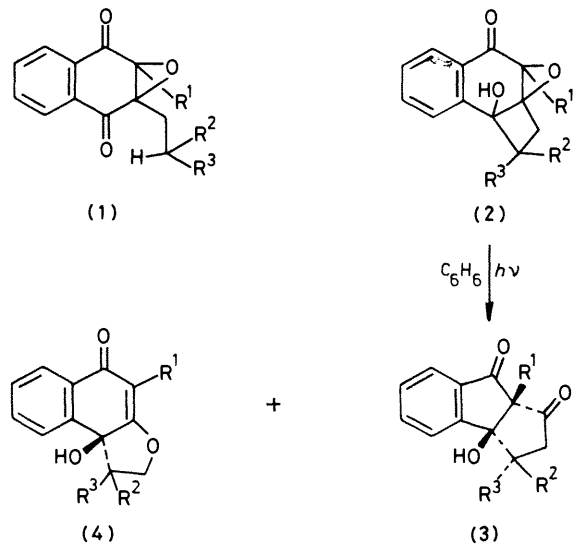
Type II Photoreaction of 1a,7a-Dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-diones: Photochemical Generation of Type II Biradicals from Cyclobutanols

Atsuhiro Osuka,* Hirohito Shimizu, Marli H. Chiba, and Hitomi Suzuki
Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790, Japan
Kazuhiro Maruyama
Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

Irradiation of the title cyclopropa[*b*]naphthalene-2,7-diones (5a—d) in benzene or benzene–Bu^{t}OH (1 : 1) gave the cyclobutanols (6a—d) and the unsaturated keto alcohols (7a—c). The former are Norrish type II cyclisation products, while the latter may be formed by reverse disproportionation of the type II biradical (9). Irradiation of the 1a-methylcyclopropa[*b*]naphthalene-2,7-diones (5e—h) gave the bicyclic diketones (16e—h) *via* hydroxymethylcyclopropyl rearrangement of the type II biradicals (9), in addition to the corresponding cyclobutanols (6e—g) and keto alcohols (7e—g). Photoexcitation of the cyclobutanols (6a—g) exclusively led to the cleavage of the cyclobutane ring, giving rise to type II biradicals (9) whose fates were solvent-dependent. The relative decay rates of the type II biradical (9), by disproportionation, cyclisation, reverse disproportionation, and hydroxymethylcyclopropyl rearrangement, were determined on the basis of the product distribution in separate photolyses of compounds (5) and (6) in benzene.

Recently, we reported the photorearrangement of the cyclobutanol (2) which is obtained from the type II photocyclisation of epoxynaphthoquinones (1).[1] The photorearrangement is presumed to begin with C(α)–O bond cleavage, giving rise to the tricyclic β-diketone (3) and the β-alkoxyenone (4) as the main rearranged products (Scheme 1). In continuation of the above studies, we have investigated the type II photoreaction of the title compounds (5a—h), in which the oxirane ring of (1) is replaced by a cyclopropane ring. These results revealed that the photochemistry of the cyclobutanol (6), a type II cyclisation product from (5), is quite different from that of the epoxide (2) in that excitation of (6) exclusively led to the generation of a type II biradical and not to the cleavage of the cyclopropane ring.[2]

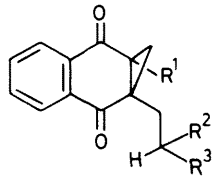


Scheme 1.

Results and Discussion

Photochemistry of 1a-*Alkyl*-1a,7a-*dihydro*-1H-*cyclopropa*[b]-*naphthalene*-2,7-*dione*.—Irradiation of 1a-(2-methylpropyl)-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (5a) in benzene or benzene–Bu^{t}OH (1 : 1) with Pyrex-filtered light furnished a mixture of the cyclobutanol (6a) and the unsaturated keto alcohol (7a), which was separated by chromatography on silica gel. The structures assigned to (6a) and (7a) were in accordance with both their spectral and chemical data. The i.r. spectrum of (6a) showed characteristic bands at 3 400 (hydroxy) and 1 660 (conjugated ketone) cm^{-1}; the ^{1}H n.m.r. ($CDCl_3$) spectrum indicated the presence of two singlet methyl groups at δ 0.90 and 1.34, and diastereoisotopic methylene hydrogens at δ 1.73 and 2.71 (ABq, *J* 11 Hz, 2 H); the ^{13}C n.m.r. ($CDCl_3$) spectrum was consistent with the assigned structure, δ 196.2 (s, ketone), 76.8 (s), 44.7 (s), 40.7 (t), 29.5 (s), 29.2 (d), 26.3 (q), 22.3 (q), and 12.5 (t) (available as a Supplementary Publication, see Experimental section). The i.r. spectrum of (7a) showed characteristic bands at 3 400 (hydroxy) and 1 660 (conjugated ketone) cm^{-1}; the ^{1}H n.m.r. ($CDCl_3$) spectrum revealed the presence of an allylic methyl group at δ 1.80, allylic methylene group at 1.93 and 2.90 (ABq, *J* 15 Hz, 2 H), an *exo*-methylene group at 4.95 (br s, 2 H), and a hydroxybenzyl methine proton at 5.20; the ^{13}C n.m.r. ($CDCl_3$) spectrum revealed the presence of a ketone at δ 196.2, a hydroxybenzyl carbon at 66.8 (d), cyclopropane carbons at 33.5 (d), 27.7 (s), and 18.5 (t), and methylallyl carbons at 141.3 (s), 112.3 (t), 43.6 (t), and 22.4 p.p.m. (q). Further, the structure of (7a) was firmly established by oxidation (CrO_3–pyridine) to a diketone (8a) which, on hydrogenation (Pd–C–EtOH), was converted back into (5a). The indicated stereochemistry of the hydroxy group in (7a) is that expected to arise from the type II biradical (9a), since the second intramolecular transfer of hydrogen from the δ-position of the side-chain to the ring radical centre should result in this hydrogen lying *cis* to the alkyl side-chain. This assignment was supported by the Eu(dpm)$_3$ shift data shown in Figure 1.

