Synthetic Photochemistry. Part 1. Generation of Benzocycloalkenones by the Ring-opening of Benzocyclobutenols. Evidence for an *ortho*-Quinodimethane Intermediate

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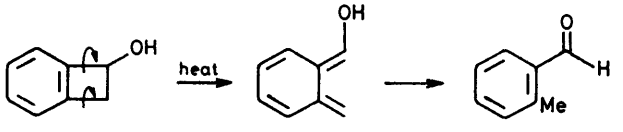
Photolysis of benzocyclobutenols (4) constitutes a new synthetic approach to the benzocycloalkenones (5). A singlet excited state is implicated in these reactions. Quenching by oxygen leads to the hydroxyperoxides (15). Incorporation of deuterium provides evidence for the intermediary of dienols; these may evolve by either (i) direct protonation producing the ketones (5b) or (ii) an intramolecular hydrogen shift forming the enols of the ketones (5a). The general character of these photolyses is emphasized by the study of several benzocyclobutenols (16) and (17), naphthocyclobutenols (22), and methyl ether derivatives (12).

FROM the work of Sammes *et al.*,[1,2] it appears that thermolysis of the benzocyclobutenol (1) produces *o*-methylbenzaldehyde (3) *via* a conrotatory opening to the *E*-dienol (2) (Scheme 1).

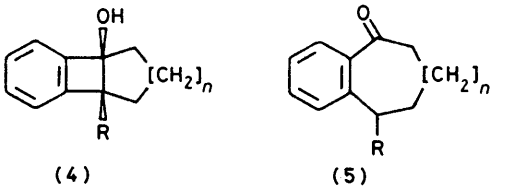


(1) (2) (3)

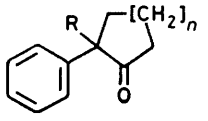
SCHEME 1

In another work, Quinkert *et al.*[3] performed the flash photolysis of several benzocyclobutenes and evidenced the formation of *o*-quinodimethane derivatives. In those cases, disrotatory opening of the strained ring is expected for a concerted reaction.

Recently, generation of *o*-xylylenes by photochemical and/or thermal treatment of polycyclic cyclobutenes [4] and by photolysis of indan-2-ones [5] has been reported. Although benzocyclobutenols have been invoked in some photoenolizations,[2] examination of the literature shows that their photolysis has not been studied. We have investigated the photolysis of benzocyclobutenols (4) [6] as part of a general study of their chemical properties.[7] Our aims were to obtain information about the photochemical behaviour of these compounds and possibly to design a new synthetic approach to the benzocycloalkenones (5). Indeed, we previously reported that basic treatment of (4; n = 1—3) produces the corresponding (5) and/or phenylcycloalkanones (6) depending on the experimental conditions.[7] However, similar reactions with (4; R ≠ H, n = 2) led only to the ketones (6).

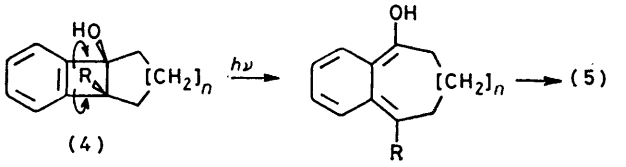


(4) (5)



(6)

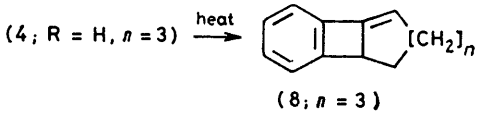
Referring to the data in the literature cited above, we might expect a disrotatory opening of (4; R = H, n = 1—3) into a dienol. Owing to the *cis* junction in (4) and steric restrictions, the dienols, if formed, should have *E,E* stereochemistry as depicted in Scheme 2.



(4) (7)

SCHEME 2

It must be noted that a thermal opening following Scheme 1 would be very difficult since, such a reaction would lead to compounds with *trans* unsaturation.



(8; n = 3)

SCHEME 3

Thus, for example, thermolysis of the alcohol (4; R = H, n = 3) leads to the ethylenic hydrocarbon (8) (Scheme 3).

We now report the photolysis of benzo- and naphthocyclobutenols.[8]

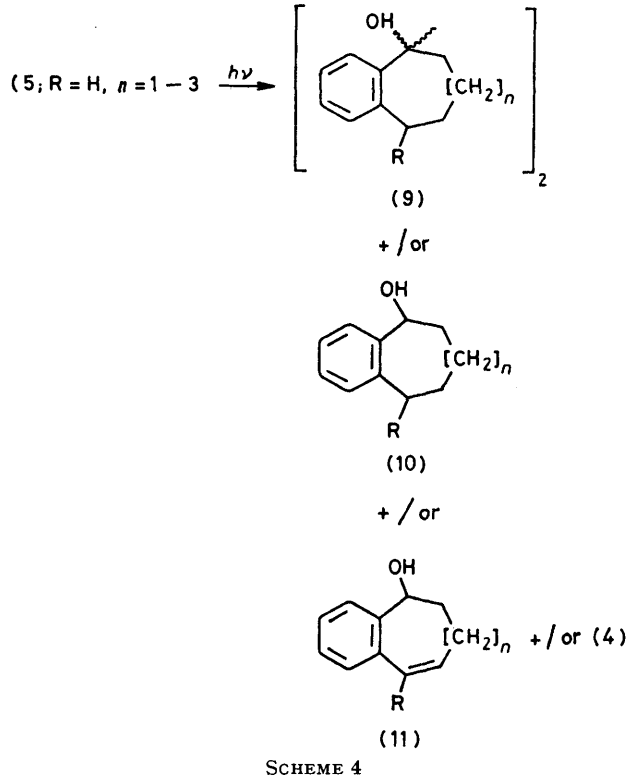
Photolysis of the Benzocyclobutenols (4; R = H, n = 1—3).—*Results.* Table 1 shows the results of the photolysis in non-polar solvents. It was thought that

TABLE 1

Photolysis of benzocyclobutenols (4; R = H, n = 1—3) in non-polar solvents

					Products(%)	
			Concentration/	Time/	Unchanged alcohol	Ketone
Run	n	Solvent	10^2M	h	(4)	(5)
1	1	Cyclohexane	4.2	3	28	21
2	2	Benzene	3.45	4	17	48
3	3	Benzene	1.65	6	13	23

by-products were being formed due to photolysis of the ketones (5) themselves. This assumption was verified



SCHEME 4

by irradiating the ketones at 2 537 and 3 000 Å. The latter wavelength was chosen to avoid photochemical reactions other than those involving the carbonyl group The major part of the study was performed with light of 3 000 Å (Scheme 4 and Table 2).

Alcohol (11; R = H, $n = 3$), formed in run 6, might be generated by a hydrogen shift in the dienol (7; R = H, $n = 3$) or by the intermediacy of a biradical.[2] These results led us to photolyse the ketones (5; R = H, $n = 2$ or 3) in t-butyl alcohol, a poor hydrogen donor. This led to a large decrease in photoreduction and for (5; R = H, $n = 3$) a simultaneous increase in the yields of (4; R = H, $n = 3$) and (11; R = H, $n = 3$) (Table 3).

Taking into account these observations and the literature data, it might be thought that the triplet excited states of the ketones (5) were the intermediates in their photolysis. Thus the addition of a triplet inhibitor should prevent photoreaction; accordingly piperylene was added which quenched formation of the intermolecular products (9) and (10), but led only to a decrease in the yields of intramolecular products for (5; R = H, $n = 3$). This observation may be correlated with the work of Wagner *et al.*[11] concerning the existence of two triplets for *o*-alkyl aromatic ketones.

The benzocyclobutenols (4; R = H, $n = 1$—3) were also photolysed in t-butyl alcohol containing piperylene. As may be seen from Table 4, the ketones (5) were the only products.

