3$ and 2-Me), 1.05 (9 H, s, Bu^t), 2.89 (0.7 H) and 3.68 (0.7 H) (AB-system, *J* 14) and 3.00 (0.3 H) and 3.70 (0.3 H) (AB-system, *J* 14) (2′-H$_2$), 3.53 (0.7 H, br s) and 3.97 (1.3 H, br s) (2 × OH), 3.73 (1 H, s, 3-H) and 7.2–7.5 (4 H, m, ArH).

trans-3,3-*Dimethyl*-1-(o-*methylphenyl*)-2-*phenylcyclopropane*-1,2-*diol* **2g**.† Oil; δ_C(60 MHz) 1.20 (3 H, s) and 1.25 (3 H, s) (3-Me$_2$), 1.85 (2 H, br s, 2 × OH), 2.44 (3 H, s, ArMe) and 7.1–7.8 (9 H, m, ArH).

2-(1′-*Hydroxy*-1′,2′-*dihydrobenzocyclobuten*-1′-*yl*)-2-*methyl*-1-*phenylpropan*-1-*ol* **4g**. Obtained as a 7:3 mixture of two stereoisomers. M.p. 142–145 °C (from hexane–benzene) (Found: C, 80.8; H, 7.6. $C_{18}H_{20}O_2$ requires C, 80.6; H, 7.5%); ν_{max}(CHCl$_3$)/cm^{-1} 3610 and 3450br (OH); δ_H(60 MHz) 0.49 (0.9 H, s), 0.66 (2.1 H, s), 1.01 (2.1 H, s) and 1.16 (0.9 H, s) (2-Me and 3-H$_3$), 2.87 (0.7 H) and 3.44 (0.7 H) (AB-system, *J* 14) and 3.01 (0.3 H) and 3.68 (0.3 H) (AB-system, *J* 14) (2′-H$_2$), 4.06 (1 H, br s, OH), 4.17 (1 H, br s, OH), 4.95 (0.3 H, s) and 4.99 (0.7 H, s) (1-H) and 7.1–7.5 (9 H, m, ArH).

cis-3,3-*Dimethyl*-1,2-*di*(o-*methylphenyl*)*cyclopropane*-1,2-*diol* **3h**.† M.p. 142–143 °C (from hexane–benzene); ν_{max}(CHCl$_3$)/

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* The configurations of these compounds could not be assigned.

† These compounds were obtained as oils of high purity as determined on the basis of their ^{1}H NMR spectra. However, their complete purification could not be achieved because they decomposed on distillation.

cm^{-1} 3600, 3500 and 3400br (OH); δ_H(60 MHz) 0.92 (3 H, s) and 1.41 (3 H, s) (3-Me_2), 2.49 (6 H, s, 2 × ArMe), 3.01 (2 H, s, 2 × OH) and 6.7–7.2 (8 H, m, ArH); δ_C 14.4 (q), 20.8 (q), 22.7 (q) (3-Me_2 and 2 × ArMe), 27.1 (s, C-3), 63.1 (s, C-1 and -2), 125.2 (d), 127.7 (d), 128.0 (d), 131.0 (d), 137.7 (s) and 140.0 (s) (ArC).

2-(1′-*Hydroxy*-1′,2′-*dihydrobenzocyclobuten*-1′-*yl*)-2-*methyl*-1-(o-*methylphenyl*)*propan*-1-*ol* **4h**.* M.p. 148 °C (from hexane–benzene) (Found: C, 80.6; H, 8.0. $C_{19}H_{22}O_2$ requires C, 80.8; H, 7.9%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3600 and 3400br (OH); δ_H(60 MHz) 0.54 (3 H, s) and 1.13 (3 H, s) (2-Me and 3-H_3), 2.24 (3 H, s, ArMe), 2.91 (1 H) and 3.52 (1 H) (AB-system, *J* 15, 2′-H_2), 3.80 (1 H, br s, OH), 4.38 (1 H, br s, OH), 5.45 (1 H, s, 1-H) and 7.0–7.7 (8 H, m, ArH).