The process by which the unsaturated keto alcohol (7a) is generated by hydrogen transfer from the δ-carbon to the benzylic radical is quite rare in type II biradicals, since it cannot compete with the usual type II processes such as dis-



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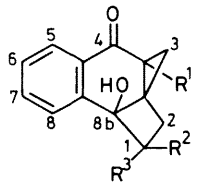

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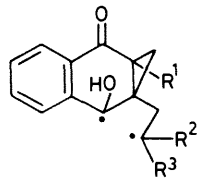
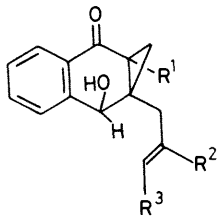


(9)

	R^1	R^2	R^3
a;	H	Me	Me
b;	H	$-(CH_2)_5-$	
c;	H	Me	H
d;	H	Ph	Ph
e;	Me	Me	Me
f;	Me	$-(CH_2)_5-$	
g;	Me	Me	H
h;	Me	Ph	Ph



(7)

	R^1	R^2	R^3
a;	H	Me	H
b;	H	$-(CH_2)_4-$	
c;	H	H	H
e;	Me	Me	H
f;	Me	$-(CH_2)_4-$	
g;	Me	H	H

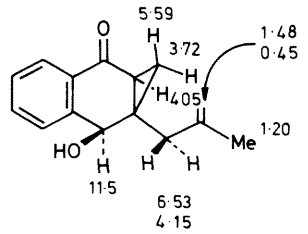


Figure 1. ^1H N.m.r. shifts induced with $Eu(dpm)_3$. The values were determined from plots of shifts (p.p.m.) *vs.* molar ratio of $Eu(dpm)_3$: (7a) by the least-squares method. Concentration of (7a) was *ca.* 0.125M in $CDCl_3$

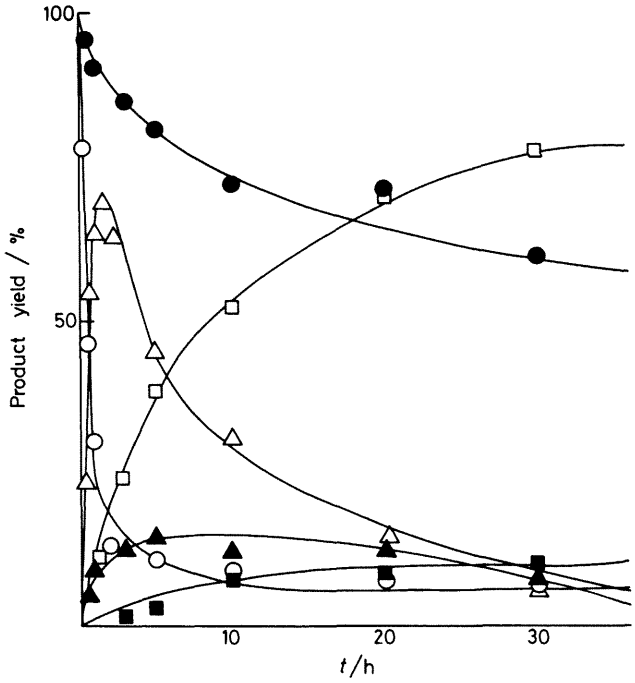
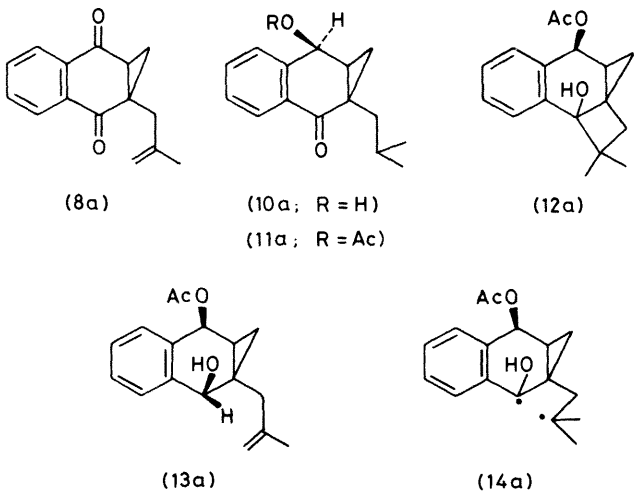


Figure 2. Dependence of the product distribution from compound (5a) on the solvent and irradiation time. Symbols ●, ▲, and ■ show the amount of (5a), (6a), and (7a) respectively in the photolysis of (5a) in benzene, while ○, △, and □, represent the amount of (5a), (6a), and (7a) respectively in the photolysis of (5a) in benzene–Bu^{t}OH (1 : 1)

proportionation, cyclisation, and elimination.[3,*] The product distribution was found to be dependent on both the solvent and the irradiation time (Figure 2). The amount of compound (6a) obtained reached a maximum (*ca.* 70%) after 1 h in benzene–Bu^{t}OH (1 : 1) or (*ca.* 17%) after 10 h in benzene, and then decreased, while the amount of the open-chain compound (7a) increased steadily. Thus, the cyclobutanol (6a) was best obtained by a short irradiation of the cyclopropanaphthalenedione (5a) in alcoholic solvent. The results in Figure 2 suggested that the photochemical production of the type II biradical (9a) occurs from the cyclobutanol (6a) as well as by the normal type II pathway from compound (5a). Interestingly, this was confirmed by irradiation of the alcohol (6a) in benzene, which readily gave the cyclopropanaphthalenedione (5a) together with a small amount of the alcohol (7a). In benzene–Bu^{t}OH (1 : 1), the irradiation of the cyclobutanol (6a) resulted in a smooth conversion into compound (7a) with concurrent formation of the diketone (5a). These results clearly indicate the intermediacy of the type II biradical (9a) in the irradiation of (6a).[4]