DISCUSSION

We have attempted to obtain information on the mechanism of these photolyses. Emission spectral studies of the alcohols (4; R = H, $n = 1$—3) give the approximate values for the singlet and triplet state energies of 98—99 and 81—82 kcal mol^{-1} respectively.

TABLE 2

Photolysis of ketones (5; R = H, $n = 1$—3) in cyclohexane

				Products (%)				
Run	n	Concentration/ 10^2M	Time/h	unchanged ketone (5)	Alcohol (4)	Alcohol (9)	Alcohol (10)	Alcohol (11)
4	1	5.89	2	75		19	4	
5	2	5.6	3	45		25	12	
6	3	5.13	4	10	20	20		10.5

The observation that alcohols (4; R = H, $n = 1$—3) ring-open even in the presence of piperylene (E_T *ca.* 59 kcal mol^{-1} [12]) and absence of acetone (E_T *ca.* 79—82 kcal mol^{-1} [12]) as photosensitizer, seems in accordance with a singlet state precursor. An attempt to trap the possible dienol (7; R = H, $n = 1$—3) precursor of the ketone (5) with dienophiles [2,13,14] was unsuccessful, even for the methyl ether derivative * (12; $n = 3$). The photolysis of (12; $n = 2$ or 3) led to the enol ether

TABLE 3

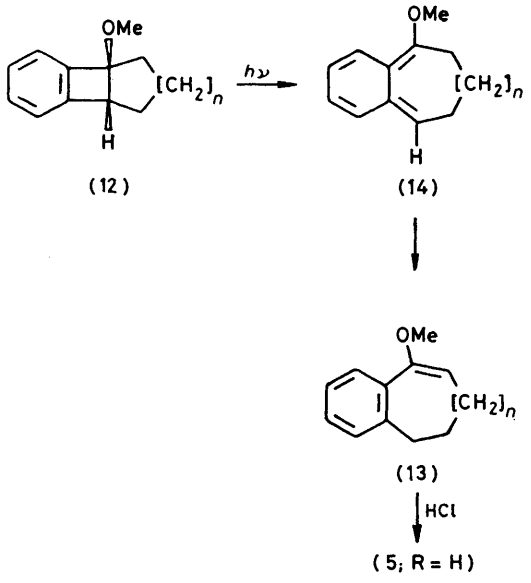
Photolysis of ketones (5; R = H, $n = 2$, 3) in t-butyl alcohol

				Products (%)				
Run	n	Concentration/ 10^2M	Time/h	Unchanged ketone (5)	Alcohol (4)	Alcohol (9)	Alcohol (10)	Alcohol (11)
7	2	1.48	4	71		20	6	
8	3	2.8	9	12	44	5		17

Obviously (9) and (10) are products of classical photoreduction of ketones.[9] Note the formation of (4; R = H, $n = 3$) in the photoreaction of benzocyclononenone (5; R = H, $n = 3$). This kind of cyclization, previously reported [2,10] for some acyclic *o*-alkylphenylketones, led us to study the photolysis of benzocycloalkenones in order to prepare benzocyclobutenols which cannot be obtained by arynic synthesis (results will be described in a future paper).

* Replacement of the hydroxy group by a methyl ether should prevent the ketonisation of the *E*-dienol and enhance the rate of Diels–Alder trapping.[15]

(13; $n = 2$ or 3) probably *via* an intramolecular hydrogen shift in the diene (14; $n = 2$ or 3) (Scheme 5).



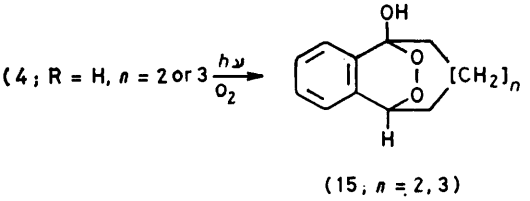
SCHEME 5

Use of oxygen, being a very good trapping agent,[16] gave hydroxyperoxides (15; $n = 2$ or 3) (Scheme 6). However, the formation of (15) does not prove the intervention of a dienol since diradical and/or electronically excited states would give the same results. In order to distinguish between dienol or diradical intermediates, photolyses were performed in the presence of MeOD and CD_3OH. The results are summarized in Table 5.

ium incorporation (see Experimental section). These results are rationalized in Scheme 7. Note that the relationship between the relative amounts formed of (5a) and (5b) with the geometry of the *E*-dienol intermediate is unknown.

Photolysis of Other Benzocyclobutenols.—As previously noted, basic treatment of (16) produces only phenylcyclohexanones. As expected, although, photolysis gave the substituted benzocycloalkenones (18) (Scheme 8 and Table 6). However, we also observed a formation of the ethylenic alcohols (19), which could be formed *via* a thermal intramolecular hydrogen shift in the intermediary dienol. Note that from a synthetic viewpoint, alcohols (19) may be easily converted to ketones (18) by hydrogenation followed by Jones oxidation. (See Experimental section). For structural elucidation, the alcohols (19) were also oxidized to the ketones (20) followed by hydrogenation to the ketones (18).

As expected, the photochemical conversion of alcohols (16) into ketones (18) is effective as a synthetic method. Irradiation of (16; $R^1 = R^2 = H$), in the presence of



SCHEME 6

MeOD confirmed the existence of the intermediate dienol (see Experimental section).

TABLE 4

Photolysis of benzocyclobutenols (4; R = H, n = 1—3) in t-butyl alcohol

Run	n	Concentration/ 10^2M	Time/h	Additional reagent	Products (%) Unchanged alcohol (4)	Ketone (5)	Alcohol (11)
9	1	2.86	3	none	28	17	
10	1	2.86	3	piperylene (10^{-1} M)	39	33	
11	2	2.86	3	none	52	28	
12	2	2.86	3	piperylene (10^{-1} M)	60	40	
13	3	2.86	3	none	62	16	7.5
14	3	2.86	3	piperylene (10^{-1} M)	58	39	

TABLE 5

Photolysis of benzocyclobutenols (4; R = H, n = 1—3) with MeOD and CD_3OH and relative distribution of deuterium in the ketones (5; R = H, n = 1—3)

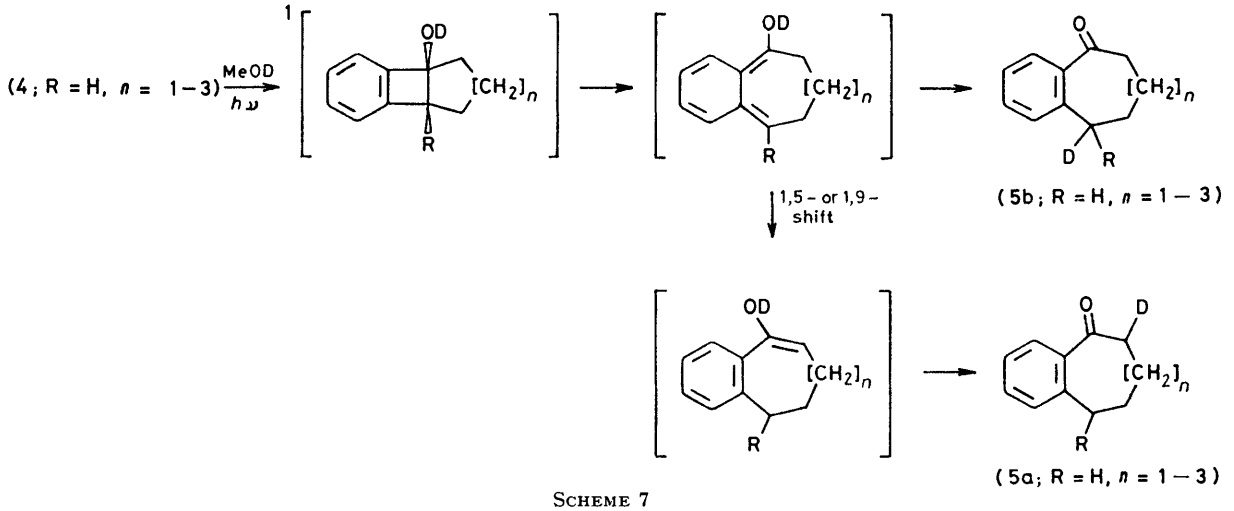
Run	n	Solvent	Concentration/ 10M	Time/h	Products (%) Unchanged Alcohol (4)	Ketone (5)	Deuterium incorporation (5a)	(5b)
15	1	MeOD	2	5	47	53	0.35	0.65
16	2	MeOD	3	7	64	32	0.31	0.69
17	3	MeOD	3	7	66	34	0.06	0.94
18	1	CD_3OH	1	7	trace	78		
19	2	CD_3OH	2.	7	50	50		