2-(1′-*Hydroxy*-1′,2′-*dihydrobenzocyclobuten*-1′-*yl*)-2-*methylpentan*-3-*ol* **4i**. Obtained as a 3:2 mixture of two stereoisomers. M.p. 96–98 °C (from hexane) (Found: C, 76.4; H, 9.2. $C_{14}H_{20}O_2$ requires C, 76.3; H, 9.2%); ν_{max}/cm^{-1} 3350br (OH); δ_H(400 MHz) 0.68 (1.8 H, s), 0.79 (1.2 H, s), 0.97 (1.2 H, s) and 1.12 (1.8 H, s) (1-H_3 and 2-Me), 1.02 (1.8 H, t, *J* 7) and 1.03 (1.2 H, t, *J* 7) (CH_2Me), 1.39 (1 H, m) and 1.59 (1 H, m) (CH_2Me), 2.93 (0.4 H) and 3.59 (0.4 H) (AB-system, *J* 14) and 3.01 (0.6 H) and 3.54 (0.6 H) (AB-system, *J* 14) (2′-H_2), 3.60 (1 H, br s, OH), 3.71 (1 H, t, *J* 8, 3-H), 4.47 (1 H, br s, OH) and 7.1–7.3 (4 H, m, ArH).

3-(1′-*Hydroxy*-1′,2′-*dihydrobenzocyclobuten*-1′-*yl*)-3-*methylbutan*-2-*ol* **4j**. Obtained as two stereoisomers **A*** and **B**.* **A**: M.p. 132–133 °C (from hexane) (Found: C, 75.5; H, 8.7. $C_{13}H_{18}O_2$ requires C, 75.7; H, 8.8%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3600 and 3450br (OH); δ_H(60 MHz) 0.69 (3 H, s) and 1.00 (3 H, s) (3-Me and 4-H_3), 1.15 (3 H, d, *J* 7, 1-H_3), 2.89 (1 H) and 3.57 (1 H) (AB-system, *J* 14, 2′-H_2), 3.91 (2 H, br s, 2 × OH), 4.08 (1 H, q, *J* 7, 2-H) and 7.0–7.3 (4 H, m, ArH). **B**: M.p. 84–85 °C (from hexane) (Found: C, 75.5; H, 8.7. $C_{13}H_{18}O_2$ requires C, 75.7; H, 8.8%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3600 and 3400br (OH); δ_H(60 MHz, CCl_4) 0.53 (3 H, s) and 1.05 (3 H, s) (3-Me and 4-H_3), 0.98 (3 H, d, *J* 7, 1-H_3), 2.88 (1 H) and 3.43 (1 H) (AB-system, *J* 14, 2′-H_2), 3.85 (1 H, q, *J* 7, 2-H), 4.88 (2 H, br s, 2 × OH) and 6.9–7.3 (4 H, m, ArH).

2-(1′-*Hydroxy*-1′,2′-*dihydrobenzocyclobuten*-1′-*yl*)-2-*methylpropan*-1-*ol* **4k**. M.p. 53–54 °C (from hexane) (Found: C, 75.1; H, 8.3. $C_{12}H_{16}O_2$ requires C, 75.0; H, 8.4%); ν_{max}/cm^{-1} 3350br (OH); δ_H(60 MHz) 0.79 (6 H, s, 2-Me and 3-H_3), 2.80 (1 H) and 3.37 (1 H) (AB-system, *J* 14, 2′-H_2), 3.39 (2 H, s, 1-H_2), 4.64 (2 H, br s, 2 × OH) and 6.9–7.3 (4 H, m, ArH).

2-(1′-*Hydroxy*-1′,2′-*dihydrobenzocyclobuten*-1′-*yl*)-4,4-*dimethylpentan*-3-*ol* **9a**.* M.p. 136 °C (from hexane) (Found: C, 76.6; H, 9.3. $C_{15}H_{22}O_2$ requires C, 76.9; H, 9.5%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3500br (OH); δ_H(400 MHz) 0.91 (9 H, s, Bu^t), 1.00 (3 H, d, *J* 7, 1-H_3), 2.16 (1 H, quint., *J* 7, 2-H), 3.07 (1 H, s, OH), 3.09 (1 H) and 3.46 (1 H) (AB-system, *J* 14, 2′-H_2), 3.38 (1 H, d, *J* 7, 3-H), 3.58 (1 H, s, OH) and 7.1–7.3 (4 H, m, ArH); δ_C 18.0 (q, C-1), 26.0 (q, CMe_3), 35.9 (s, CMe_3), 39.8 (d, C-2), 44.4 (t, C-2′), 84.2 (s + d, C-1′ and -3), 122.9 (d), 123.4 (d), 127.0 (d), 128.9 (d), 142.0 (s) and 150.0 (s) (ArC).

