Synthetic Photochemistry. Part 2.[1] Generation of Benzocyclobutenols by Photocyclisation of Benzocycloalkenones

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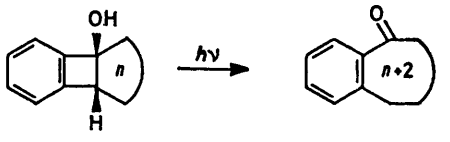
The irradiation of benzocycloalkenones (2) was examined in t-butyl alcohol and cyclisation into benzocyclobutenols (1) was observed for n = 7—9. On irradiation, substituted benzocycloalkenones (4) cyclised by an external mechanism to tricyclic benzocyclobutenols (7) and/or by an internal mechanism to alcohols (5) and/or (6), the relative ratio of these products depending on the nature of the alkyl substituent and the ring size. The results are related to the mechanism of the photoenolisation reaction.

We have previously shown that photolysis of benzocyclobutenols (1) led to benzocycloalkenones (2).[1,2]

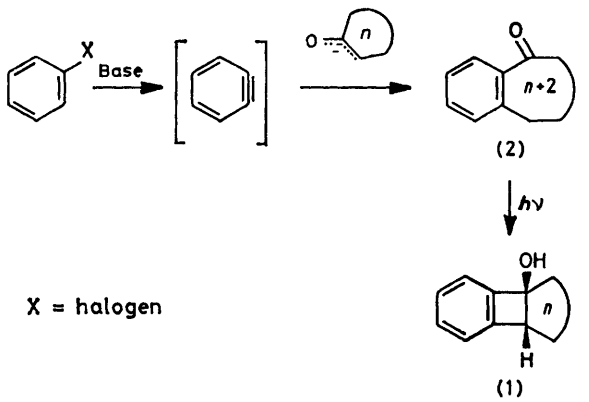
During this work, we observed that in t-butyl alcohol and without a triplet quencher, photoreaction of the benzocycloalkenones (2) may partially occur. Amongst the products isolated alcohols (1) were found, and we then



(1) (2)

n and n + 2 are the numbers of carbon atoms in the rings

undertook the study of the photolytic behaviour of ketones (2).[1,2] Indeed, alcohols (1) may be obtained by arynic additions,[3] but this is limited to values of n = 5—7. We thought that irradiations of ketones (2)



SCHEME 1

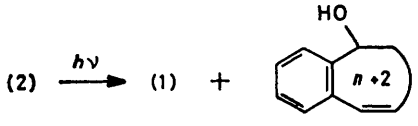
might constitute a new synthetic pathway; moreover ketones (2) are easily obtained by means of arynic additions.[4,5] Thus a general synthetic approach to the alcohols (1) as shown in Scheme 1 might be feasible.

We were also interested in the alcohols (1) because they were unknown for $n > 7$, and also because they showed some interesting pharmacological properties.[6] Finally, irradiations of *ortho*-alkylaryl ketones have been frequently studied,[7,8] and the mechanistic aspect of these reactions much discussed.[8,9] However, studies of the benzocycloalkenones (2) with $n \geqslant 5$ have not been described in the literature and thus we hoped to obtain some information about the irradiation of these compounds.

RESULTS

Irradiation of Benzocycloalkenones (2).—Irradiations were performed in t-butyl alcohol in order to diminish the classical photoreduction [10] products observed with these ketones.[1] When cyclisation does occur, the only products formed are alcohols (1) and, in a few cases, alcohols (3). The main results obtained are summarised in Table 1; they will be discussed later.

Irradiation of Alkylbenzocycloalkenones (4).—In order to prepare several substituted benzocyclobutenols and to



(3)

obtain some information about the influence of an alkyl substituent on the irradiation of benzocycloalkenones, we studied the ketones (4).[5] Two cyclisation pathways are possible (Scheme 2), an internal reaction leading to (5) and/or (6), and an external reaction leading to (7).

Note that almost simultaneously with our first publication,[1] one example of such an external reaction was reported by Sammes *et al.*[11]

Our own results are summarised in Tables 2 and 3 and will

TABLE 1

Products from the irradiation of benzocycloalkenones (2) in t-butyl alcohol [a]

Run	Ketone (2) n-value	Recovered ketone (2) (%)	Products formed (%) [c] Alcohol (1)	Alcohol (3)	ϕ Value of ketone (2)
R-1	6 [b]	71			
R-2	7 [b]	25	37 [d] (49)	16 [d] (21)	0.063
R-3	8	59	40 (98)		0.034
R-4	9	50	45 (90)		0.021
R-5	10	*ca.* 100			
R-6	12	*ca.* 100			

[a] See Experimental section for irradiating procedure and conditions. [b] Results previously reported.[1] [c] In parentheses is given the percentage conversion based on consumed ketone (2). [d] Respective yields determined by n.m.r. analysis.

TABLE 2

Irradiation of alkylbenzocycloalkenones (4) in t-butyl alcohol

Substituent	*n*-Value	Run	Recovered ketone (4) %	ϕ Value	Alcohol (7) %	Alcohols [a] (5) and/or (6) (%)	Total alcohols [b] formed (%)	Ratio (7) : (5) + (6)
$R^1 = R^2 = H$	6	R-7 [c]	41	0.050	58	0	98	100 : 0
	7	R-8	25	0.067	73	0	98	100 : 0
	8	R-9	50	0.042	7	39 (17 *trans*, 22 *cis*)	92	15 : 85
	9	R-10	7	0.032	32	60 (*cis*)	99	35 : 65
	10	R-11	61	0.033	0	39 (*cis*)	100	0 : 100
	12	R-12	83	0.015	0	17 (*cis*)	100	0 : 100
$R^1 = H$, $R^2 = Me$ [d]	6	R-13	38	0.006	58	0	94	100 : 0
	7	R-14	41	0.049	58 (37 *cis*, 21 *trans*)	0	98	100 : 0
	8	R-15	41	0.049	19 (16 *cis*, 3 *trans*)	39 (15 *trans*, 24 *cis*)	98	33 : 77
	9	R-16	34	0.020	37 (*cis*)	30 (*cis*)	100	55 : 45
	10	R-17	19	0.013	28 (*cis*)	41 (*cis*)	85	41 : 59
	12	R-18	55	0.009	30(*cis*)	10 (*cis*)	89	75 : 25
$R^1 = R^2 = Me$	6	R-19	53	0.006	32	0	68	100 : 0
	7	R-20	19	0.036	77	0	95	100 : 0
	8	R-21	12	0.073	56	32 (5 *trans*, 27 *cis*)	100	64 : 36
	9	R-22	10	0.016	55	35 (*cis*)	100	61 : 39
	10	R-23	56	0.022	27	15 (*cis*)	96	64 : 36
	12	R-24	75	0.007	15	7 (*cis*)	88	68 : 32

[a] In parentheses, the respective yield for *trans* (5) and *cis* (6). [b] Yield based on consumed ketones (4). [c] Results previously reported.[1] [d] Mixture of *cis*- (H,OH) and *trans*- alcohols (respective yields, if determined, in parentheses).