Similarly, irradiation of the cyclopropanaphthalenediones (5b) and (5c) in benzene–Bu^{t}OH (1 : 1) afforded the corresponding cyclobutanols (6b), (6c-*en*), and (6c-*ex*), and the unsaturated keto alcohols (7b) and (7c). The structure assignments of the epimeric cyclobutanols (6c) is based on the ^1H n.m.r. chemical shifts of the methyl protons at C(8). The methyl protons of (6c-*en*) appeared at higher field (0.82) owing to the shielding effects of the benzene ring, compared with those of (6c-*ex*) which appeared at δ 1.20. On excitation, the cyclobutanols (6b), (6c-*en*), and (6c-*ex*) generated the type II biradicals (9b) and (9c), respectively, a large portion of which reverted to the starting diketones (5b) and (5c) by disproportionation in benzene. Upon irradiation in alcoholic solvents the cyclobutanol (6b) was smoothly converted into

* Cycloundecen-4-ol was reported as a minor product (8%) in the photochemical reaction of cycloundecanone in benzene, K. Matsui, T. Mori, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 3440. To our knowledge, this is the only reported case of reverse disproportionation in type II biradicals.



(8a) (10a; R = H) (11a; R = Ac) (12a)

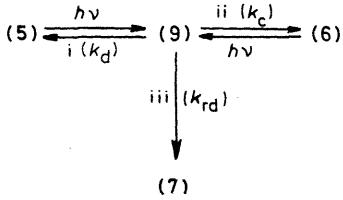
(13a) (14a)

the unsaturated keto alcohol (7b), while (6c-*ex*) was largely epimerised to give a mixture of (6c-*ex*) and (6c-*en*) accompanied by a small amount of (7c).

Irradiation of the 2,2-diphenylethyl substituted compound (5d) in benzene for 5 h furnished a photostationary mixture of (5d) (80%) and (6d) (20%). Extended irradiation of this mixture did not enhance the degree of conversion. A separate irradiation of the cyclobutanol (6d) in benzene also led to a mixture of (5d) and (6d) with the same composition after 3 h. The ratio of (6d) to (5d) increased significantly with added alcohol; (6d) : (5d) = 4 in benzene–Bu^{t}OH (1 : 1) and 9 in MeOH.

In order to inspect the effect of the carbonyl group at C(3), we examined the photoreaction of the keto acetate (11a). The cyclopropanaphthalenedione (5a) was reduced with $NaBH_4$ to yield the keto alcohol (10a) as the major reduction product, which was acetylated (Ac_2O–pyridine) to give the acetate (11a). Irradiation of (11a) for 2 h gave the cyclobutanol (12a) and the unsaturated alcohol (13a); the ratio of (12a) : (13a) was 6.5 in MeOH and 5 in benzene–Bu^{t}OH (1 : 1). Since the cyclobutanol (12a) and the unsaturated alcohol (13a) were quite stable under the irradiation conditions and no interconversion of (11a), (12a), or (13a) was operative, the ratio of (12a) to (13a) may be seen to reflect the relative rates of cyclisation and reverse disproportionation in the type II biradical (14a).

Photochemistry of 1a-*Alkyl*-7a-*methyl*-1a,7a-*dihydro*-1H-*cyclopropa*[b]*naphthalene*-2,7-*dione*.—The fact that the type II biradicals (9a—d) did not give appreciable amounts of products derived from the opening of the cyclopropane ring indicated that the rate of hydroxymethylcyclopropyl rearrangement was negligible compared with other processes. The hydroxymethylcyclopropyl rearrangement was expected to be accelerated by the introduction of a methyl group at C(7a) since, in the rearranged radical (15), the radical centre α to the carbonyl group would be better stabilised by the methyl group, and we therefore investigated the photochemical reactions of the cyclopropanaphthalenediones (5e—h). The photochemistry of (5h) stands in sharp contrast to that of (5d) in that irradiation of (5h) in benzene for 30 h gave exclusively the bicyclic diketone (16h) in 83% isolated yield. In this case, the formation of the corresponding cyclobutanol (6h) was not detected during the course of the reaction. The structure of (16h) was assigned on the basis of its spectral data and elemental analysis. The i.r. spectrum showed characteristic bands at 1 695 and 1 655 (conjugated ketones) cm^{-1}; the ^1H n.m.r. ($CDCl_3$) spectrum showed