In all cases, experiments carried out with MeOD led to the incorporation of one deuterium atom. On the contrary, photolysis with CD_3OH did not show any deuter-

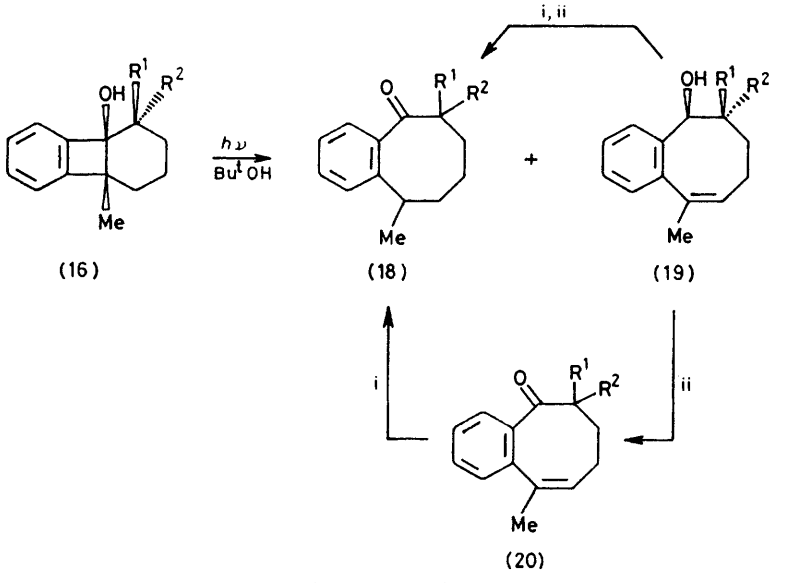
We have previously shown that irradiation of *o*-alkyl-substituted benzocycloalkenones [17] (21; R^2 = Me, Et, Pr^i, n = 2—6 or 8) provides new benzocyclobutenols [8]

(17). Interestingly, we were able to perform the reverse reaction and so demonstrate the general character of the photochemistry of benzocyclobutenols (Scheme 9).

naphthocyclobutenols (22; R = H, n = 3) [18] with light of 2 537 or 3 000 Å in t-butyl alcohol, with or without added piperylene * led to the known naphthocyclo-



SCHEME 7



SCHEME 8 *i*, hydrogenation; *ii*, Jones oxidation

Moreover, photolysis of (17; R^1 = H, n = 2), performed with MeOD, afforded (21; R^2 = Me, n = 2) with nonenone [18] (23; R = H, n = 3) (Scheme 10). That the reaction came from the singlet (E_S *ca.* 89 kcal mol^{-1}) and

TABLE 6

Photolysis of benzocyclobutenols (16) in t-butyl alcohol containing piperylene

Run	Compound (16)	Concentration/ 10^2M	Time/h	Products (%) Unchanged alcohol (16)	Ketone (18)	Alcohol (19)	Overall ketone (18) [a]
20	$R^1 = R^2 = H$	1.75	6	4.5	60	4.5	
21	$R^1 = R^2 = Me$	3.90	3	32	35	19	51
22	$R^1 = H, R^2 = Me$	3.15	4.5	13	36 [b]	48	69

[a] After further conversion of the alcohol (19) into the ketone (18). [b] As a mixture of the two isomers.

introduction of *ca.* 0.8 D in the *ortho* methyl group. A *Z*-dienol intermediate [11] should occur in this reaction.

Photolysis of Naphthocyclobutenols.—Irradiation of the

not from the triplet state (E_T *ca.* 59 kcal mol^{-1}) was evidenced by the absence of reaction upon irradiation

* It is not necessary to add piperylene, as the naphthocycloalkenones formed are photostable.

sensitized with acetophenone (E_T 74.1 kcal mol^{-1} [12]) or benzophenone (E_T 69.2 kcal mol^{-1} [12]) (Table 7).

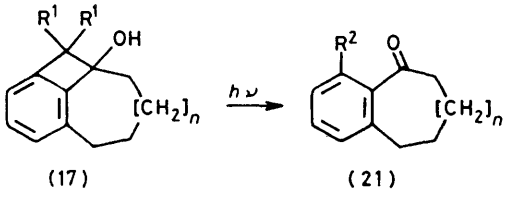
TABLE 7

Photolysis of naphthocyclobutenols

Run	Compound (22) R	n	Solvent	Concentration/ 10^2M	Time/h	λ/Å	Additional reagent	Products (%) Unchanged alcohol (22)	Ketone (23)
23	H	3	But^{t}OH [a]	1.38	3	3 000	none	57.5	38
24	H	3	But^{t}OH [a]	1.38	3	3 000	piperylene	56	37
25	H	3	But^{t}OH	0.606	6.5	3 600	acetophenone	81	0
26	H	3	But^{t}OH	0.597	6.5	3 600	benzophenone	94	0
27	H	3	benzene MeOD	6.95	8	3 000	none	82.5	14
28	Me	2	But^{t}OH	5.14	3	2 537	piperylene	37	44.5

[a] Simultaneous experiments.

When the irradiation was performed in the presence of MeOD, the ketone (23; R = H, n = 3) incorporated one

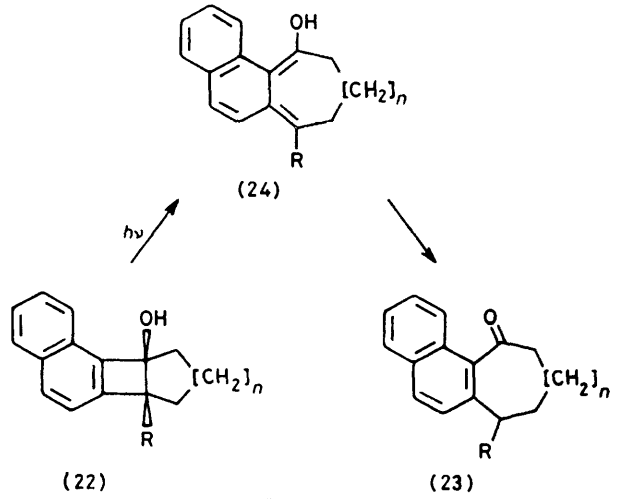


(17) (21)

R^1	n	R^2	n
H	2	Me	2 (38%)
Me	3	Pr^i	3 (50%)

SCHEME 9

deuterium atom at the benzylic position showing the 1,2-naphthoquinodimethane (24; R = H, n = 3) to be



(22) (23)

SCHEME 10

an intermediate. For the purposes of synthesis (22; R = Me, n = 2) was photolysed into (23; R = Me, n = 2) (Table 7). This ring-opening was not obtained by basic treatment of the corresponding alcohol.

It then appears that photochemical opening of benzocyclobutenols constitutes a new synthetic route to benzocycloalkenones and is particularly useful in the synthesis of several substituted benzocyclenones. Conversely, photolysis of benzocycloalkenones may constitute a good synthetic approach to benzocyclobutenols. These results will appear in a future publication.