TABLE 3

Irradiations of alkylbenzocycloalkenones (4) in acetone

Run [a]	Ketone (4) R^1	Ketone (4) R^2	Ketone (4) *n*	ϕ Value	Recovered ketone (4) (%)	Alcohol (7) [b] (%)	Alcohol [c] (5) and/or (6) (%)	Total alcohols [d] formed (%)	Ratio (7) : (5) + (6)
R-24 (R-8)	H	H	7	0.085	0	90	0	90	100 : 0
R-26 (R-13)	H	Me	6	0.026	6	84 (*cis* 75, *trans* 9)	0	89	100 : 0
R-27 (R-14)	H	Me	7	0.043	6	91 (*cis* 62, *trans* 29)	0	97	100 : 0
R-28 (R-17)	H	Me	10	0.028	20	64 (*cis*)	15 (*cis*)	99	81 : 19
R-29 (R-18)	H	Me	12	0.020	19	53 (*cis*)	19 (*cis*)	89	74 : 26
R-30 (R-19)	Me	Me	6	0.022	23	66	0	86	100 : 0
R-31 (R-20)	Me	Me	7	0.052	23	72	0	93	100 : 0
R-32 (R-23)	Me	Me	10	0.020	16	74	10 (*cis*)	100	88 : 12
R-33 (R-24)	Me	Me	12	0.016	31	56	12 (*cis*)	99	82 : 18

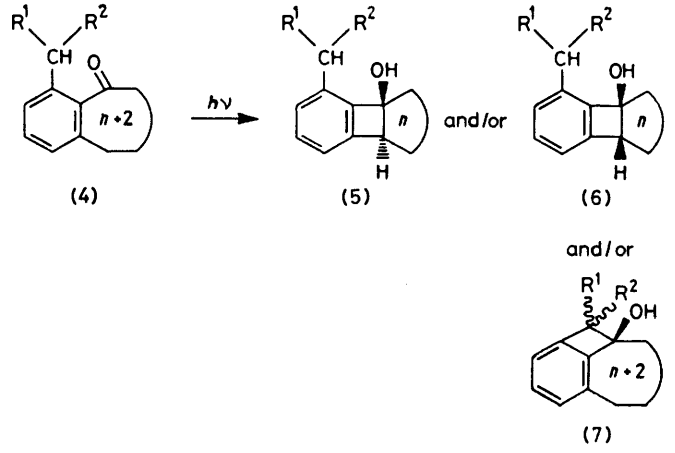
[a] Corresponding run in t-butyl alcohol in parentheses. [b] Mixture of *cis*-(H,OH) and *trans* alcohols for $R^1 = H$, $R^2 = Me$ (relative yields in parentheses). [c] In parentheses, the nature of the alcohol with the respective yields for *trans* (5) and *cis* (6). [d] Yield based on consumed ketones (4).

be discussed later. Most of the irradiations were performed in t-butyl alcohol (Table 2); however, for some ketones we observed poor conversion yields, which was avoided by using acetone as a solvent (Table 3) (note that acetone may have several effects, *e.g.* energy transfer or stabilisation of intermediates [12]).

For the ketones (4; $R^1 = H$, $R^2 = Me$), (7) was generally a mixture of *cis* and *trans* isomers, the ratio depending on the solvent (Table 2, runs 14 and 15; Table 3, runs 26 and 27). Such an effect has previously been observed by other authors.[7b,13] Alcohols (5) were only observed for $n = 8$; they constitute the first example of fused benzocyclobutenols with a *trans* ring-junction.

DISCUSSION

Photoenolisation is a classical reaction,[8] but its mechanism is still subject to much controversy; the mechanism of benzocyclobutenol formation is thus no better explained. The alcohol could be formed (Scheme



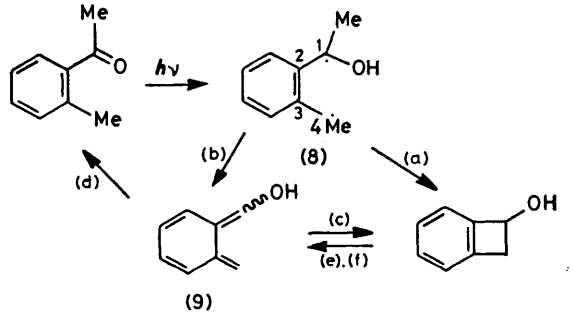
SCHEME 2

3) either by direct cyclisation (path a) from a diradical * (8) or by a two-step process (paths b and c) involving intermediate dienols (9) (both the *E* and *Z* isomers of the dienol could be formed [9]).

Although our results were mainly directed towards synthetic utility, we can put forward some mechanistic comments on the photocylisation of benzocycloalkenones.

First, let us examine the results obtained with unsubstituted ketones (2; $n = 6$—10 and 12) (see Table 1). The smallest ring ketone (2; $n = 6$) slowly disappeared by reduction and pinacolisation,[1] without cyclisation. However, the benzocyclobutenol (1; $n = 6$) has been synthesised.[3] Thus it may be suggested that it is steric hindrance which prevents intramolecular benzylic hydrogen abstraction. The lack of peroxide formation and deuterium incorporation during irradiation, in the presence of oxygen and CH_3OD respectively, agrees with the lack of dienol formation.

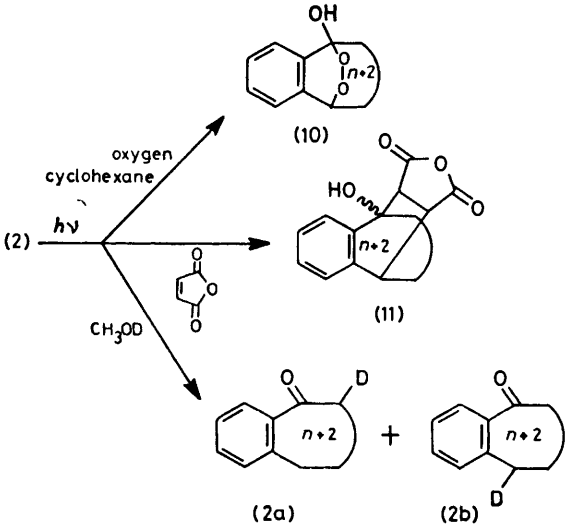
Concerning the other ketones, we also performed some complementary experiments (Scheme 4). Thus irradiation of ketones (2; $n = 7$, 10, or 12) in the presence of oxygen leads to peroxide (10). In the presence of CH_3OD, irradiation of ketones (2; $n = 7$, 8, 10, or 12) leads to the incorporation of deuterium. These observations are in agreement with dienol formation, which were confirmed by dienophile addition for (2; $n = 10$ or 12).



SCHEME 3 (a) Direct cyclisation; (b) dienol formation; (c) dienol cyclisation; (d) hydrogen transfer; (e) thermal conrotary opening; (f) photochemical disrotary opening

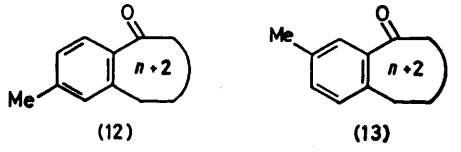
Taking into account the fact that cyclisations are only observed for (2; $n = 7$—9), and that cyclisation decreases with increase of ring size, the results can be interpreted as follows. As the ring size increases, the rotational freedom around the C(1)–C(2) and C(3)–C(4) bonds in the diradical (8) increases, which leads to easier dienol formation. If we assume that the dienol (9) leads only to the starting ketone, and the benzocyclobutenol is only formed from the diradical (8),[14] the observations cited above reflect competition between paths (a) and (b) (Scheme 3).

Note that the results obtained for (2; $n = 10$ or 12) support this conclusion; with these large-ring ketones, no cyclisation was observed. However, we cannot



SCHEME 4

completely eliminate the possibility that the absence of benzocyclobutenols is in fact simply a consequence of their instability.



Some interesting observations may be made for alkylbenzocycloalkenones. From the literature,[7b] it appeared that the presence of an alkyl substituent on the aromatic ring of a phenyl alkyl ketone favours the photocyclisation into benzocyclobutenols. This result was explained in terms of differences in the nature of the excited states (n,π^* or π,π^*). Such an effect does not seem to occur here. Indeed, the ketones (12; $n = 10$ or 12) and (13; $n = 12$) did not give any benzocyclobutenol [*cf.* the unsubstituted ketones (2; $n = 10$ or 12)]. Of

* The literature data reflect the controversy about both the nature of the biradicals and their origin: *e.g.* the nature of the excited state (n,π^* or π,π^*), and its multiplicity. On the other hand, recent theoretical calculations on a methylacetophenone agree with the process in (path a).[14]

course, in the present work, the presence of an alkyl substituent leads to competition between internal and external cyclisations.

First, we shall discuss the results for a variation in ring size for a given substituent. With $n = 6$, as would be expected from the results obtained with the corresponding unsubstituted ketone, the only product formed is (7) (external cyclisation). With $n = 7$, again only external cyclisation is observed. Molecular models showed that steric effects strongly favour hydrogen abstraction as well as cyclisation on the alkyl substituent relatively to the benzylic position of the ring. For $n = 8$ and 9 competition occurs but the variation in the relative proportions is not easily interpreted.