Scheme 2. i, Disproportionation; ii, cyclization; iii, reverse disproportionation

signals at δ 1.18 (s, Me), 2.28 (d, *J* 15 Hz, 1 H), 2.60 (dd, *J* 8, 15 Hz, 1 H), 2.88 (dd, *J* 4, 16 Hz, 1 H), 3.42 (dd, *J* 10, 16 Hz, 1 H), and 3.62 (m, 1 H), indicating the presence of a CH_2CH-CH_2 group; the ^{13}C n.m.r. ($CDCl_3$) spectrum revealed the presence of two ketones at δ 204.4 and 199.2, two quaternary carbons at 63.9 and 60.7, one methine carbon at 50.2, two methylene carbons at 45.2 and 42.1, and a methyl carbon at 22.7 p.p.m., besides aromatic carbon atoms. As shown in Scheme 3, the formation of compound (16h) can be best explained by a mechanism involving hydroxymethylcyclopropyl rearrangement of the type II biradical (9h) to (15h) followed by radical recombination. Similar irradiation of compound (5e) in benzene–Bu^{t}OH (1 : 1) for 5 h gave the cyclobutanol (6e) (17%), the unsaturated keto alcohol (7e) (11%), the bicyclic diketone (16e) (30%), and the alkylidene phthalide (17e) (9%). The last compound is a secondary photoproduct derived from (16e). This was confirmed by exposure of (16e) to the irradiation conditions, which readily produced (17e). Irradiation of the cyclohexylmethyl substituted compound (5f) in benzene–Bu^{t}OH (1 : 1) gave the cyclobutanol (6f) (61%), the unsaturated keto alcohol (7f) (18%), and the alkylidene phthalide (17f) (2%). The hydroxymethylcyclopropyl rearrangement is probably of minor importance in (9f) because of efficient reverse disproportionation. Irradiation of the diketone (5g) in benzene–Bu^{t}OH (1 : 1) gave the cyclobutanols (6g-*ex*) (48%) and (6g-*en*) (9%), the unsaturated keto alcohol (7g) (4%), and an epimeric mixture of the bicyclic diketone (16g) (15%).

Reaction Mechanism.—Previously, we suggested that 10% of the type II biradical (18) derived from epoxynaphthoquinone (1) underwent a type II elimination to give the phthiocol *via* an allene oxide intermediate (19).[1] In contrast, the type II biradical (9) did not give appreciable amounts of elimination products. We examined the crude photolysate of (5d) or (5h) by gas chromatography in detail, but we could not detect even traces of 1,1-diphenylethylene. The reluctance to undergo elimination may be due to the high internal energy of the expected elimination product with a bridgehead double bond.

Quantum yields for the disappearance of the diketone (5) in benzene and benzene–Bu^{t}OH (1 : 1) were determined at low conversions (*ca.* 10%) by using valerophenone as the chemical actinometer.[5] The values were reproducible, but would be slightly smaller than the real ones since the cyclobutanol (6) efficiently reproduces the starting diketone (5) under the irradiation conditions. The results are shown in Table 1. The increase in quantum yield with added alcohol can be attributed to biradical solvation, which suppressed reversion of the biradical to ground-state cyclopropanaphthalenedione. Quantum yields of compounds (5e) and (5f) in benzene–Bu^{t}OH (1 : 1) were smaller than those of (5a) and (5b). We are uncertain which step is affected by the presence of the methyl group at C(2a).

Since the photoexcitation of conjugated cyclopropyl ketones usually leads to the opening of the three-membered ring, it is quite interesting to realize that irradiation of the

Table 1. Quantum yields (φ) for the disappearance of the cyclopropanaphthalenediones (5) [a]

	φ		
	C_6H_6	C_6H_6–Bu^tOH (1 : 1)	$k_q\tau$ [b]
(5a)	0.017	0.37	
(5b)	0.052	0.23	
(5c)	0.073	0.40	
(5d)	0.11	0.18	
(5e)	0.016	0.18	16
(5f)	0.021	0.12	16

[a] 0.015M-Solutions of (5) were used. [b] Least-squares slopes of linear Stern–Volmer plots in benzene solutions using naphthalene as the triplet quencher, ±10%.

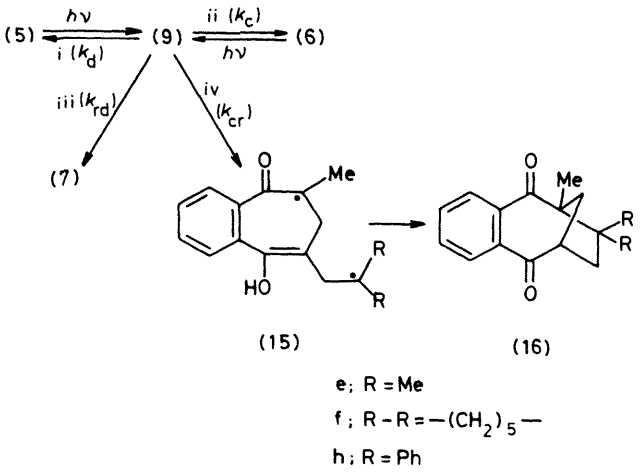
Table 2. Quantum yields (φ) and kinetic data for the photochemical reaction of the cyclobutanols (6) [a]

Cyclobutanol	φ [b]	$k_q\tau$ (mol^{-1} l) [c]	10^{-6} 1/τ(s^{-1}) [d]
(6a)	0.21	228	22
(6b)	0.21	157	32
(6c-*ex*)	0.023	460	11
(6d)	0.23	10	500
(6e)	0.44	242	21
(6f)	0.58	119	42

[a] 0.015M-Benzene solutions of (6) were used. [b] Quantum yields for the formation of (5), ±5%. [c] Least-squares slopes of linear Stern–Volmer plots in benzene solutions using naphthalene quencher, ±10%. [d] Assuming $k_q = 5 \times 10^9$ mol^{-1} l s^{-1}.