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 either Varian A60 or Perkin-Elmer R12B instruments with tetramethylsilane as internal reference. Emission spectra (fluorescence and phosphorescence) were recorded on a Mark I, Farrand spectrofluorometer. Analyses were performed by Mr. Dorme, microanalytical laboratory, Paris VI. 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 run on silica gel Merck (0.05—0.2 mm), normally using light petroleum–ether. Irradiations were carried out in a rayonet type Srinivasan–Griffin photochemical reactor RPR 100, using quartz (irradiation at 2 537 Å) and Pyrex vessels (irradiations at 3 000 and 3 500 Å). Solutions were purged with nitrogen before photolysis.

Photolysis of benzocyclobutenols (4; R = H, n = 1, 2, 3). (a) *In non-polar and polar solvents* (*Tables* 1 *and* 4). All irradiations were performed at 2 537 Å. The solvent was removed *in vacuo* and the ketone and starting alcohol were separated by column chromatography, the ketone being eluted first.

Run 1. Alcohol (4; R = H, n = 1) (234 mg, 1.46 mmol) in cyclohexane (35 ml) gave the ketone (5; R = H, n = 1) (50 mg, 21%) as an oil, identical with an authentic specimen,[6] and the starting alcohol (66 mg, 28%).

Run 2. Alcohol (4; R = H, n = 2) (601 mg, 3.45 mmol) in benzene (100 ml) gave the ketone (5; R = H, n = 2) (286 mg, 48%) as an oil, identical with an authentic sample,[6] and the starting alcohol (103 mg, 17%).

Run 3. Alcohol (4; R = H, n = 3) (623 mg, 3.31 mmol) in benzene (200 ml) gave the ketone (5; R = H, n = 3) (144 mg, 23%) as an oil, identical with an authentic sample,[6] and the starting alcohol (81 mg, 13%).

Run 9. Alcohol (4; R = H, n = 1) (160 mg, 1 mmol) in t-butyl alcohol (35 ml) gave the ketone (5; R = H, n = 1) (27 mg, 17%) and the starting alcohol (45 mg, 28%).

Run 10. Alcohol (4; R = H, n = 1) (320 mg, 2 mmol) in t butyl alcohol (70 ml) gave the ketone (5; R = H, n = 1) (106 mg, 33%) and the starting alcohol (125 mg, 39%).

Run 11. Alcohol (4; R = H, n = 2) (174 mg, 1 mmol) in t-butyl alcohol (35 ml) gave the ketone (5; R = H, n = 2) (48 mg, 28%) and the starting alcohol (91 mg, 52%).

Run 12. Alcohol (4; R = H, n = 2) (174 mg, 1 mmol) in t-butyl alcohol (35 ml) gave the ketone (5; R = H, n = 2) (70 mg, 40%) and the starting alcohol (105 mg, 60%).

Run 13. Alcohol (4; R = H, n = 3) (188 mg, 1 mmol) in t-butyl alcohol (35 ml) gave the ketone (5; R = H, n = 3) (30 mg, 16%), the starting alcohol (116 mg, 62%), and the alcohol (11; R = H, n = 3) (14 mg, 7.5%).

Run 14. Alcohol (4; R = H, n = 3) (188 mg, 1 mmol) in t-butyl alcohol (35 ml) gave the ketone (5; R = H, n = 3) (73 mg, 39%) and the starting alcohol (109 mg, 58%).

(b) *In acetone.* A solution of (4; R = H, n = 3) (1.014 g, 5.39 mmol) in acetone (140 ml) was irradiated at 3 000 Å for 3 h. No appreciable quantity of the ketone (5; R = H, n = 3) was detected.

(c) *With dienophile agents.* Irradiations of alcohol (4; R = H) with maleic anhydride, dimethyl butynedioate, *N*-ethylmaleimide, and *N*-phenylmaleimide in various solvents (cyclohexane, dioxan, THF, benzene) gave no detectable adducts.

(d) *With oxygen* (*Scheme* 6). The alcohol (4; R = H, n = 2) (1.450 g, 8.33 mmol) was irradiated in cyclohexane (200 ml) at 2 537 Å for 2 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 successively the ketone (5; R = H, n = 2) (175 mg, 12%), the starting alcohol (1.130 g, 78%), and 5,10-*epidioxy*-5,6,7,8,9,10-*hexahydrobenzocyclo-octen*-5-*ol* (15; R = H, n = 2) (68 mg, 5%) which showed a positive starch–iodide test, m.p. 131° (from light petroleum), $\nu_{max.}$ (CCl_4) 3 580, 3 350, 1 120, 1 060, 1 030, and 930 cm^{-1}, δ(CCl_4) 1.0—2.2 (8 H, m, 4 × CH_2), 3.8 (1 H, br s, exchanged with D_2O, OH), 5.0 (1 H, br d, Ar–C*H*O–O–), and 6.8—7.2 (4 H, m, Ar) (Found: C, 69.65; H, 7.1. $C_{12}H_{14}O_3$ requires C, 69.88; H, 6.84%).

In a similar experiment, the alcohol (4; R = H, n = 3) (1.030 g, 5.5 mmol) in cyclohexane (200 ml) was irradiated for 2 h to give the ketone (5; R = H, n = 3) (107 mg, 10%), the starting alcohol (760 mg, 74%), and 5,11-*epidioxy*-6,7,8,9,10,11-*hexahydro*-5H-*benzocyclononen*-5-*ol* (15; R = H, n = 3) (51 mg, 5%) giving a positive starch–iodide test, m.p. 109° (from light petroleum), $\nu_{max.}$ (CCl_4) 3 590, 3 450, and 1 050 cm^{-1}, δ(CCl_4) 1.1—2.5 (10 H, m, 5 × CH_2), 3.2 (1 H, br s, exchanged with D_2O, OH), 5.0—5.2 (1 H, m, Ar–C*H*O–O–), and 7.0—7.75 (4 H, m, Ar) (Found: C, 71.1; H, 7.2. $C_{13}H_{16}O_3$ requires C, 70.89; H, 7.32%).

(e) *In* CD_3OH (*Table* 5). The alcohols (4; R = H, n = 1 or 2) in benzene (4.5 ml) and CD_3OH (0.5 ml) with added piperylene (10^{-1}M) were irradiated at 2 537 Å. In neither case was incorporation of deuterium into the ketones (5; R = H, n = 1 or 2) observed (^{1}H n.m.r.).

(f) *In* CH_3OD (*Table* 5). The alcohols (4; R = H, n = 1—3) in benzene (4.5 ml) and MeOD (0.5 ml) with added piperylene (10^{-1}M) were irradiated at 2 537 Å. Incorporation of deuterium into the ketones (5; R = H, n = 1—3) was determined by ^{1}H n.m.r. as follows. (i) Comparison of integrations; CH_2 (benzylic + α to carbonyl) *versus* aromatic showed one deuterium atom per molecule of ketone (5). (ii) Complete exchange of residual hydrogen at the α-position to the carbonyl group by treatment with Na and D_2O, and comparison of the above integrations gave the proportion of deuterium incorporated at the benzylic position. (iii) Complete exchange of introduced deuterium at the α-position to the carbonyl group gave the proportion of (5b). (iv) Use of $Eu(fod)_3$ to separate the signals due to the benzylic CH_2 and the α-CH_2 to the carbonyl group gave by integration the ratio [5a] : [5b].

Photolysis of the Benzocyclenones (5; R = H, n = 1—3) (*Tables* 2 *and* 3).—Solutions were irradiated at 3 000 Å. The solvent was then removed *in vacuo* and the products isolated by column chromatography.