The results obtained with $n = 10$ and 12 should appear surprising, in comparison with those described for unsubstituted corresponding ketones. The induction of cyclisation in these larger rings by the *ortho*-substituent could be interpreted as follows: the presence of the alkyl group diminishes the rotational freedom around the C(1)–C(2) bond, forcing the carbonyl group to turn toward the benzylic carbon atom of the ring, thus reducing dienol formation and favouring internal cyclisation. However, it is possible that the presence of the alkyl group stabilises the benzocyclobutenol itself.

The differences observed in the results for variation of the *ortho*-alkyl substituent are a consequence of the superimposition of two classical effects: (i) efficiency of hydrogen abstraction relative to the strength of the CH bond (primary, secondary, tertiary) under attack, and to the statistical factor; and (ii) increasing back shift of the abstracted hydrogen with increasing stability of the formed diradical.[15] No quantitative explanation of our results relative to these parameters can be given; however they agree qualitatively, as might be expected.

In conclusion, irradiations of benzocycloalkenones appears to be a good synthetic pathway to benzocyclobutenols of the type (1) and (7). Our results seem to be in agreement with diradical formation followed by two competing pathways: cyclisation into benzocyclobutenol and dienol formation. Moreover, our qualitative analysis seems to show that steric factors play an important part in these reactions.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. I.r. spectra were recorded on a Perkin-Elmer 457 spectrophotometer, and u.v. spectra with a Beckman D.K. 2A spectrophotometer. ^{1}H N.m.r. spectra were determined on a Varian A 60 or a Perkin-Elmer R 12 B instrument, with tetramethylsilane as internal reference. Analyses were performed by the microanalytical laboratory of Paris VI of M. Dorme. Solvents were distilled and dried before use. T.l.c. was carried out on silica gel Merck G, normally using cyclohexane–ethyl acetate. Column chromatography was on silica gel Merck (0.05—0.2 mm), normally using light petroleum–ether mixtures.

Irradiations were carried out using 300-nm radiation, in a rayonet-type Srinivasan–Griffin photochemical reactor RPR 100, equipped with a merry-go-round. Solutions of the ketones in t-butyl alcohol or acetone were purged with nitrogen before irradiation. After irradiating for the appropriate time, the solvent was removed *in vacuo* and the residue was subjected to column chromatography. Each run (which represents an average of several experiments) will be described as follows: nature and concentration of starting ketone, irradiation time, nature of *n* isolated products with physical properties for new compounds, and chemical reactions for their characterisation,* if any. Quantum yields were measured using uranyl oxalate actinometry.[16]

Irradiation of Ketones (2) *in t-Butyl Alcohol* (*Table* 1).—Run 3: ketone (2; $n = 8$) 1 010 mg, 5 mmol, 2.5×10^{-2}M), 5 h. Elution gave the starting ketone (593 mg, 59%), and the alcohol (1; $n = 8$) (407 mg, 40%), m.p. 62 °C (from pentane).[6]

Run 4: ketone (2; $n = 9$) (218 mg, 1 mmol, 1.25×10^{-2}M), 5 h. Elution gave the starting ketone (110 mg, 50%), and the alcohol (1; $n = 8$) (98 mg, 45%) as an oil; $\nu_{max.}$ (film) 3 600—3 200 cm^{-1}; $\lambda_{max.}$ (MeOH) 273 (776), 266 (955), and 260 nm (ε 851); δ(CCl_4) 1.0—2.2 (14 H, m, 7 × CH_2), 2.85—3.25 (2 H, m, with 2.9, s, exchanged with D_2O, OH, Ar-C*H*), and 6.75—7.30 (4 H, m, Ar) (Found: C, 82.76; H, 9.52. $C_{15}H_{20}O$ requires C, 83.28; H, 9.32%).

Treatment of (1; $n = 9$) with $NaNH_2$ in THF afforded the ketone (2; $n = 9$) as an oil, identical with an authentic sample.

Run 5: ketone (2; $n = 10$) (207 mg, 0.9 mmol, 2.25×10^{-2}M), 58 h. Elution gave only the starting ketone.

Run 6: ketone (2; $n = 12$) (265 mg, 1.03 mmol, 1.28×10^{-2}M), 20 h. Elution gave only the starting ketone.

Irradiation of Ketones (4) *in t-Butyl Alcohol* (*Table* 2).—Run 8: ketone (4; $R^1 = R^2 = H$, $n = 7$) (429 mg, 2.12 mmol, 2.65×10^{-2}M), 5 h. Elution gave the starting ketone (107 mg, 25%) and the alcohol (7; $R^1 = R^2 = H$, $n = 7$) (315 mg, 73%), m.p. 72 °C (from pentane); $\nu_{max.}$ (film) 3 600—3 100 cm^{-1}, $\lambda_{max.}$ (MeOH) 273 (719), 266 (753), and 261 nm (ε 578); δ(CCl_4) 0.92—2.0 (10 H, m, 5 × CH_2), 2.5—2.83 (2 H, m, Ar-CH_2, nine-membered ring), 3.01 (2 H, s, Ar-CH_2, four-membered ring), 3.5 (1 H, s, exchanged with D_2O, OH), and 6.66—7.25 (3 H, m, Ar) (Found: C, 83.25; H, 8.95. $C_{14}H_{18}O$ requires C, 83.12; H, 8.97%). Treatment of (7; $R^1 = R^2 = H$, $n = 7$) with $NaNH_2$ in THF gave ketone (4; $R^1 = R^2 = H$, $n = 7$), m.p. 48 °C (from pentane), identical with an authentic sample.

Run 9: ketone (4; $R^1 = R^2 = H$, $n = 8$) (1 300 mg, 6.02 mmol, 2.5×10^{-2}M), 5 h. Elution gave a mixture (A9) of the starting ketone and the alcohol (5; $R^1 = R^2 = H$, $n = 8$) (877 mg, 67%) (see later for separation); the alcohol (6; $R^1 = R^2 = H$, $n = 8$) (286 mg, 22%) as an oil; $\nu_{max.}$ (film) 3 600—3 200 cm^{-1}; $\lambda_{max.}$ (MeOH) 274 (920), 267 (865), and 261 nm (ε 706); δ(CCl_4) 1.16—2.16 (13 H, m, with 1.97, s, exchanged with D_2O, OH, 6 × CH_2), 2.23 (3 H, s, Ar-*Me*), 2.75—3.17 (1 H, m, Ar-C*H*), and 6.66—7.16 (3 H, m, Ar) (Found: C, 82.96; H, 9.40. $C_{15}H_{20}O$ requires C, 83.28; H, 9.32%); and the alcohol (7; $R^1 = R^2 = H$, $n = 8$) (94 mg, 7%), m.p. 133 °C (from pentane); $\nu_{max.}$ (CCl_4) 3 610 and 3 600—3 200 cm^{-1}; $\lambda_{max.}$ (MeOH) 275 (766), 267 (713), and 262 nm (ε 527); δ(CCl_4) 0.83—2.83 (13 H, m, with 2.79, s, exchanged with D_2O, OH, 7 × CH_2), 2.92—3.16 (2 H, m, pseudo-d, *J* 7.5 Hz, Ar-CH_2, four-membered

* ^{1}H N.m.r. spectra for structure elucidation were recorded in the presence of [Eu(fod)$_3$].

ring), and 6.66—7.33 (3 H, m, Ar) (Found: C, 83.18; H, 9.41. $C_{15}H_{20}O$ requires C, 83.28; H, 9.32%).

Reduction of the mixture A9 with $LiAlH_4$ in ether at room temperature and column chromatography gave the alcohol (5; $R^1 = R^2 = H$, $n = 8$) (220 mg, 17%), m.p. 69 °C (from pentane); $\nu_{max.}$ (film) 3 600—3 200 cm^{-1}; $\lambda_{max.}$ (MeOH) 275 (980), 267 (886), and 262 nm (ε 653); δ (CCl_4) 1.25—2.08 (12 H, m, 6 × CH_2), 2.23 (4 H, s, exchanged with D_2O, OH, Ar-*Me*), 3.37—3.75 (1 H, m, Ar-C*H*), and 6.66—7.16 (3 H, m, Ar) (Found: C, 82.67; H, 9.78. $C_{15}H_{20}O$ requires C, 83.28; H, 9.32%), and the methylbenzocyclodecenol, which upon Jones oxidation gave the starting ketone (4; $R^1 = R^2 = H$, $n = 8$) (650 mg, 50%). Treatment of (5, 6, or 7; $R^1 = R^2 = H$, $n = 8$) with $NaNH_2$ in THF gave the ketone (4; $R^1 = R^2 = H$, $n = 8$) as an oil, identical with an authentic sample.