cyclobutanol (6) does not lead to this opening, but instead to cleavage of the cyclobutane ring which is situated away from the carbonyl group. The photoreactions of the cyclobutanol (6) were quenched by naphthalene or penta-1,3-diene, and were sensitised by xanthone, thus indicating the occurrence of a triplet reaction. Quantum yields for the formation of the diketone (5) from the cyclobutanol (6) and $k_q\tau$ values, standard Stern–Volmer slopes, were determined by the use of the valerophenone actinometer and the naphthalene quencher. The data are collected in Table 2. Apparently, the life times of the cyclobutanols (6) are determined primarily by the C(1)–C(8b) bond strength. Therefore, the cyclobutanol (6d) is the most reactive and its triplet life time can be calculated to be as short as 2×10^{-9} s based on $k_q = 5 \times 10^9$ mol^{-1} l s^{-1}.[6] The marked stability of the acetate (12a) under the irradiation conditions indicates that the carbonyl group at C(4) is necessary for the photochemical generation of the type II biradical (9). We believe that C(1)–C(8b) bond rupture may be brought about as a result of intramolecular energy transfer through the cyclopropane ring or through the π-electron systems of the benzene ring. In the cyclobutanol (6), the highly efficient cleavage of the C(1)–C(8b) bond which is remote from the chromophore, indicates that this bond is the weakest in (6). The cyclopropane ring appears to weaken this bond by conjugative or inductive effects, in co-operation with the aromatic ring and the hydroxy group.

It is of mechanistic interest to estimate the relative rates of type II biradical reactions such as disproportionation (k_d), cyclisation (k_c), reverse disproportionation (k_{rd}), and hydroxymethylcyclopropyl rearrangement (k_{cr}). The importance of disproportionation relative to cyclisation or elimination was usually deduced from the differences in efficiency of type II reactions, when irradiation is performed in benzene or alcoholic solvents. It is generally accepted that disproportionation is completely suppressed in alcoholic media with simple aryl alkyl ketones,[3,4] and we were interested to see whether this is true even for sterically hindered ketones such as (5). For this purpose, the cyclobutanol (6), a precursor of the type II biradical (9), was selected. Irradiation of compound (6e) in MeOH gave products (5e), (7e), and (16e) (Scheme 3) in the ratio 9.5 : 1 : 4.5, indicating that disproportionation was not completely suppressed in this solvent. This is probably due to the steric hindrance around the hydroxy group, which does not allow the hydrogen bonding by the solvent necessary to prevent disproportionation. We determined the following product ratios; (5) : (7) : (16) from the irradiation of compound (6), and (6) : (7) : (16) in the irradiation of (5) in benzene, at low conversions, by gas chromatography. Then, based on these results, the relative importance of the type II reaction for compound (9) was calculated (Table 3). It would be very difficult to evaluate each rate constant for the same unit only on the basis of the data in Table 3, because we do not have exact values for the life time of compound (9); but, several qualitative comparisons could be made. Recently, Wagner and Scaiano have shown that monoradical reactions of the biradicals proceed with the characteristic rate constants of the reactions of analogous monoradicals.[7,8] It has been shown that the rate constant for the reaction with octanethiol of the alkyl radical in the type II biradical derived from valerophenone is slightly larger than that from γ-methylvalerophenone.[8] These results suggest that the secondary alkyl radical in (9c) may be more reactive toward hydrogen abstraction than the tertiary alkyl radicals in (9a) and (9b). Thus, the decreased propensity of (9c) to disproportionate may be brought about as a result of the enhanced rate constant for cyclisation. The increased percentages of reverse disproportionation in (9b) and (9f) compared with (9a) and (9e) can be accounted for by considering the smaller δ C–H bond energies in the former compounds. Compared with compounds (9a), (9b), and (9c), larger proportions of (9e) and (9f) underwent disproportionation, which is related with the high quantum yields of the cyclobutanols (6e) and (6f) for the formation of the corresponding cyclopropanaphthalenediones. These facts might be explained by considering the conformation of the biradical. Conformation A, where disproportionation is more feasible owing to the proximity of the hydroxy group and alkyl radical centre, would be more favoured in (9e) and (9f) where the methyl group is attached at the cyclopropane ring; [10] usual type II processes leading to products (cyclisation and elimination) from (9) would be

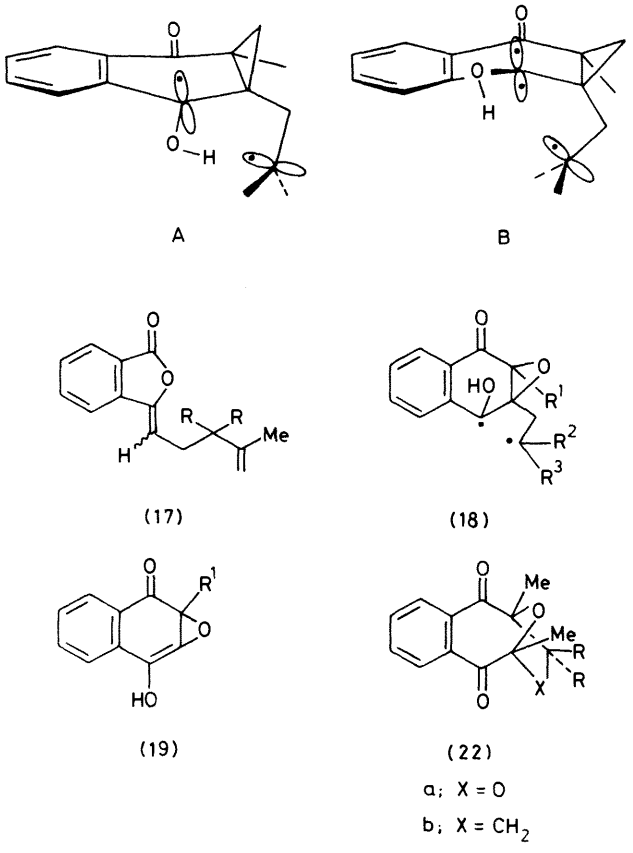


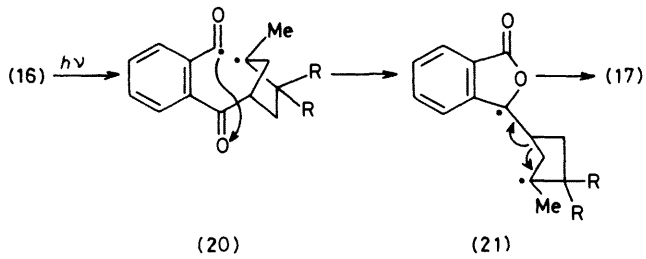
Scheme 3. i, Disproportionation; ii, cyclization; iii, reverse disproportionation; iv, hydroxymethylcyclopropyl rearrangement