Run 4. The ketone (5; R = H, n = 1) (3.016 g, 18.85 mmol) in cyclohexane (320 ml) gave [5,5′-*bi*-6,7,8,9-*tetrahydro*-5H-*benzocycloheptene*]-5,5′-*diol* (9a; R = H, n = 1) (303 mg, 10%), m.p. 137° (from light petroleum), $\nu_{max.}$ (CCl_4) 3 600 and 3 580 cm^{-1}, δ($CDCl_3$) 1.3—1.95 (12 H, m, 6 × CH_2), 2.16—2.85 [6 H, m including 2.68, s, exchanged with D_2O, ArCH_2 + (2 × OH)], and 6.83—7.58 (8 H, m, Ar) (Found: C, 82.05; H, 8.15. $C_{22}H_{26}O_2$ requires C, 81.95; H, 8.13%), the starting ketone (2.260 g, 75%), the *isomeric pinacol* (9b; R = H, n = 1) (282 mg, 9%), m.p. 217° (from light petroleum), $\nu_{max.}$ ($CHCl_3$) 3 580 cm^{-1}, δ([$^2H_6$]-DMSO) 1.2—2.5 [16 H, m, (6 × CH_2) + ArCH_2], 4.67 (2 H, s, exchanged with D_2O, 2 × OH), and 6.7—7.2 (8 H, m, Ar) (Found: C, 81.9; H, 8.25, and the alcohol (10; R = H, n = 1) (120 mg, 4%), m.p. 100—101° (from light petroleum) (lit.,[19] 110—111°).

Run 5. The ketone (5; R = H, n = 2) (2.910 g, 16.7 mmol) in cyclohexane (300 ml) gave the starting ketone (1.32 g, 45%), a mixture of the two isomers of [5,5′-*bi*-5,6,7,8,9,10-*hexahydrobenzocyclo-octene*]-5,5′-*diol* (9a, b; R = H, n = 2) (730 mg, 25%), $\nu_{max.}$ ($CHCl_3$) 3 580 cm^{-1}, δ($CDCl_3$) 1.0—2.0 (16 H, m, 8 × CH_2), 2.1 (2 H, s, exchanged with D_2O, 2 × OH), 2.3—3.2 (4 H, m, ArCH_2), 6.8—7.5 (8 H, m, Ar) (Found: C, 82.15; H, 8.85. $C_{24}H_{30}O_2$ requires C, 82.24; H, 8.63%), and the alcohol (10; R = H, n = 2) (342 mg, 12%), m.p. 77° (from light petroleum), identical with an authentic sample obtained by reduction of the ketone (5; R = H, n = 2) with $LiAlH_4$ in ether.

Run 6. The ketone (5; R = H, n = 3) (3.040 g, 16.17 mmol) in cyclohexane (315 ml) gave [5,5′-*bi*-6,7,8,9,10,11-*hexahydro*-5H-*benzocyclononene*]-5,5′-*diol* (9a; R = H, n = 3) (322 mg, 10.5%), m.p. 206° (from light petroleum), $\nu_{max.}$ ($CHCl_3$) 3 590 cm^{-1}, δ($CDCl_3$) 1.0—1.6 (20 H, m, 10 × CH_2), 1.75 (2 H, s, exchanged with D_2O, 2 × OH), 2.3—3.6 (4 H, m, ArCH_2), 7.0—7.3 (6 H, m, Ar), and 7.6—7.8 (2 H, m, Ar) (Found: C, 82.6; H, 9.15. $C_{26}H_{34}O_2$ requires C, 82.49; H, 9.05%), the starting ketone (310 mg, 10%), the *isomeric pinacol* (9b; R = H, n = 3) (292 mg, 9.5%), m.p. 165° (from light petroleum), $\nu_{max.}$ (CCl_4) 3 580 cm^{-1}, δ($CDCl_3$) 1.0—2.1 (20 H, m, 10 × CH_2), 2.2—2.5 (4 H, m, ArCH_2), 2.55 (2 H, s, exchanged with D_2O, 2 × OH), 6.8—7.3 (6 H, m, Ar), and 7.75—8.05 (2 H, m, Ar) (Found: C, 82.3; H, 8.95), and a mixture of the two alcohols (4; R = H, n = 3) and (11; R = H, n = 3) (1.018 g, 33.5%) which were separated by conversion into their acetates: the alcohols were heated at reflux for 5 h in chloroform (10 ml) containing *NN*-dimethylaniline (2 ml) and acetyl chloride (1 ml); after addition of dilute HCl, and extraction with ether, the dried extract was evaporated and the residue chromatographed to give the acetate of (11; R = H, n = 3) as an oil, $\nu_{max.}$ (film) 1 735 cm^{-1}, δ(CCl_4) 1.2—2.1 [11 H, m with 1.9, s, (4 × CH_2) + O·CO-CH_3], 5.6—6.1 (2 H, m, Ar–CH=C*H* + Ar–C*H*–OCOCH$_3$), 6.66 (1 H, d, Ar–C*H*=CH), and 6.9—7.3 (4 H, m, Ar), and the acetate of (4; R = H, n = 3) as an oil, identical with an authentic sample.[6]

Further reduction with lithium aluminium hydride in ether of each of the two acetates gave 6,7,8,9-*tetrahydro*-5H-*benzocyclononen*-5-*ol* (11; R = H, n = 3) (319 mg, 10.5%), m.p. 100—101°, $\nu_{max.}$ (CCl_4) 3 610 cm^{-1}, δ(CCl_4) 1.0—2.4 (8 H, m, 4 × CH_2), 2.8 (1 H, s, exchanged with D_2O, OH), 4.58—4.85 (1 H, m, ArC*H*OH), 5.55—6.06

(1 H, m, Ar–CH=C*H*–), 6.5 (1 H, d, Ar–CH=CH–), and 6.7—7.5 (4 H, m, Ar) (Found: C, 83.25; H, 8.75. $C_{13}H_{16}O$ requires C, 82.93; H, 8.57%), and the alcohol (4; R = H, n = 3) (610 mg, 20%), m.p. 96°, identical with an authentic sample.

The alcohol (11; R = H, n = 3) in acetone, when oxidized with Jones reagent, gave the ethylenic ketone as an oil, $\nu_{max.}$ (film) 1 675 cm^{-1}, $\delta(CCl_4)$ 1.20—2.36 (6 H, m, 3 × CH_2), 2.6—2.9 (2 H, m, Ar–CO–CH_2), 5.5—6.1 (1 H, m, Ar–CH=C*H*), 6.5 (1 H, d, Ar–C*H*=CH–), and 7.0—7.6 (4 H, m, Ar). The ethylenic ketone in ethyl acetate was rapidly converted by hydrogenation over 5% palladium–charcoal at room temperature and atmospheric pressure into the ketone (5; R = H, n = 3), an oil, identical with an authentic specimen.

Run 7. The ketone (5; R = H, n = 2) (103 mg, 0.59 mmol) in t-butyl alcohol (40 ml) gave the starting ketone (73 mg, 71%), the mixture of the two pinacols (9a, b; R = H, n = 2) (21 mg, 20%), and the alcohol (10; R = H, n = 2) (7 mg, 6%).

Run 8. The ketone (5; R = H, n = 3) (1.316 g, 7 mmol) in t-butyl alcohol (250 ml) gave the starting ketone (157 mg, 12%) and a mixture of the two alcohols (4; R = H, n = 3) and (11; R = H, n = 3) (800 mg, 61%) in the ratio 72 : 28 (^{1}H n.m.r.).

Pinacols (9; R = H, n = 1—3).—A solution of the ketone (5; R = H, n = 1—3) (1 g) in tetrahydrofuran (30 ml), was added with stirring to a Mg–$HgCl_2$ amalgam [20] at room temperature for 5 h. The products formed were separated by column chromatography. The results for each ketone are as follows. (*a*) n = 1; two pinacols in the ratio 85 : 15, (9a; R = H, n = 1) (754 mg, 75%), m.p. 138—139° (from light petroleum), and (9b; R = H, n = 1) (116 mg, 12%), m.p. 217—218° (from light petroleum); (*b*) n = 2; mixture of two pinacols (9a, b; R = H, n = 2) (603 mg, 60%); (*c*) n = 3; two pinacols in the ratio 27 : 73, (9a; R = H, n = 3) (208 mg, 21%), m.p. 210° (from light petroleum), and (9b; R = H, n = 3) (555 mg, 55%), m.p. 162° (from light petroleum).