2-(1′-*Hydroxy*-1′,4′-*dihydrobenzo*[d][1,2]*dioxin*-1′-*yl*)-4,4-*dimethylpentan*-3-*ol* **10**.* M.p. 125–127 °C (from hexane) (Found: C, 67.6; H, 8.3. $C_{15}H_{22}O_4$ requires C, 67.7; H, 8.3%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3600 and 3400br (OH); δ_H(400 MHz) 0.65 (3 H, d, *J* 7, 1-H_3), 1.02 (9 H, s, Bu^t), 2.56 (1 H, quint, *J* 7, 2-H), 2.91 (1 H, d, *J* 4, 3-OH), 3.51 (1 H, dd, *J* 7 and 4, 3-H), 4.89 (1 H) and 5.41 (1 H) (AB-system, *J* 15, 4′-H_2), 6.50 (1 H, s, 1′-OH) and 7.1–7.5 (4 H, m, ArH); δ_C 17.2 (q, C-1), 26.0 (q, CMe_3), 36.0 (s, CMe_3), 42.5 (d, C-2), 71.7 (t, C-4′), 82.7 (d, C-3), 104.9 (s, C-1′), 124.2 (d), 126.1 (d), 127.6 (d), 127.8 (d), 132.9 (s) and 134.4 (s) (ArC).

3-(3′-*Hydroxy*-4′,4′-*dimethylpentan*-2′-*yl*)*phthalide* **11a**. Obtained as a 2:1 mixture of two stereoisomers. Oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 3600 and 3500br (OH) and 1765 (C=O); δ_H(60 MHz) 0.60 (2.0 H, d, *J* 7) and 0.66 (1.0 H, d, *J* 7) (1′-Me), 1.04 (9 H, s, Bu^t), 2.06 (1 H, br s, OH), 2.1–2.8 (1 H, m, 1′-H), 3.33 (0.3 H, d, *J* 5) and 3.41 (0.7 H, d, *J* 8) (2′-H), 5.87 (0.3 H, d, *J* 4) and 5.99 (0.7 H, d, *J* 1) (3-H) and 7.1–8.0 (4 H, m, ArH).

1-(1′-*Hydroxy*-5′-*methyl*-1′,2′-*dihydrobenzocyclobuten*-1′-*yl*)-3,3-*dimethylbutan*-2-*ol* **9b**.* M.p. 110 °C (from hexane) (Found: C, 76.8; H, 9.5. $C_{15}H_{22}O_2$ requires C, 76.9; H, 9.5%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3450br (OH); δ_H(400 MHz) 0.89 (9 H, s, Bu^t), 1.88 (1 H, dd, *J* 14 and 2) and 2.07 (1 H, dd, *J* 14 and 11) (1-H_2), 2.35 (3 H, s, 5′-Me), 3.16 (1 H) and 3.26 (1 H) (AB-system, *J* 14) (2′-H_2), 3.18 (1 H, br s, OH), 3.77 (1 H, dd, *J* 11 and 2, 2-H), 3.94 (1 H, br s, OH) and 7.0–7.2 (3 H, m, ArH); δ_C 22.0 (q, Me), 25.6 (q, CMe_3), 34.7 (s, CMe_3), 39.0 (t) and 47.3 (t) (C-1 and C-2′), 78.7 (d, C-2), 80.9 (s, C-1′), 122.0 (d), 123.7 (d), 130.1 (d), 136.9 (s), 138.0 (s) and 149.8 (s) (ArC).

3-(2′-*Hydroxy*-3′,3′-*dimethylbutyl*)-5-*methylphthalide* **11b**.* M.p. 128 °C (from hexane–acetone) (Found: C, 72.6; H, 8.1. $C_{15}H_{20}O_3$ requires C, 72.6; H, 8.1%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3600 (OH) and 1760 (C=O); δ_H(400 MHz) 0.94 (9 H, s, Bu^t), 1.90 (1 H, ddd, *J* 14, 10 and 7) and 2.12 (1 H, ddd, *J* 14, 5 and 2) (1′-H_2), 2.14 (1 H, s, OH), 2.51 (3 H, s, 5-Me), 3.62 (1 H, dd, *J* 10 and 2, 2′-H), 5.59 (1 H, dd, *J* 7 and 5, 3-H) and 7.3–7.8 (3 H, m, ArH); δ_C 22.1 (q, Me), 25.5 (q, CMe_3), 35.0 (s, CMe_3), 36.9 (t, C-1′), 77.0 (d) and 80.8 (d) (C-2′ and C-3), 122.5 (d), 125.6 (d), 130.4 (d), 123.2 (s), 145.3 (s) and 150.5 (s) (ArC) and 170.1 (s, C=O).