Table 3. Determination of the relative rate constants of the type II biradicals (9)

Run	Starting material	Product distribution (%) (5)	(6)	(7)	(16)	Type II biradical	Relative rate constant [a] k_d	k_c	k_{rd}	k_{cr}
1	(5a)		90	10		(9a)	78	20	2	
2	(6a)	97.2		2.8						
3	(5b)		63	37		(9b)	82	12	7	
4	(6b)	92.3		7.7						
5	(5c)		97 [b]	3		(9c) [f]	65	33 [g]	2.5	
6	(6c-*ex*)	86	10 [c]	3.4						
7	(6c-*en*)	69	28 [d]	2.8						
8	(5e)		80	*e*	30	(9e)	91	6	0.005	2.5
9	(6e)	96.8		0.6	2.6					
10	(5f)		56.5	*e*	43.5	(9f)	93	2.2	2.7	1.7
11	(6f)	95.5		2.8	1.7					

[a] Arbitrary unit. [b] The ratio of (6c-*ex*) to (6c-*en*) = 5.4. [c] Yield of (6c-*en*). [d] Yield of (6c-*ex*). [e] Trace amounts. [f] Based on runs 6 and 7. [g] The ratio of $k_{c\text{-}ex}$ to $k_{c\text{-}en}$ = 3.3.





Scheme 4.

greatly retarded by steric congestion and reduced conformational mobility. We believe that this is a major reason for the occurrence of unusual type II processes such as reverse disproportionation and hydroxymethylcyclopropyl rearrangement at the ketyl radical site.

Finally, the secondary photorearrangement of the bicyclic diketone (16) to the alkylidene phthalide (17) could be explained by the mechanism shown in Scheme 4. The rearrangement could begin with α-cleavage, followed by lactonisation to give the 1,4-biradical (21) which then cleaves to give (17). We previously reported similar photorearrangements of compounds (22a) and (22b) having oxygen atoms β to the carbonyl group. However, the results from the diketone (16) suggest that the photorearrangement of the bicyclic diketone to the alkylidene phthalide is general for these strained bicyclic diketones, and the β-oxygen atoms are not essential.

Experimental

M.p.s were measured on a Yanagimoto micro melting point apparatus and are uncorrected. I.r. spectra were recorded on a Hitachi Model 260-10. ^{1}H N.m.r. spectra were recorded on a JEOL JMN-C-60HL instrument and chemical shifts are reported in p.p.m. on the δ scale from internal Me_4Si. ^{13}C N.m.r. spectra were recorded on a JEOL FX-100 spectrometer. G.c. analyses were performed on a Hitachi Model 163, using a 3φ × 1-m stainless-steel column packed with 10% SE-30 on Celite 545 AW. High-pressure liquid chromatography (h.p.l.c.) analyses were performed on a JASCO Model FLC A-700 equipped with a u.v. detector (Model UVIDEC-100). The separations were carried out on a 500 × 2-mm stainless column packed with JASCO-Pack SS-05 with water-saturated hexane–diethyl ether as the eluant. Preparative separations were performed by column chromatography over silica gel (Wakogel C-200). U.v. irradiations were carried out in a Pyrex vessel (Eikosha EHB-WF) under argon with an Eikosha 300-W high-pressure Hg lamp.

Preparation of 1a,7a-*Dihydro*-1H-*cyclopropa*[b]*naphthalene*-2,7-*dione* (5a—h).—The diketones (5) used were prepared by the method of Buchanan.[11] Isolated yields and physical properties are summarised in Table 4.

General Procedure for the Photochemical Reaction of the Diketones (5).—Solvent benzene was purified by distillation from diphenyl ketyl solution. Bu^{t}OH was distilled over CaO. For preparative purpose, irradiations were carried out in benzene–Bu^{t}OH (1 : 1). Argon was bubbled through a solu-

Table 4. Yields and physical properties of cyclopropanaphthalenediones (5)