Photolysis of Methyl Ethers (12; n = 2 *or* 3).—(a) *Synthesis.* By the method of Sammes *et al.*,[15] a solution of the alcohol (4; R = H, n = 2) (355 mg, 2.04 mmol) in chloroform (25 ml) with methyl iodide (1 ml) and freshly prepared silver oxide [21] (510 mg) was stirred at room temperature for 24 h. filtration, evaporation, and chromatography gave 1,2,3,4,-4a,8b-*hexahydro*-4a-*methoxy*-cis-*biphenylene* (12; n = 2) as an oil, (350 mg, 91%), $\nu_{max.}$ (film) 1 180, 1 105, and 1 095sh cm^{-1}, $\lambda_{max.}$ (MeOH) 274 (ε 1 645), 267 (1 710), and 261 nm (1 135), $\delta(CCl_4)$ 1.0—1.66 (4 H, m, 2 × CH_2), 1.66—2.25 (4 H, m, 2 × CH_2), 3.30 (3 H, s, OMe), 3.47—3.82 (1 H, m, ArC*H*), and 6.90—7.70 (4 H, m including 7.30 br s, Ar) (Found: C, 83.0; H, 8.75. $C_{13}H_{16}O$ requires C, 82.93; H, 8.57%). By a similar procedure the alcohol (4; R = H, n = 3) gave 5,6,7,8,9,9a-*hexahydro*-4b-*methoxy*-cis-4bH-*benzo*[a]*cyclohepta*[c]*cyclobutene* (12; n = 3) as an oil (85%), $\nu_{max.}$ (film) 1 090 cm^{-1}, $\lambda_{max.}$ (MeOH) 273 (ε 1 675), 266 (1 775), and 260 nm (1 153), $\delta(CCl_4)$ 1.0—2.57 (10 H, m, 5 × CH_2), 3.3 (3 H, s, OMe), 3.42—3.90 (1 H, m, ArC*H*), and 7.18—7.54 (4 H, m including 7.27 br s, Ar) (Found: C, 82.85; H, 9.1. $C_{14}H_{18}O$ requires C, 83.12; H, 8.97%).

(b) *Photolysis.* The methyl ether (12; n = 2) (294 mg, 1.56 mmol) in cyclohexane (100 ml) was irradiated at 2 537 Å for 3.5 h. Analysis of the reaction by v.p.c. (QF_1, 170°) showed 42% conversion. The solvent was then removed *in vacuo* and the products were isolated by column chromatography. Elution gave successively the enol ether (13; n = 2) as an oil, $\nu_{max.}$ (film) 1 655, 1 235, 1 135, and 1 095 cm^{-1}, $\lambda_{max.}$ (cyclohexane) 250 nm (ε 4 400), $\delta(CCl_4)$ 1.0—2.4 (6 H, m, 3 × CH_2), 2.6—3.0 (2 H, m, ArCH_2), 3.70 (3 H, s, OMe), 4.75—5.17 [1 H, m, Ar–C(OMe)=C*H*], and 7.1—7.6 (4 H, m including 7.35 br s, Ar), a mixture of (13; n = 2) and the starting material, and finally the ketone (5; R = H, n = 2) resulting from partial hydrolysis of (13; n = 2) on the column.

Similar irradiation of (12, n = 3) (139 mg, 0.688 mmol) in cyclohexane (70 ml) for 2 h gave the enol ether (13; n = 3) as an oil (40 mg, 29%), $\nu_{max.}$ (film) 1 660, 1 220, 1 130, 1 110, and 1 090 cm^{-1}, $\lambda_{max.}$ (cyclohexane) 240sh nm (ε 2 039), $\delta(CCl_4)$ 1.0—2.0 (8 H, m, 4 × CH_2), 2.75—2.91 (2 H, m, ArCH_2), 3.67 (3 H, s, OMe), 4.55—4.92 [1 H, m, ArC(OMe)=C*H*], and 7.18 (4 H, s, Ar).

(c) *Hydrolysis of the enol ether* (13; n = 2 or 3). The ketones (5; R = H, n = 2 or 3) were obtained by hydrolysis with dilute hydrochloric acid in acetone.

Photolysis of Substituted Benzocyclobutenols (16).—(*a*). Photolyses were performed at 2 537 Å (concentration and time indicated in Table 6) with added, piperylene (10^{-1}M). The solvent was removed *in vacuo* and the products isolated by column chromatography. Elution gave first the ketone (18) and then a mixture of the two alcohols (19) and (16). Their ratio was evaluated from their ^{1}H n.m.r. spectra [olefinic hydrogen in (19) *versus* total aromatic hydrogens]. Separation was realized by selective acetylation of the secondary alcohol with acetic anhydride in pyridine at room temperature, isolation of the acetate by column chromatography, and reduction by $LiAlH_4$ in ether to produce the alcohol (19).

Run 20. The alcohol (16; R^1 = R^2 = H) (660 mg, 3.51 mmol) in Bu^tOH (200 ml) gave the ketone (18; R^1 = R^2 = H) (395 mg, 60%) as an oil, $\nu_{max.}$ (film) 1 690 cm^{-1}, $\delta(CCl_4)$ 0.75—2.17 [9 H, m with 1.28, d, J 7 Hz, (3 × CH_2) + ArCHCH_3], 2.33—3.25 (3 H, m, ArC*H*CH_3 + Ar–CO–CH_2), 6.92—7.50 (4 H, m, Ar), and a mixture of (19; R^1 = R^2 = H) and starting alcohol (61 mg, 9%). ^{1}H N.m.r. showed an approximate ratio of 1 : 1. Selective acetylation of the products from several experiments led to the acetate of the alcohol (19; R^1 = R^2 = H), an oil, $\nu_{max.}$ (film) 1 740, 1 240, and 1 025 cm^{-1}, $\delta(CCl_4)$ 0.65—2.75 (12 H, m, with 1.95, s, OCOCH_3), 2.03 [s, ArCCH_3 + (3 × CH_2)], 5.45—5.95 (2 H, m, ArC*H*OAc + ArCCH_3=C*H*), and 6.85—7.50 (4 H, m, Ar). Further reduction gave the corresponding alcohol (19; R^1 = R^2 = H), $\nu_{max.}$ (film) 3 340 cm^{-1}, $\delta(CCl_4)$ 0.69—2.30 [9 H, m with 1.98, s, ArC(CH_3)= + (3 × CH_2)], 3.04 (1 H, s exchanged with D_2O, OH), 4.45—4.80 (1 H, m, ArC*H*OH), 5.31—5.73 (1 H, m, ArC(CH_3)=C*H*), 6.76—7.62 (4 H, m with 7.07, s, Ar).