Run 10: ketone (4; $R^1 = R^2 = H$, $n = 9$) (228 mg, 1 mmol, 1.25 × 10^{-2}M), 6 h. Elution gave the starting ketone (16 mg, 7%), the alcohol (6; $R^1 = R^2 = H$, $n = 9$) (136 mg, 60%), m.p. 98 °C (from light petroleum); $\nu_{max.}$ (CCl_4) 3 605 cm^{-1}; $\lambda_{max.}$ (MeOH) 274 (880), 266 (829), and 261 nm (ε 619); δ($CDCl_4$) 1.0—2.61 (18 H, m, with 2.19, s, Ar-*Me*, and 2.36, s, exchanged with D_2O, OH, 7 × CH_2), 2.84—3.16 (1 H, m, pseudo-t, Ar-C*H*), and 6.49—7.29 (3 H, m, Ar) (Found: C, 83.44; H, 9.72. $C_{16}H_{22}O$ requires C, 83.43; H, 9.63%); and the alcohol (7; $R^1 = R^2 = H$, $n = 9$) (73 mg, 32%), m.p. 79 °C (from pentane); $\nu_{max.}$ (CCl_4) 3 160 and 3 600—3 200 cm^{-1}; $\lambda_{max.}$ (MeOH) 275 (729), 267 (762), and 262 nm (ε 569); δ(CCl_4) 1.0—3.99 (19 H, m; with 2.80 and 3.18, AB quartet, *J* 14 Hz, Ar-CH_2, four-membered ring; and 2.83, s, exchanged with D_2O, OH; and 8 × CH_2), and 6.55—7.25 (3 H, m, Ar) (Found: C, 83.49; H, 9.62. $C_{16}H_{22}O$ requires C, 83.43; H, 9.63%). Treatment of (6 or 7; $R^1 = R^2 = H$, $n = 9$) with $NaNH_2$ in THF gave ketone (4; $R^1 = R_2 = H$, $n = 9$), m.p. 77 °C (from light petroleum), identical with an authentic sample.

Run 11: ketone (4; $R^1 = R^2 = H$, $n = 10$) (244 mg, 1 mmol, 2.5 × 10^{-2}M), 5 h. Elution gave the starting ketone (148 mg, 61%) and the alcohol (6; $R^1 = R^2 = H$, $n = 10$) (96 mg, 39%) as an oil; $\nu_{max.}$ (film) 3 640—3 100 cm^{-1}, $\lambda_{max.}$ (MeOH) 274 (721), 267 (715), and 261 nm (ε 571); δ(CCl_4) 1.0—2.08 (16 H, m, 8 × CH_2), 2.2 (3 H, s, Ar-*Me*), 2.73 (1 H, s, exchanged with D_2O, OH), 3.0—3.46 (1 H, m, Ar-C*H*), and 6.66—7.14 (3 H, m, Ar), for which a correct elemental analysis was not obtained.

Run 12: ketone (4; $R^1 = R^2 = H$, $n = 12$) (278 mg, 1.02 mmol, 2.55 × 10^{-2}M), 5 h. Elution gave the starting ketone (230 mg, 83%) and the alcohol (6; $R^1 = R^2 = H$, $n = 12$) (47 mg, 17%) as an oil; $\nu_{max.}$ (film) 3 600—3 100 cm^{-1}; $\lambda_{max.}$ (MeOH) 273 (715), 266 (727), and 260 nm (ε 604); δ(CCl_4) 1.08—1.92 (20 H, m, 10 × CH_2), 2.07 (1 H, s, exchanged with D_2O, OH), 2.22 (3 H, s, Ar-*Me*), 2.92—3.25 (1 H, m, Ar-C*H*), and 6.64—7.12 (3 H, m, Ar) (Found: C, 82.61; H, 10.20. $C_{19}H_{28}O$ requires C, 83.77; H, 10.36%).

Run 13: ketone (4; $R^1 = H$, $R^2 = Me$, $n = 6$) (200 mg, 0.99 mmol, 1.1 × 10^{-2}M), 18 h. Elution gave the starting ketone (76 mg, 38%) and an isomeric mixture of the alcohols (7; $R^1 = H$, $R^2 = Me$, $n = 6$) (116 mg, 58%) as an oil. See Run 26, below for the physical properties of the isomers.

Run 14: ketone (4; $R^1 = H$, $R^2 = Me$, $n = 7$) (436 mg, 2.02 mmol, 2.52 × 10^{-2}M), 5 h. Elution gave the starting ketone (181 mg, 41%); the alcohol *trans*-(7; $R^1 = H$, $R^2 = Me$, $n = 7$) (91 mg, 21%), m.p. 122 °C (from pentane); $\nu_{max.}$ (CCl_4) 3 615 and 3 520—3 300 cm^{-1}; $\lambda_{max.}$ (MeOH) 273 (796), 266 (796), and 261 nm (ε 589); δ(CCl_4) 1.0—2.15 (14 H, m; with 1.22, d, *J* 7.5 Hz, Ar-CH*Me*; 1.95, s, exchanged with D_2O, OH; and 5 × CH_2), 2.50—2.83 (2 H, m, Ar-CH_2), 3.3 (1 H, q, *J* 7.5 Hz, Ar-C*H*Me), and 6.66—7.22 (3 H, m, Ar) (Found; C, 83.22; H, 9.51. $C_{15}H_{20}O$ requires C, 83.28; H, 9.32%); and the alcohol *cis*-(7; $R^1 = H$, $R^2 = Me$, $n = 7$) (161 mg, 37%), m.p. 112 °C (from pentane); $\nu_{max.}$ (CCl_4) 3 610 and 3 580—3 200 cm^{-1}; $\lambda_{max.}$ (MeOH) 273 (746), 266 (757), and 261 nm (ε 579); δ(CCl_4) 1.0—2.17 (13 H, m; with 1.23, d, *J* 7.5 Hz, Ar-CH*Me*; and 5 × CH_2), 2.5—3.0 (3 H, m; with 2.8, s, exchanged with D_2O, OH; and Ar-CH_2), 3.22 (1 H, q, *J* 7.5 Hz, Ar-C*H*Me), and 6.66—7.25 (3 H, m, Ar) (Found: C, 82.97; H, 9.28. $C_{15}H_{20}O$ requires C, 83.28; H, 9.32%).