Compound	Yield (%)	M.p. (°C) [b.p. (°C/mmHg)] [a]	Elemental analysis Found (%)	Required (%)	I.r. $\nu_{max.}$ (cm^{-1})((KBr)	^1H N.m.r. δ(p.p.m.) ($CDCl_3$) (*J* in Hz)
(5a)	55	[165—170/2]	C; 78.7 H; 7.3	78.92 7.06	1 680, 1 600, 1 340, 1 300, 1 270, 970, 790, 720	0.92 (d, *J* 6, 6 H), 0.6—1.1 (m, 2 H), 1.50 (dd, *J* 4 and 9, 1 H), 1.7—2.1 (m, 1 H), 2.3—2.6 (m, 2 H), and 7.5—8.0 (m, 4 H)
(5b)	57	81—82	C; 80.5 H; 7.7	80.56 7.51	1 680, 1 595, 1 450, 1 300, 1 130, 970, 795, 720	0.8—1.9 (m, 14 H), 2.3—2.4 (m, 1 H), 2.42 (d, *J* 14, 1 H), 2.50 (dd, *J* 6 and 9, 1 H), and 7.5—8.1 (m, 4 H)
(5c)	54	[150—157/2]	C; 78.3 H; 6.45	78.48 6.59	1 680, 1 595, 1 295, 1 260, 960, 790, 715	0.95 (t, *J* 6, 3 H), 1.2—1.8 (m, 5 H), 2.1—2.4 (m, 1 H), 2.61 (dd, *J* 6 and 9, 1 H), and 7.5—8.1 (m, 4 H)
(5d)	42	130—131	C; 85.15 H; 5.65	85.20 5.72	1 680, 1 600, 1 360, 1 300, 1 265, 980, 755, 720, 705	1.2—2.1 (m, 4 H), 3.26 (dd, *J* 6 and 13, 1 H), 4.55 (dd, *J* 6 and 9, 1 H), 7.0—7.2 (m, 10 H), and 7.5—8.0 (m, 4 H)
(5e)	82	[155—160/1.5]	C; 79.35 H; 7.55	79.31 7.49	1 680, 1 595, 1 470, 1 385, 1 305, 990, 720	0.94 (d, *J* 6, 6 H), 1.58 (s, 3 H), 1.30 and 1.80 (ABq, *J* 5, 2 H), 1.6—2.4 (m, 3 H), and 7.5—8.0 (m, 4 H)
(5f)	72	[170—180/1]	C; 80.65 H; 7.9	80.81 7.85	1 670, 1 590, 1 445, 1 295, 1 270, 985, 720	1.24 and 1.71 (ABq, *J* 5, 2 H), 1.54 (s, 3 H), 0.8—2.2 (m, 13 H), and 7.5—8.0 (m, 4 H)
(5g)	59	[140—147/1]	C; 79.0 H; 7.05	78.92 7.06	1 675, 1 595, 1 465, 1 305, 1 185, 985, 720	0.98 (t, *J* 6, 3 H), 1.25 and 1.73 (ABq, *J* 5, 2 H), 1.56 (s, 3 H), 1.2—1.6 (m, 2 H), 1.9—2.5 (m, 2 H), and 7.4—8.0 (m, 4 H)
(5h)	55	Oil	C; 85.25 H; 6.15	85.21 6.05	1 680, 1 600, 1 495, 1 455, 1 305, 995, 725, 705	0.97 and 1.57 (ABq, *J* 5, 2 H), 1.17 (s, 3 H), 2.52 (dd, *J* 7 and 14, 1 H), 2.86 (dd, *J* 7 and 14, 1 H), 4.52 (t, *J* 7, 1 H), 7.16 (m, 10 H), and 7.5—8.0 (m, 4 H)

[a] B.p.s were measured by Kugelrohr apparatus.

tion of the diketone (5) (1 g) in benzene (200 ml) and Bu^{t}OH (200 ml) in a Pyrex vessel for 10 min and then irradiated with cooling water for an appropriate period of time. The progress of the reaction was followed by t.l.c. After removal of the solvent, the residual oil was chromatographed on a silica gel column, using hexane–diethyl ether as the eluant. Final purification was usually accomplished by recrystallisation. M.p.s, i.r. and ^1H n.m.r. spectral results and the elemental analyses of the photoproducts are summarised in Table 4—7. ^{13}C N.m.r. data of selected photoproducts are available as a Supplementary Publication * (SUP. No. 23622, 3 pages).

*Conversion of 7-Hydroxy-*7a-(2-*methylprop-*2-*enyl*)-1,1a,7,-7a-*tetrahydrocyclopropa*[b]*naphthalen-*2-*one* (7a) *into the Cyclopropanaphthalenedione* (5a).—Chromium trioxide–pyridine complex was prepared from CrO_3 (10 mg) and pyridine (5 ml). To this stirred slurry was added a solution of the alcohol (7a) (50 mg, 0.22 mmol) in pyridine (5 ml). After the mixture had been stirred for 24 h, water (20 ml) was added and the solution extracted with diethyl ether (four 20 ml portions). The combined ether solution was shaken in turn with water, sulphuric acid (1.8M), water, sodium hydrogencarbonate solution, and water, the solution was dried (Na_2SO_4), and the solvent evaporated to give the diketone (8a) as a colourless oil (42 mg, 85%).

Hydrogenation of the unsaturated diketone (8a) (45 mg, 0.2 mmol) over 5% Pd/C (10 mg) in ethanol (20 ml) under hydrogen (1 atm) for 2 h, followed by filtration and removal of the solvent, gave almost pure diketone (5a) (43 mg, 92%).

7a-(2-*Methylprop-*2-*enyl*)-1a,7a-*dihydro-*1H-*cyclopropa*[b]-*naphthalene-*2,7-*dione* (8a), colourless oil; $\nu_{max.}$ (NaCl) 3 060, 2 900, 1 680 (CO), 1 590, 1 450, 1 350, 1 300, and 1 260 cm^{-1}; δ($CDCl_3$) 1.6 (m, 2 H), 1.8 (C=CMe), 2.10 and 3.21 (ABq, *J* 15 Hz, 2 H), 2.63 (dd, *J* 5 and 8 Hz, 1 H), 4.70 (br s, 1 H), 4.82 (br s, 1 H), and 7.6—8.2 (m, 4 H) (Found: C, 79.45; H, 6.35. $C_{15}H_{14}O_2$ requires C, 79.62; H, 6.24%).

Preparation of the Keto Ester (11a).—A mixture of the diketone (5a) (1 g, 6.58 mmol) and $NaBH_4$ (700 mg, 1.85 mmol) in methanol (40 ml) was stirred for 1.5 h at room temperature, then water (20 ml) was added to the reaction mixture, and it was extracted with diethyl ether (three 30-ml portions). After the solution had been dried (Na_2SO_4), evaporation of the solvent gave the residual oil, which was separated by column chromatography over silica gel to give the keto alcohol (10a) (594 mg, 61%), together with the regioisomeric alcohol (10a′) whose structure has not been elucidated yet.