Run 21. The alcohol (16; R^1 = R^2 = Me) (589 mg, 2.73 mmol) in Bu^tOH (70 ml) gave the ketone (18; R^1 = R^2 = Me) (208 mg, 35%) as an oil, $\nu_{max.}$ (film) 1 685 cm^{-1}, $\delta(CCl_4)$ 1.05—1.18 [6 H, s, Ar–CO–C(CH_3)$_2$], 1.18 (3 H, d, J 7 Hz, ArCHCH_3), 1.35—1.85 (6 H, m, 3 × CH_2), 2.5—3.1 (1 H, m, ArC*H*CH_3), and 6.65—7.25 (4 H, m, Ar); a mixture of (19; R^1 = R^2 = Me) and starting alcohol (302 mg, 51%), in the ratio 37 : 63 (^{1}H n.m.r.). Selective acetylation of the preceding mixture led to the acetate of the alcohol (19; R^1 = R^2 = Me) as an oil, $\nu_{max.}$ (film) 1 740 and 1 245 cm^{-1}, $\delta(CCl_4)$ 0.75—1.40 [10 H, m with 0.85, s and 1.03, s, ArCOH-CHC(CH_3)$_2$ + (2 × CH_2)], 1.98 (3 H, s, OCOCH_3), 2.06 (3 H, br s, ArCCH_3=), 5.65—5.90 (2 H, m with 5.87, s, ArC*H*OAc + ArCCH_3=C*H*), and 6.95—7.35 (4 H, m with

7.15 br s, Ar). Reduction of the above acetate led to the alcohol (19; $R^1 = R^2 = Me$) as an oil, $\nu_{max.}$ (film) 3 450 cm^{-1}, $\delta(CCl_4)$ 0.65—1.5 [10 H, m with 0.73, br s, and 1.05, s, $ArCHOHC(CH_3)_2$ + (2 × CH_2)], 1.95 (3 H, s, $ArCCH_3$=), 2.27 (1 H, s, exchanged with D_2O, OH), 4.72 (1 H, s, ArCH-OH), 5.5—5.82 (1 H, m, $ArCCH_3$=CH), and 6.84—7.55 (4 H, m, Ar).

Run 22. The alcohol (16; $R^1 = H$, $R^2 = Me$) (891 mg, 4.41 mmol) in Bu^tOH (140 ml) gave the ketone (18; $R^1 = H$, $R^2 = Me$) (320 mg, 36%) as an oil composed of an inseparable mixture of two isomers, A and B, in the ratio 35 : 65 (v.p.c.), $\nu_{max.}$ (film) 1 690 cm^{-1}, $\delta(CCl_4)$ 1.0—1.95 [12 H, m with 1.09, d, *J* 7 Hz, 1.18, d, *J* 7 Hz and 1.22, d, *J* 7 Hz, Ar–CO–$CHCH_3$ + $ArCHCH_3$ + (3 × CH_2)], 2.35—3.30 (2 H, m, Ar–CO–$CHCH_3$ + $ArCHCH_3$), and 6.92—7.50 (4 H, m, Ar). Hydrogenation of the unsaturated ketone (20; $R^1 = H$, $R^2 = CH_3$) in ethyl acetate over 5% palladium–charcoal led to the single isomer A, an oil, $\nu_{max.}$ (film) 1 690 cm^{-1}, $\delta(CCl_4)$ 1.0—1.91 [12 H, m, including 1.09, d, *J* 7 Hz, and 1.22, d, *J* 7 Hz, Ar–CO–$CHCH_3$ and $ArCHCH_3$ + (3 × CH_2)], 2.32—3.05 (2 H, m, Ar–CO–$CHCH_3$ + $ArCHCH_3$), and 6.71—7.31 (4 H, m, Ar). Further treatment of this isomer with base led to a mixture of the two isomers (18 A and B; $R^1 = H$, $R^2 = Me$). Further elution of the chromatogram from run 22, gave a mixture of (19; $R^1 = Me$, $R^2 = H$) and starting alcohol (543 mg, 61%) in the ratio 78 : 22 (^1H n.m.r.). Selective acetylation of the mixture led to the acetate of the alcohol (19; $R^1 = Me$, $R^2 = H$) which was an oil, $\nu_{max.}$ (film) 1 740 and 1 240 cm^{-1}, $\delta(CCl_4)$ 0.81 [3 H, d, *J* 7 Hz, $ArCH(OAc)CHCH_3$], 1.15—2.25 [11 H, m including 1.98, s, and 2.05, br s, $OCOCH_3$, $ArCCH_3$, and Ar–$CHOAcCHCH_3$ + (2 × CH_2)], 5.55—5.87 [1 H, m, $Ar–C(CH_3)$=CH], 5.93 (1 H, d, *J* 2.5 Hz, ArCHOAc), and 7.05—7.45 (4 H, m, Ar). Reduction of the acetate gave the alcohol (19; $R^1 = Me$, $R^2 = H$), m.p. 79—80°, $\nu_{max.}$ (film) 3 460 cm^{-1}, $\delta(CCl_4)$ 0.70 [3 H, d, *J* 7 Hz, $ArCH(OH)CHCH_3$], 0.80—2.65 [9 H, m including 1.96, s, $ArCCH_3$= and 2.42, s, exchanged with D_2O, OH, $ArCH(OH)CHCH_3$ + (2 × CH_2)], 4.88 (1 H, d, *J* 2.5 Hz, ArCHOH), 5.30—5.77 (1 H, m, $ArCCH_3$=CH), and 6.90—7.60 (4 H, m, Ar).

(*b*) *Transformation of* (19) *into* (18). Alcohol (19) in ethyl acetate was rapidly hydrogenated over 5% palladium–charcoal at room temperature and atmospheric pressure. After filtration and evaporation of the solvent, the crude product in acetone was oxidized with Jones reagent. Column chromatography gave the ketone (18). The reverse order of the two reactions, *i.e.* Jones oxidation followed by hydrogenation, was also performed, the intermediary unsaturated ketones (20) being isolated in the case of (20; $R^1 = R^2 = Me$) as an oil, $\nu_{max.}$ (film) 1 685 and 1 600 cm^{-1}, $\delta(CCl_4)$ 0.9—2.30 [13 H, m including 1.17, s, $ArC(O)C(CH_3)_2$ and 1.95, br s, $ArCCH_3$= + (2 × CH_2)], 5.25—5.60 (1 H, m, $ArC(CH_3)$=CH), and 6.80—7.35 (4 H, m, Ar), and (20; $R^1 = H$, $R^2 = Me$) as an oil, $\nu_{max.}$ (film) 1 695 and 1 665 cm^{-1}, $\delta(CCl_4)$ 1.0—2.30 [10 H, m including 1.12, d, *J* 7 Hz, $ArC(O)CHCH_3$ and 2.20, br s, $ArCCH_3$= + (2 × CH_2)], 2.67—3.58 [1 H, m, $ArC(O)CHCH_3$], 5.50—5.90 (1 H, m, $ArCCH_3$=CH), 7.0—7.40 (3 H, m, Ar), and 7.50—7.85 (1 H, m, *ortho*-H of Ar). Jones oxidation of (19) led to by-products, probably due to oxidation of the double bond. The transformation of (19) into (18) can be carried out on the crude photolysed mixture of alcohols but it is better to use CrO_3–pyridine as the oxidising agent, in the second step, to prevent oxidation of the benzocyclobutenols.

(*c*) The structure of (19; $R^1 = Me$, $R^2 = H$) was elucidated by selective reduction of the unsaturated ketone (20; $R^1 = H$, $R^2 = Me$) (310 mg, 1.55 mmol) in tetrahydrofuran (20 ml) at −40 °C for 30 min, with lithium tris-s-butyl borohydride [22] (3 ml, 3 mmol). Further oxidation (H_2O_2, NaOH) gave the alcohol (19; $R^1 = Me$, $R^2 = H$) (300 mg, 95%), m.p. 79—80° (from pentane), identical with the sample obtained by photolysis.

Two other reductions of the ketone (20, $R^1 = H$, $R^2 = Me$) were performed, giving a mixture of the two isomeric alcohols (19 *trans*; $R^1 = H$, $R^2 = Me$) and (19 *cis*; $R^1 = Me$, $R^2 = H$) which were separated by l.c. The relative ratio was determined by v.p.c. (QF_1); reduction by $LiAlH_4$ in ether gave a *trans* : *cis* ratio of 53 : 47; reduction by $NaBH_4$ in ethanol gave *trans* : *cis* 40 : 60; [*cis*-(19)] $\delta(CCl_4)$ 0.80—2.35 [11 H, m, including 1.10, d, *J* 7 Hz, ArCHOH-$CHCH_3$ and 1.95, s, $ArCCH_3$= + (2 × CH_2) + ArCHOH–$CHCH_3$], 2.85 (1 H, s, exchanged with D_2O, OH), 4.55 (1 H, d, *J* 9 Hz, Ar–CHOH), 5.45—5.77 [1 H, m, $ArC(CH_3)CH$], and 6.92—7.62 (4 H, m, Ar) [*trans*-(19), *vide supra*].