Run 15: ketone (4; $R^1 = H$, $R^2 = Me$, $n = 8$) (924 mg, 4.02 mmol, 2.51 × 10^{-2}M), 5 h. Elution gave a mixture (A15) of the starting ketone and the alcohol (5; $R^1 = H$, $R^2 = Me$, $n = 8$) (522 mg, 56%) (see later for separation); the alcohol (6; $R^1 = H$, $R^2 = Me$, $n = 8$) (225 mg, 24%), m.p. 55 °C (from pentane); $\nu_{max.}$ (film) 3 600—3 200 cm^{-1}; $\lambda_{max.}$ (MeOH) 273 (852), 266 (856), and 262 nm (ε 626); δ(CCl_4) 0.67—3.17 (19 H, m; with 1.21, t, *J* 7.5 Hz, Ar-CH_2*Me*; 2.55, s, exchanged with D_2O, OH; and 2.62 q, *J* 7.5 Hz, Ar-CH_2Me; Ar-C*H*; and 6 × CH_2), and 6.76—7.5 (3 H, m, Ar) (Found: C, 83.60; H, 9.84. $C_{16}H_{22}O$ requires C, 83.43; H, 9.63%); the alcohol *trans*-(7; $R^1 = H$, $R^2 = Me$, $n = 8$) (30 mg, 3%) as an oil; $\nu_{max.}$ (film) 3 600—3 200 cm^{-1}; $\lambda_{max.}$ (MeOH) 276 (929), 267 (983), and 261 nm (ε 920); δ(CCl_4) 0.67—2.06 (15 H, m; with 1.19, d, *J* 7.5 Hz, Ar-CH*Me*; and 6 × CH_2), 2.27 (1 H, s, exchanged with D_2O, OH), 2.5—2.8 (2 H, m, Ar-CH_2), 3.27 (1 H, q, *J* 7.5 Hz, Ar-C*H*Me), and 6.5—7.26 (3 H, m, Ar) (Found: C, 83.87; H, 9.93. $C_{16}H_{22}O$ requires C, 83.43; H, 9.63%); and the alcohol *cis*-(7; $R^1 = H$, $R^2 = Me$, $n = 8$) (148 mg, 16%), m.p. 116 °C (from pentane); $\nu_{max.}$ (CCl_4) 3 610 and 3 600—3 200 cm^{-1}; $\lambda_{max.}$ (MeOH) 275 (866), 267 (825), and 262 nm (ε 592); δ(CCl_4) 0.66—2.17 (15 H, m; with 1.26, d, *J* 7.5 Hz, Ar-CH*Me*; and 6 × CH_2), 2.5—2.84 (2 H, m, Ar-CH_2), 3.04—3.43 (2 H, m; with 3.25, q, *J* 7.5 Hz, Ar-C*H*Me; and 3.31, s, exchanged with D_2O, OH), and 6.82—7.57 (3 H, m, Ar) (Found: C, 83.46; H, 9.77. $C_{16}H_{22}O$ requires C, 83.43; H, 9.63%).

Reduction of the mixture A15 with $LiAlH_4$ in ether at room temperature and column chromatography gave the alcohol (5; $R^1 = H$, $R^2 = Me$, $n = 8$) (140 mg, 15%) as an oil; $\nu_{max.}$ (film) 3 600—3 300 cm^{-1}, $\lambda_{max.}$ (MeOH) 274 (903), 267 (878), and 260 nm (ε 657); δ (CCl_4) 0.82—2.92 (18 H, m; with 1.26, t, *J* 7.5 Hz, Ar-CH_2*Me*; 2.05, s, exchanged with D_2O, OH; 2.64, q, *J* 7.5 Hz, Ar-CH_2Me; and 6 × CH_2), 3.43—3.82 (1 H, m, Ar-C*H*), and 6.82—7.5 (3 H, m, Ar) (Found: C, 83.09; H, 9.62. $C_{16}H_{22}O$ requires C, 83.43; H, 9.63%) and the ethylbenzocyclodecenol, which upon Jones oxidation gave the starting ketone (4; $R^1 = H$, $R^2 = Me$, $n = 8$) (382 mg, 41%).

Run 16: ketone (4; $R^1 = H$, $R^2 = Me$, $n = 9$) (244 mg, 1 mmol, 1.25 × 10^{-2}M), 7 h. Elution gave the starting ketone (82 mg, 34%): the alcohol (6; $R^1 = H$, $R^2 = Me$, $n = 9$) (74 mg, 30%), m.p. 59 °C (from pentane); $\nu_{max.}$ (CCl_4) 3 610 and 3 600—3 200 cm^{-1}; $\lambda_{max.}$ (MeOH) 273 (921), 266 (906), and 261 nm (ε 666); δ(CCl_4) 1.0—2.79 (20 H, m; with 1.2, t, *J* 7.5 Hz, Ar-CH_2*Me*; 2.24, s, exchanged with D_2O, OH; 2.54, q, *J* 7.5 Hz, Ar-CH_2Me; and 7 × CH_2), 2.82—3.22 (1 H, m, Ar-C*H*), and 6.6—7.3 (3 H, m, Ar) (Found: C, 83.33; H, 9.76. $C_{17}H_{24}O$ requires C, 83.55; H, 9.90%) and the alcohol *cis*-(7; $R^1 = H$, $R^2 = Me$, $n = 9$) (90 mg, 37%), m.p. 111 °C (from pentane); $\nu_{max.}$

(CCl_4) 3 605 and 3 600—3 200 cm^{-1}; $\lambda_{max.}$ (MeOH) 274 (655), 267 (730), and 261 nm (ε 554); δ(CCl_4 1.0—3.36 (21 H, m; with 1.22, d, *J* 7.5 Hz, Ar-CH*Me*; 2.42, s, exchanged with D_2O, OH; 2.35—2.87, m, Ar-CH_2; 3.11, q, *J* 7.5 Hz, Ar-C*H*Me; and 7 × CH_2), and 6.51—7.31 (3 H, m, Ar) (Found: C, 83.55; H, 9.82. $C_{17}H_{24}O$ requires C, 83.55; H, 9.90%). Treatment of (6 or 7; R^1 = H, R^2 = Me, *n* = 9) with $NaNH_2$ in THF gave ketone (4; R^1 = H, R^2 = Me, *n* = 9), m.p. 59 °C (from light petroleum), identical with an authentic sample.

Run 17: ketone (4; R^1 = H, R^2 = Me, *n* = 10) (510 mg, 1.98 mmol, 1.65 × 10^{-2}M), 8 h. Elution gave the starting ketone (95 mg, 19%); the alcohol (6; R^1 = H, R^2 = Me, *n* = 10) (210 mg, 41%) as an oil; $\nu_{max.}$ (film) 3 600—3 100 cm^{-1}, $\lambda_{max.}$ (MeOH) 274 (515), 266 (534), and 260 nm (ε 453); δ(CCl_4) 0.82—2.93 (22 H, m; with 1.21, t, *J* 7.5 Hz, Ar-CH_2*Me*; 2.31, s, exchanged with D_2O, OH; 2.58, q, *J* 7.5 Hz, Ar-CH_2Me; and 8 × CH_2), 2.93—3.38 (1 H, m, Ar-C*H*), and 6.67—7.29 (3 H, m, Ar) (a correct elemental analysis was not obtained); and the alcohol *cis*-(7, R^1 = H, R^2 = Me, *n* = 10) (140 mg, 28%) as an oil; $\nu_{max.}$ (film) 3 680—3 100 cm^{-1}, $\lambda_{max.}$ (MeOH) 274 (688), 266 (712), and 260 nm (ε 542), δ(CCl_4) 1.0—3.37 (23 H, m; with 1.27, d, *J* 7.5 Hz, Ar-CH*Me*; 2.4, s, exchanged with D_2O, OH; 3.11, q, *J* 7.5 Hz, Ar-C*H*Me; and 9 × CH_2), and 6.67—7.27 (3 H, m, Ar) (Found: C, 83.81; H, 10.03. $C_{18}H_{26}O$ requires C, 83.66; H, 10.14%).

Run 18: ketone (4; R^1 = H, R^2 = Me, *n* = 12) (1 030 mg, 3.6 mmol, 1.8 × 10^{-2}M), 7 h. Elution gave the starting ketone (569 mg, 55%); the alcohol (6; R^1 = H, R^2 = Me, *n* = 12) (103 mg, 10%) as an oil; $\nu_{max.}$ (film) 3 650—3 150 cm^{-1}; $\lambda_{max.}$ (MeOH) 274 (879), 266 (896), and 260 nm (ε 723); δ(CCl_4) 1.0—2.19 (24 H, m; with 1.2, t, *J* 7.5 Hz, Ar-CH_2*Me*; 1.91, s, exchanged with D_2O, OH; and 10 × CH_2), 2.55 (2 H, q, *J* 7.5 Hz, Ar-CH_2Me), 2.96—3.24 (1 H, m, Ar-C*H*), and 6.69—7.24 (3 H, m, Ar) (a satisfactory microanalysis was not obtained); and the alcohol *cis*-(7, R^1 = H, R^2 = Me, *n* = 12) (308 mg, 30%) as an oil; $\nu_{max.}$ (film) 3 680—3 120 cm^{-1}; $\lambda_{max.}$ (MeOH) 274 (709), 266 (767), and 260 nm (ε 590); δ(CCl_4) 1.0—2.01 (23 H, m; with 1.27, d, *J* 7.5 Hz, Ar-CH*Me*; and 10 × CH_2), 2.21—2.81 (3 H, m; with 2.47, s, exchanged with D_2O, OH; and Ar-CH_2), 3.5 (1 H, q, *J* 7.5 Hz, Ar-C*H*Me), and 6.64—7.24 (3 H, m, Ar) (Found: C, 83.10; H, 10.51. $C_{18}H_{30}O$ requires C, 83.86; H, 10.56%).