trans-3,3-*Dimethyl*-1,2-*diphenylcyclopropane*-1,2-*diol* **13a**.† Oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 3600 and 3450br (OH); δ_H(60 MHz) 1.22 (6 H, s, 3-Me_2), 2.24 (2 H, br s, 2 × OH) and 7.2–7.7 (10 H, m, ArH).

cis-3,3-*Dimethyl*-1,2-*diphenylcyclopropane*-1,2-*diol* **14**.† Oil (lit.,[9] white solid, m.p. 132 °C); δ_H(60 MHz) 1.09 (3 H, s, 3-Me), 1.41 (3 H, s, 3-Me), 3.43 (2 H, br s, 2 × OH) and 7.1–7.7 (10 H, m, ArH).

trans-1-*Isopropyl*-3,3-*dimethyl*-2-*phenylcyclopropane*-1,2-*diol* **13b**.† Oil; ν_{max}/cm^{-1} 3630 and 3500br (OH); δ_H(400 MHz) 1.04 (3 H, s) and 1.33 (3 H, s) (3-Me_2), 1.05 (3 H, d, *J* 7) and 1.22 (3 H, d, *J* 7) ($CHMe_2$), 1.40 (1 H, s, OH), 1.47 (1 H, s, OH), 2.28 (1 H, sept., *J* 7, $CHMe_2$) and 7.3–7.5 (5 H, m, ArH).

Reaction of Cyclopropane-1,2-*diol* **3a** *with Phenylboronic Acid*.—A solution of compound **3a** (65 mg, 0.27 mmol) and phenylboronic acid (37 mg, 0.30 mmol) in dry benzene (5 cm^3) was stirred at room temperature for 2 h. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel [hexane–ethyl acetate (30:1)] to give the ester **6**.

1-*Isopropyl*-6,6-*dimethyl*-5-(o-*methylphenyl*)-3-*phenyl*-2,4-*dioxa*-3-*borabicyclo*[3.1.0]*hexane* **6**. M.p. 66–67 °C (Found: C, 78.9; H, 7.9. $C_{21}H_{25}BO_2$ requires C, 78.8; H, 7.9%); δ_H(400 MHz) 0.86 (3 H, s) and 1.11 (3 H, s) (6-Me_2), 1.24 (3 H, d, *J* 7) and 1.39 (3 H, d, *J* 7) ($CHMe_2$), 2.12 (1 H, sept, *J* 7, $CHMe_2$), 2.45 (3 H, s, ArMe) and 7.1–7.9 (9 H, m, ArH); δ_C 13.4 (q), 17.2 (q), 19.6 (q), 19.8 (q), 19.9 (q) (5 × Me), 23.6 (s, C-6), 28.1 (d, $CHMe_2$), 73.6 (s) and 75.6 (s) (C-1 and -5), 125.5 (d), 127.7 (d), 128.4 (d), 128.5 (d), 130.8 (d), 131.3 (d), 134.8 (d), 134.0 (s) and 140.0 (s) (ArC).

Oxidation of Benzocyclobutenol **4a**.—To a solution of compound **4a** (50 mg, 0.22 mmol) in acetone (1 cm^3) was added

* The configurations of these compounds could not be assigned.

† These compounds were so sensitive to air that they were rapidly oxidized to give 1,3-diketones. Even the ^1H NMR spectra just after isolation showed peaks due to the 1,3-diketone as well as peaks due to the cyclopropane-1,2-diol. The ^1H NMR spectral data of these compounds were obtained by subtraction of peaks due to the 1,3-diketone.

slowly Jones reagent (2.57 mol dm^{-3} solution; 0.06 cm^3, 0.15 mmol) with ice-cooling. The mixture was stirred with ice-cooling for 1 h. The acetone solution was separated from the solid and worked up. The ^1H NMR analysis of the crude mixture revealed that compound **4a** was oxidized to the ketone **7**.[5]

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