(*d*) *Photolysis of* (16; $R^1 = R^2 = H$) *in presence of* CH_3OD. The alcohol (282 mg, 1.5 mmol) in benzene (4.5 ml) and MeOD (0.5 ml) containing piperylene (0.5 ml) was irradiated at 2 537 Å for 7 h. The solvent was removed *in vacuo* and the products were separated by chromatography to give the ketone (18; $R^1 = R^2 = H$) (93 mg, 33%) and a mixture of (19; $R^1 = R^2 = H$) and the starting alcohol (179 mg, 63.5%) in the ratio 40 : 60 (^1H n.m.r.). ^1H N.m.r. of the ketone showed the introduction of one deuterium atom, by comparison of the signals at 2.33—3.25 p.p.m. and in the aromatic region. Addition of $(Eufod)_3$ caused the appearance of two different signals for $ArCOCH_2(CHD)$ and $ArCHCH_3(CDCH_3)$ in the ratio 80 : 20.

Photolysis of Benzocyclobutenols (17).—(a) *Synthesis.* The ketone (21; $R^2 = Me$, $n = 2$) (380 mg, 2.02 mmol) in t-butyl alcohol (80 ml) was irradiated at 3 000 Å for 5 h. The solvent was removed *in vacuo* and the products chromatographed to afford the starting ketone (156 mg, 41%) and 5,6,7,8,9,9a-*hexahydro*-1H-*cyclobuta*[de]*benzocyclo-octen*-9a-*ol* (17; $R^1 = H$, $n = 2$) (219 mg, 57.5%), m.p. 93—94° (from pentane), $\nu_{max.}$ (CCl_4) 3 610, 3 600, and 3 200 cm^{-1}, $\lambda_{max.}$ (MeOH) 273 (ε 772), 266 (723), and 261 nm (537), $\delta(CCl_4)$ 1.17—2.23 (8 H, m, 4 × CH_2), 2.33—2.87 (2 H, m, $ArCH_2$, 8-membered ring), 3.05 (3 H, s, exchanged with D_2O, OH + CH_2, 4-membered ring), and 6.67—7.17 (3 H, m, Ar) (Found: C, 82.5; H, 8.7. $C_{13}H_{16}O$ requires C, 82.93; H, 8.57%). The two benzylic CH_2 groups were differentiated by addition of the shift reagent $Eu(dpm)_3$. Finally, treatment of (17, $R^1 = H$, $n = 2$) with base [7] led to the ketone (21; $R^2 = Me$, $n = 2$). The same procedure, applied to the ketone (21; $R^2 = Pr^i$, $n = 3$) (230 mg, 1 mmol) in t-butyl alcohol (40 ml) for 5 h, led to the starting ketone (43 mg, 19%) and 1,5,6,7,8,9,10,10a-*octahydrocyclo-buta*[de]*benzocyclononen*-10a-*ol* (17; $R^1 = Me$, $n = 3$) (176 mg, 76.5%), m.p. 131° (from pentane), $\nu_{max.}$ (CCl_4) 3 620, 3 540, and 3 320 cm^{-1}, $\lambda_{max.}$ (MeOH) 273 (ε 780), 265 (773) and 260 nm (557), $\delta(CCl_4)$ 1.15—2.22 [17 H, m including 1.25 and 1.32, s, 2 × Me, with 2.09, s, exchanged with D_2O, OH + (5 × CH_2)], 2.55—3.0 (2 H, m, $ArCH_2$), and 6.74—7.31 (3 H, m, Ar) (Found: C, 83.65: H, 9.45. $C_{16}H_{22}O$ requires C, 83.43; H, 9.63%).

(b) *Photolysis.* The alcohol (17, $R^1 = H$, $n = 2$) (50 mg, 0.266 mmol) in t-butyl alcohol (35 ml) with added piperylene (10^{-1}M) was irradiated at 2 537 Å for 3 h. The solvent was removed *in vacuo* and the products isolated by chro-

matography; elution gave successively the ketone (21; R^2 = Me, n = 2) (19 mg, 38%) and the starting alcohol (23 mg, 46%).

The same procedure, applied to the alcohol (17, R^1 = Me, n = 3) (250 mg, 1.09 mmol) in t-butyl alcohol (30 ml) with added piperylene (10^{-1}M) when irradiated for 2.5 h gave the ketone (21; R^2 = Pr^i, n = 3) (126 mg, 50%) and the starting alcohol (123 mg, 49%).

Photolysis of the Naphthocyclobutenols (22).—Photolyses were performed under the conditions reported in Table 7. The solvent was removed *in vacuo* and the products isolated by column chromatography.

Run 23. Alcohol (22; R = H, n = 3) (132 mg, 0.55 mmol) in Bu^tOH (40 ml) gave the ketone (23; R = H, n = 3) (50 mg, 38%), m.p. 70°, identical with an authentic specimen,[18] and the starting alcohol (76 mg, 57.5%).

Run 24. Alcohol (22; R = H, n = 3) (132 mg, 0.55 mmol) in Bu^tOH (40 ml) with piperylene (0.2 ml) gave the ketone (23; R = H, n = 3) (49 mg, 37%) and the starting alcohol (74 mg, 56%).

Run 25. Alcohol (22; R = H, n = 3) (26 mg, 0.109 mmol) in Bu^tOH (18 ml) with acetophenone (224 mg, 1.86 mmol) gave only starting alcohol (21 mg, 81%).

Run 26. Alcohol (22; R = H, n = 3) (47 mg, 0.197 mmol) in Bu^tOH (33 ml) with benzophenone (509 mg, 2.79 mmol) gave only starting alcohol (44 mg, 94%).

Run 27. Alcohol (22; R = H, n = 3) (364 mg, 1.53 mmol) in benzene (20 ml) and MeOD (2 ml) gave the ketone (23; R = H, n = 3) (51 mg, 14%) and the starting alcohol (300 mg, 82.5%). ^{1}H N.m.r. of the ketone showed the incorporation of one deuterium atom located at the benzylic position (n.m.r. before and after exchange with Na–D_2O).

Run 28. Alcohol (22; R = Me, n = 2) (429 mg, 1.80 mmol) in Bu^tOH (35 ml) with piperylene (0.1 ml) gave the ketone (23; R = Me, n = 2) (191 mg, 44.5%) as an oil, $\nu_{max.}$ (film) 1 690 cm^{-1}, $\lambda_{max.}$ (MeOH) 319 (ε 402), 278 (5 650), 271 (5 520), and 225 nm (78 500), δ(CCl_4) 1.08—1.9 (6 H, m, 3 × CH_2), 1.32 (3 H, d, J 7 Hz, ArCHCH_3), 2.49—3.27 (3 H, m, ArCHCH_3 + ArCOCH_2), and 7.08—7.84 (6 H, m, Ar), and the starting alcohol (158 mg, 39%).

Emission Studies.—Fluorescence spectra were measured at room temperature and phosphorescence spectra at 77 K, both in ethanol. Singlet energy was determined from the intersection of emission and absorption spectra. Triplet energy corresponded to the first absorption in the phosphorescence emission.

Thermal Treatment of Alcohol (4; R = H, n = 3).—The alcohol (122 mg, 0.65 mmol) when heated under nitrogen at 200° for 5 h, was converted into the olefin (8; n = 3), identical with an authentic sample.[6]

We thank the CNRS (M. L. V. V.) and INSERM (C. C.) for financial support.

[8/659 *Received*, 10th *April*, 1978]

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