Run 19: ketone (4; R^1 = R^2 = Me, *n* = 6) (216 mg, 1 mmol, 1.25 × 10^{-2}M), 9 h. Elution gave the starting ketone (115 mg, 53%); the alcohol (7; R^1 = R^2 = Me, *n* = 6) (69 mg, 32%), m.p. 129 °C (from pentane); $\nu_{max.}$ (CCl_4) 3 620 and 3 600—3 300 cm^{-1}; $\lambda_{max.}$ (MeOH) 273 (835), 266 (828), and 260 nm (ε 612); δ(CCl_4) 1.29 (6 H, s, Ar-C*Me*$_2$), 1.5—2.17 (9 H, m; with 2.05, s, exchanged with D_2O, OH; and 4 × CH_2), 2.4—2.9 (2 H, m, Ar-CH_2), and 6.66—7.34 (3 H, m, Ar) (Found: C, 82.59; H, 9.65. $C_{15}H_{20}O$ requires C, 83.28; H, 9.32%); and one unidentified product.

Run 20: ketone (4; R^1 = R^2 = Me, *n* = 7) (230 mg, 1 mmol, 2.5 × 10^{-2}M), 5 h. Elution gave the starting ketone (43 mg, 19%) and the alcohol (7; R^1 = R^2 = Me, *n* = 7) (176 mg, 77%), m.p. 131 °C (from pentane); $\nu_{max.}$ (CCl_4) 3 625 and 3 600—3 300 cm^{-1}; $\lambda_{max.}$ (MeOH) 273 (780), 265 (773), and 260 nm (ε 557); δ(CCl_4) 1.15—2.22 (17 H, m; with 1.25 and 1.32, s, Ar-C*Me*$_2$; 2.09, s, exchanged with D_2O, OH; and 5 × CH_2), 2.55—3 (2 H, m, Ar-CH_2), and 6.74—7.31 (3 H, m, Ar) (Found: C, 83.66; H, 9.44. $C_{16}H_{22}O$ requires C, 83.43; H, 9.63%). Treatment of (7; R^1 = R^2 = Me, *n* = 7) with $NaNH_2$ in THF gave ketone (4; R^1 = R^2 = Me, *n* = 7) as an oil, identical with an authentic sample.

Run 21: ketone (4; R^1 = R^2 = Me, *n* = 8) (716 mg, 2.93 mmol, 2.45 × 10^{-2}M), 5 h. Elution gave a mixture (A21) of the starting ketone and the alcohol (5; R^1 = R^2 = Me, *n* = 8) (132 mg, 18%) (see later for separation); the alcohol (6; R^1 = R^2 = Me, *n* = 8) (196 mg, 27%), m.p. 67 °C (from pentane); $\nu_{max.}$ (CCl_4) 3 610 and 3 600—3 300 cm^{-1}; $\lambda_{max.}$ (MeOH) 273 (1 138), 266 (1 151), and 261 nm (ε 819); δ(CCl_4) 1.0—2.5 (19 H, m; with 1.22, d, *J* 7 Hz, Ar-CH*Me*$_2$; 2.17, s, exchanged with D_2O, OH; and 6 × CH_2), 2.77—3.27 (2 H, m; with 2.97, heptuplet, *J* 7 Hz, Ar-C*H*Me$_2$; and Ar-C*H*), and 6.82—7.6 (3 H, m, Ar) (Found: C, 83.71; H, 9.88. $C_{17}H_{24}O$ requires C, 83.55; H, 9.90%); and the alcohol (7; R^1 = R^2 = Me, *n* = 8) (403 mg, 56%), m.p. 95 °C (from pentane); $\nu_{max.}$ (CCl_4) 3 620 and 3 600—3 300 cm^{-1}; $\lambda_{max.}$ (MeOH) 273 (879), 266 (848), and 261 nm (ε 610); δ(CCl_4) 0.62—2.22 (18 H, m; with 1.19 and 1.29 s, Ar-C*Me*$_2$; and 6 × CH_2), 2.4—3.12 (3 H, m; with 2.51, s, exchanged with D_2O, OH; and Ar-CH_2), and 6.82—7.5 (3 H, m, Ar) (Found: C, 83.31; H, 10.02. $C_{17}H_{24}O$ requires C, 83.55; H, 9.90%). Treatment of (7; R^1 = R^2 = Me, *n* = 8) with $NaNH_2$ in THF gave ketone (4; R^1 = R^2 = Me, *n* = 8) as an oil, identical with an authentic sample.

Reduction of the mixture A21 with $LiAlH_4$ in ether at room temperature and column chromatography gave the alcohol (5; R^1 = R^2 = Me, *n* = 8) (35 mg, 5%) as an oil; $\nu_{max.}$ (film) 3 600—3 300 cm^{-1}; $\lambda_{max.}$ (MeOH) 274 (900), 266 (928), and 261 nm (ε 682); δ(CCl_4) 0.79—3 (20 H, m; with 1.26, d; *J* 7 Hz, Ar-CH*Me*$_2$; 2.25, s, exchanged with D_2O, OH; Ar-C*H*Me$_2$; and 6 × CH_2), 3.32—3.8 (1 H, m, Ar-C*H*), and 6.72—7.36 (3 H, m, Ar) (Found C, 82.60; H, 9.97. $C_{17}H_{24}O$ requires C, 83.55; H, 9.90%); and the isopropylbenzocyclodecenol, which upon Jones oxidation gave the starting ketone (4; R^1 = R^2 = Me, *n* = 8) (85 mg, 12%).

Run 22: ketone (4; R^1 = R^2 = Me, *n* = 9) (258 mg, 1 mmol, 1.25 × 10^{-2}M), 11 h. Elution gave the starting ketone (26 mg, 10%); the alcohol (6; R^1 = R^2 = Me, *n* = 9) (91 mg, 35%), m.p. 64 °C (from pentane); $\nu_{max.}$ (CCl_4) 3 610 and 3 600—3 200 cm^{-1}; $\lambda_{max.}$ (MeOH) 274 (903), 266 (966), and 260 nm (ε 732); δ(CCl_4) 1.0—2.5 (21 H, m; with 1.2, d, *J* 7 Hz, Ar-CH*Me*$_2$; 2.11, s, exchanged with D_2O, OH; and 7 × CH_2), 2.64—3.38 (2 H, m; a heptuplet, *J* 7 Hz, Ar-C*H*Me$_2$, and Ar-C*H*), and 6.62—7.38 (3 H, m, Ar) (Found: C, 83.64; H, 10.18. $C_{18}H_{26}O$ requires C, 83.66; H, 10.14%); and the alcohol (7; R^1 = R^2 = Me, *n* = 9) (142 mg, 55%), m.p. 92 °C (from pentane); $\nu_{max.}$ (CCl_4) 3 620 and 3 600—3 200 cm^{-1}; $\nu_{max.}$ (MeOH) 273 (658), 266 (732), and 260 nm (ε 534); δ(CCl_4) 1.0—3.0 (23 H, m; with 1.19 and 1.28, s, Ar-C*Me*$_2$; 1.97, s, exchanged with D_2O, OH; and 8 × CH_2), and 6.7—7.3 (3 H, m, Ar) (Found: C, 83.59; H, 10.00. $C_{18}H_{26}O$ requires C, 83.66; H, 10.14%). Treatment of (6 or 7; R^1 = R^2 = Me, *n* = 9) with $NaNH_2$ in THF gave ketone (4; R^1 = R^2 = Me, *n* = 9), m.p. 67 °C (from light petroleum), identical with an authentic sample.

Run 23: ketone (4; R^1 = R^2 = Me, *n* = 10) (325 mg, 1.19 mmol, 1.49 × 10^{-2}M), 5 h. Elution gave the starting ketone (182 mg, 56%); the alcohol (7; R^1 = R^2 = Me, *n* = 10) (87 mg, 27%), m.p. 84 °C (from pentane); $\nu_{max.}$ (film) 3 640—3 100 cm^{-1}; $\lambda_{max.}$ (MeOH) 273 (747), 266 (787), and 260 nm (ε 587); δ(CCl_4) 1—2 (22 H, m; with 1.2 and 1.3, s, Ar-C*Me*$_2$; and 8 × CH_2), 2.07 (1 H, s, exchanged

with D_2O, OH), 2.2—3.0 (2 H, m, Ar-CH_2), and 6.65—7.32 (3 H, m, Ar) (Found: C, 83.48; H, 10.29. $C_{19}H_{28}O$ requires C, 83.77; H, 10.36%), and the alcohol (6; R^1 = R^2 = Me, n = 10) (49 mg, 15%) as an oil; $\nu_{max.}$ (CCl_4) 3 630 and 3 600—3 300 cm^{-1}; δ(CCl_4) 0.84—2.16 (22 H, m; with 1.25, d, J 7.5 Hz, Ar-CH*Me*$_2$; and 8 × CH_2), 2.32 (1 H, s, exchanged with D_2O, OH), 2.58—3.4 (2 H, m, Ar-C*H*Me$_2$ and Ar-C*H*), and 6.64—7.24 (3 H, m, Ar) (a correct elemental analysis was not obtained).

Run 24: ketone (4; R^1 = R^2 = Me, n = 12) (400 mg, 1.33 mmol, 0.84 × 10^{-2}M), 5 h. Elution gave the starting ketone (302 mg, 75%); the alcohol (7; R^1 = R^2 = Me, n = 12) (61 mg, 15%) as an oil; $\nu_{max.}$ (film) 3 600—3 200 cm^{-1}; $\lambda_{max.}$ (MeOH) 273 (826), 266 (851), and 260 nm (ε 835); δ(CCl_4 1.0—2.05 (27 H, m; with 1.26 and 1.35, s, Ar-C*Me*$_2$; 1.95, s, exchanged with D_2O, OH; and 10 × CH_2), 2.2—2.9 (2 H, m, Ar-CH_2), and 6.7—7.2 (3 H, m, Ar) (Found: C, 83.03; H, 10.34. $C_{21}H_{32}O$ requires C, 83.94; H, 10.73%); and the alcohol (6; R^1 = R^2 = Me, n = 12) (29 mg, 7%) as an oil; $\nu_{max.}$ (film) 3 640—3 200 cm^{-1}; $\lambda_{max.}$ (MeOH) 273 (658), 266 (690), and 260 nm (ε 544); δ(CCl_4) 0.84—2.16 (26 H, m; with 1.26, d, J 7.5 Hz, Ar-CHMe$_2$; and 10 × CH_2), 2.36 (1 H, s, exchanged with D_2O, OH), 2.7—3.5 (2 H, m, Ar-C*H*Me$_2$ and Ar-C*H*), and 6.72—7.26 (3 H, m, Ar) (a satisfactory microanalysis was not obtained).

Irradiation of Ketones (4) *in Acetone* (*Table* 3).—Run 25: ketone (4; R^1 = R^2 = H, n = 7) (2 300 mg, 10.05 mmol, 3.59 × 10^{-2}M), 5 h. Elution gave the alcohol (7; R^1 = R^2 = H, n = 7) (1 831 mg, 90%).

Run 26: ketone (4; R^1 = H, R^2 = Me, n = 6) (303 mg, 1.5 mmol, 1.25 × 10^{-2}M), 4 h. Elution gave the starting ketone (18 mg, 6%); the alcohol *trans*-(7; R^1 = H, R^2 = Me, n = 6) (28 mg, 9%) as an oil; $\nu_{max.}$ (CCl_4) 3 620 and 3 600—3 200 cm^{-1}; $\lambda_{max.}$ (MeOH) 274 (682), 266 (710), and 260 nm (ε 642); δ(CCl_4), 1.0—2.16 (11 H, m; with 1.24, d, J 7.5 Hz, Ar-CH*Me*; and 4 × CH_2), 2.45—3.0 (3 H, m; with 2.86, s, exchanged with D_2O, OH; and Ar-CH_2), 3.27 (1 H, q, J 7.5 Hz, Ar-C*H*Me), and 6.70—7.35 (3 H, m, Ar); and the alcohol *cis*-(7; R^1 = H, R^2 = Me, n = 6) (226 mg, 75%), m.p. 129 °C (from pentane); $\nu_{max.}$ (CCl_4) 3 610 and 3 600—3 200 cm^{-1}; $\lambda_{max.}$ (MeOH) 273 (752), 266 (725), and 260 nm (ε 523); δ(CCl_4) 1.0—2.25 (11 H, m; with 1.24, d, J 5 Hz, Ar-CH*Me*; and 4 × CH_2), 2.45—2.9 (3 H, m; with 2.72, s, exchanged with D_2O, OH; and Ar-CH_2), 3.25 (1 H, q, J 7.5 Hz, Ar-C*H*Me), and 6.57—7.30 (3 H, m, Ar) (Found: C, 83.09; H, 8.85. $C_{14}H_{18}O$ requires C, 83.12; H, 8.97%).

Run 27: ketone (4; R^1 = H, R^2 = Me, n = 7) (2 405 mg, 11 and 13 mmol, 3.48 × 10^{-2}M), 7 h. Elution gave the starting ketone (152 mg, 6%): the alcohol *trans*-(7; R^1 = H, R^2 = Me, n = 7) (687 mg, 29%): and the alcohol *cis*-(7; R^1 = H, R^2 = Me, n = 7) (1 502 mg, 62%).

Run 28: ketone (4; R^1 = H, R^2 = Me, n = 10) (827 mg, 3.20 mmol, 1.60 × 10^{-2}M), 5 h. Elution gave the starting ketone (167 mg, 20%); the alcohol (6; R^1 = H, R^2 = Me, n = 10) (128 mg, 15%); and the alcohol *cis*-(7; R^1 = H, R^2 = Me, n = 10) (532 mg, 64%).

Run 29: ketone (4; R^1 = H, R^2 = Me, n = 12) (636 mg, 2.22 mmol, 1.39 × 10^{-2}M), 5 h. Elution gave the starting ketone (123 mg, 19%); the alcohol (6; R^1 = H, R^2 = Me, n = 12) (121 mg, 19%); and the alcohol *cis*-(7; R^1 = H, R^2 = Me, n = 12) (335 mg, 53%).

Run 30: ketone (4; R^1 = R^2 = Me, n = 6) (216 mg, 1 mmol, 1.25 × 10^{-2}M), 4 h. Elution gave the starting ketone (50 mg, 23%) and the alcohol (7; R^1 = R^2 = Me, n = 6) (143 mg, 66%).

Run 31: ketone (4; R^1 = R^2 = Me, n = 7) (2 667 mg, 11.6 mmol, 3.62 × 10^{-2}M), 5 h. Elution gave the starting ketone (610 mg, 23%) and the alcohol (7; R^1 = R^2 =Me, n = 7) (1 912 mg, 72%).

Run 32: ketone (4; R^1 = R^2 = Me, n = 10) (272 mg, 1 mmol, 1.25 × 10^{-2}M), 5 h. Elution gave the starting ketone (43 mg, 16%); the alcohol (7; R^1 = R^2 = Me, n = 10) (201 mg, 74%); and the alcohol (6; R^1 = R^2 = Me, n = 10) (28 mg, 10%).

Run 23: ketone (4; R^1 = R^2 = Me, n = 12) (153 mg, 0.51 mmol, 1.27 × 10^{-2}M), 5 h. Elution gave the starting ketone (47 mg, 31%); the alcohol (7; R^1 = R^2 = Me, n = 12) (96 mg, 56%); and the alcohol (6; R^1 = R^2 = Me, n = 12) (18 mg, 12%).

Photolysis of Ketones (2) *with Trapping Agents*.—(a) *With oxygen*. The ketone (2; n = 7) (2 400 mg, 12.8 mmol) was irradiated in cyclohexane (200 ml) for 3 h, whilst passing a stream of pure oxygen through the solution. The solvent was removed *in vacuo* and the products isolated by column chromatography: elution gave the starting ketone (1 815 mg, 76%), alcohols which were not identified, and the peroxide (10; n = 7) (310 mg, 13%), m.p. 109 °C, identical to an authentic sample.[2]

Similar treatment of ketone (2; n = 10) (400 mg, 1.74 mmol, 1.16 × 10^{-2}M) during 4.5 h, gave the starting ketone (292 mg, 73%) and the corresponding peroxide (10; n = 10) (124 mg, 27%) as an oil, showing a positive starch–iodide test; $\nu_{max.}$ (film) 3 640—3 100, 1 100, 1 040, and 1 010 cm^{-1}; δ(CCl_4) 0.6—2.42 (16 H, m, 8 × CH_2), 3.4—3.91 (1 H, m, exchanged with D_2O, OH), 4.83 (1 H, m, pseudo-t, Ar–C*H*O–O), and 6.76—7.56 (4 H, m, Ar).

Similar treatment of ketone (2; n = 12) (188 mg, 0.73 mmol, 1.2 × 10^{-2}M) during 4.5 h, gave the starting ketone (113 mg, 60%), and the corresponding peroxide (10; n = 12) (84 mg, 40%) as an oil, showing a positive starch–iodide test; $\nu_{max.}$ (film) 3 640—3 140, 1 115, 1 095, 1 055, and 1 025 cm^{-1}; δ(CCl_4) 0.76—2.56 (20 H, m, 10 × CH_2), 3.6—4.38 (1 H, m, exchanged with D_2O, OH), 4.42—4.76 (1 H, m, Ar–C*H*O–O), and 6.73—7.47 (4 H, m, Ar).

(b) *With the dienophile maleic anhydride*. The ketone (2; n = 10) (235 mg, 1.02 mmol) and maleic anhydride (487 mg, 5 mmol) were irradiated in cyclohexane (40 ml) for 15 h. The solvent was removed *in vacuo* and elution on column chromatography gave the starting ketone (179 mg, 76%), and the anhydride (11; n = 10) (22 mg, 7%) as an oil; $\nu_{max.}$ (film) 3 640—3 100, 1 730, and 1 685 cm^{-1}; δ(CCl_4) 0.78—2.40 (18 H, m, 8 × CH_2, 2 × C*H*–C=O), 2.96—3.40 (1 H, m, exchanged with D_2O, OH), 4.89 (1 H, m, pseudo-t, Ar-C*H*), and 6.80—7.58 (4 H, m, Ar).

The ketone (2; n = 12) (261 mg, 1.01 mmol) and maleic anhydride (490 mg, 5 mmol) were irradiated in benzene (40 ml) for 15 h. The solvent was removed *in vacuo* and column chromatography gave the starting ketone (170 mg, 65%), and the anhydride (11; n = 12) (31 mg, 9%) as an oil; $\nu_{max.}$ (film) 3 580—3 240, 1 740, and 1 690 cm^{-1}; δ(CCl_4) 0.71—2.47 (22 H, m; 10 × CH_2, 2 × C*H*–C=O), 3.0—3.4 (1 H, m, exchanged with D_2O, OH), 4.44—4.78 (1 H, m, Ar-C*H*), and 6.78—7.49 (4 H, m, Ar).

(c) *With* CH_3OD. The ketones (2) in benzene (4.5 ml) and CH_3OD (0.5 ml) were irradiated during the appropriate time. Incorporation of deuterium into the recovered ketones (2) was determined by ^1H n.m.r. analysis; the position of incorporated deuterium was established as

previously described;[2] the results for each ketone (2) considered are as follows: ketone (2; $n = 6$) (88 mg, 0.51 mmol), 5 h: no deuterium incorporation; ketone (2; $n = 7$) (188 mg, 1 mmol), 5 h: incorporation of 0.5 D, *i.e.* (2b) 0.21 D, and (2a) 0.29 D; ketone (2; $n = 8$) (202 mg, 1 mmol), 7 h: incorporation of 0.46 D, *i.e.* (2b) 0.11 D, and (2a) 0.35 D; ketone (2; $n = 10$) (115 mg, 0.5 mmol), 7 h: incorporation of 0.57 D, *i.e.* (2b) 0.04 D and (2a) 0.53 D; and ketone (2; $n = 12$) (130 mg, 0.5 mmol), 7 h: incorporation of 0.5 D as (2a).

Irradiation of Ketones (12) *and* (13).—Arynic addition of the enolate of cyclodecanone to *meta*-methylbenzyne (generated from *p*-bromotoluene by $NaNH_2$ in dimethoxyethane, at 45 °C for 4 h) led to a mixture of ketones, which were separated by method C of ref. 5.

Amongst the reduced products were the 2-methylbenzocyclododecen-5-ol; δ($CDCl_3$) 1.15—3.16 (22 H, m; with 2.29, s, Me; 9 × CH_2; and OH), 4.97—5.24 (1 H, m, pseudo-t, Ar-C*H*OH), and 6.93—7.56 (3 H, m, Ar); ^1H n.m.r. with [Eu(fod)$_3$], downfield shift of the *ortho*-aromatic hydrogen to the carbonyl group as a doublet, J 8 Hz; and the 3-methylbenzocyclododecen-5-ol; δ($CDCl_3$) 1.07—3.11 (22 H, m; with 2.29, s, Me; 9 × CH_2; and OH), 4.95—5.22 (1 H, m, pseudo-t, Ar-C*H*OH), and 6.98—7.38 (3 H, m, Ar); ^1H n.m.r. with [Eu(fod)$_3$]: downfield shift of the *ortho*-aromatic hydrogen to the carbonyl group as a singlet. Jones oxidation of the 2-methyl alcohol gave the ketone (12; $n = 10$) as an oil, ν (film) 1 690 cm^{-1}.

A similar arynic addition of cyclododecanone led to a mixture of ketones. Amongst the reduced products were the 2-methylbenzocyclotetradecen-5-ol, m.p. 97 °C (from pentane); ν(CCl_4) 3 620 cm^{-1}; δ($CDCl_3$) 1.17—2.93 (26 H, m; with 2.32, s, Me; 11 × CH_2; and OH), 4.83—5.23 (1 H, m, Ar-C*H*OH), 6.93—7.57 (3 H, m, Ar); ^1H n.m.r. with [Eu(fod)$_3$]: downfield shift of the *ortho*-aromatic hydrogen to the carbonyl group as a doublet, J 8 Hz; and the 3-methylbenzocyclotetradecen-5-ol, m.p. 127 °C (from pentane); ν(CCl_4) 3 620 cm^{-1}; δ($CDCl_3$) 1.06—3.0 (26 H, m; with 2.35, s, Me; 11 × CH_2; and OH), 4.83—5.27 (1 H, m, Ar-C*H*OH), and 7.10—7.40 (3 H, m, Ar); ^1H n.m.r. with [Eu(fod)$_3$]: downfield shift of the *ortho*-aromatic hydrogen to the carbonyl group as a singlet. Jones oxidation of the 2-methyl alcohol gave the ketone (12; $n = 12$) as an oil, ν (film) 1 690 cm^{-1}; $\lambda_{max.}$ (Bu^tOH) 282sh (1 284), 252 (7 857), and 210 nm (ε 21 230); δ($CDCl_3$) 1—2 (18 H, m, 9 × CH_2), 2.35 (3 H, s, Me), 2.65—3.10 (4 H, m, Ar-CH_2 and Ar-CO-CH_2, and 6.90—7.51 (3 H, m, Ar); ^1H n.m.r. with [Eu(fod)$_3$]: downfield shift of the *ortho*-aromatic hydrogen to the carbonyl group as a doublet.

Irradiation. Ketones (12; $n = 10$ or 12) (9 × 10^{-3}M), in t-butyl alcohol were irradiated for 15 h; column chromatography of the crude photolysate gave only starting ketones (48 and 39%, respectively), no detectable benzocyclobutenol formation being observed.

A mixture of ketones (12; $n = 12$) and (13; $n = 12$) (1.2 × 10^{-2}M), in t-butyl alcohol was photolysed for 8 h; column chromatography gave starting ketones (69%); no benzocyclobutenol was detected.

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