A solution of the keto alcohol (10a) (594 mg) in acetic anhydride (5 ml) and pyridine (30 ml) was stirred at room temperature for 6 h; then, the reaction mixture was poured into water (100 ml), and it was extracted with diethyl ether (three 30-ml portions). The combined ether solution was shaken in turn with water, sulphuric acid (1.8M), water, sodium hydrogencarbonate solution, and water. Removal of the solvent gave a yellow oil, which was purified by column chromatography over silica gel to yield the keto ester (11a) (542 mg, 77%).

7-*Hydroxy-*1a-(2-*methylpropyl*)-1,1a,7,7a-*tetrahydrocyclopropa*[b]*naphthalen-*2-*one* (10a), colourless oil; $\nu_{max.}$ 3 400 (OH), 3 050, 1 680, and 1 600 cm^{-1}; δ(CCl_4) 0.88 (d, *J* 6 Hz, 6 H), 0.6—0.9 (m, 2 H), 1.9—2.5 (m, 4 H), 3.6 (mobile, 1 H), 5.3 (d, *J* 6 Hz, 1 H), and 7.2—7.8 (m, 4 H) (Found: C, 78.15; H, 7.9. $C_{15}H_{18}O_2$ requires C, 78.23; H, 7.88%). 7-*Acetoxy-*1a-(2-*methylpropyl*)-1,1a,7,7a-*tetrahydrocyclopropa*[b]*naphthalen-*2-*one* (11a), colourless oil; $\nu_{max.}$ 2 950, 1 740 (ester), 1 675 (a conjugated ketone), 1 370, and 1 230 cm^{-1}; δ($CDCl_3$) 0.90 (d, *J* 6 Hz, 3 H), 0.95 (d, *J* 6 Hz, 3 H), 1.1 (m, 2 H), 2.0—2.5 (m, 4 H), 2.23 (s, OCOMe), 7.1—7.5 (m, 3 H), and

* For details of the Supplementary Publications Scheme, see Instructions to Authors (1983), *J. Chem. Soc., Perkin Trans. 1*, 1983, Issue 1.

Table 5. Physical properties of the cyclobutanols (6)

Cyclobutanol	M.p. (°C)	Elemental analysis Found (%)	Required (%)	I.r. $\nu_{max.}$ (cm^{-1}) (KBr)	^1H N.m.r. δ(p.p.m.) ($CDCl_3$) (*J* in Hz)
(6a)	107—108	C; 78.8 H; 7.1	78.92 7.06	3 400, 2 940, 1 660, 1 600, 1 300, 790	0.90 (s, 3 H), 1.34 (s, 3 H), 1.12 (d, *J* 6, 1 H), 1.26 (d, *J* 9, 1 H), 1.98 (dd, *J* 6 and 9, 1 H), 1.73 and 2.71 (ABq, *J* 11, 2 H), 2.90 (mobile, 1 H), 7.20—7.70 (m, 3 H), and 7.9—8.0 (m, 1 H)
(6b)	205—206	C; 80.4 H; 7.65	80.56 7.51	3 400, 1 650, 1 600, 1 290, 755, 730	0.7—2.4 (m, 14 H), 2.57 (d, *J* 11, 1 H), 7.2—7.6 (m, 3 H), and 7.8—8.0 (m, 1 H)
(6c-*ex*)	167—168	C; 78.45 H; 6.55	78.48 6.59	3 420, 1 650, 1 600, 1 290, 1 100, 1 000, 970, 760	1.26 (d, *J* 6, 3 H), 1.1—1.4 (m, 2 H), 1.98 (dd, *J* 6 and 9, 1 H), 2.19 (dd, *J* 7 and 16, 1 H), 2.5—3.0 (m, 2 H), 7.1—7.6 (m, 3 H), and 7.8—8.0 (m, 1 H)
(6c-*en*)	85—86	C; 78.55 H; 6.45	78.48 6.59	3 420, 1 640, 1 600, 1 290, 1 090, 1 010, 980, 780	0.87 (d, *J* 7, 3 H), 1.1—1.4 (m, 2 H), 1.56 (dd, *J* 2 and 11, 1 H), 1.98 (dd, *J* 6 and 8, 1 H), 2.5—3.1 (m, 1 H), 3.12 (dd, *J* 8 and 11, 1 H), 7.1—7.6 (m, 3 H), and 7.8—8.1 (m, 1 H)
(6d)	144—146	C; 85.45 H; 5.6	85.20 5.72	3 370, 1 650, 1 600, 1 450, 1 290, 1 100, 1 020, 755	1.1 (m, 1 H), 1.4 (m, 1 H), 2.07 (dd, *J* 6 and 9, 1 H), 3.20 and 3.64 (ABq, *J* 12, 2 H), and 7.1—8.0 (m, 14 H)
(6e)	110.5—111	C; 79.35 H; 7.55	79.31 7.49	3 450, 1 650, 1 600, 1 350, 1 060, 990, 750	0.80 and 1.17 (ABq, *J* 6, 2 H), 0.82 (s, 3 H), 1.30 (s, 3 H), 1.34 (s, 3 H), 1.81 and 2.59 (ABq, *J* 11, 2 H), 2.44 (mobile, 1 H), 7.1—7.5 (m, 3 H), and 7.8—8.1 (m, 1 H)
(6f)	140.5—141	C; 81.1 H; 8.0	80.81 7.85	3 460, 1 650, 1 600, 1 050, 990, 750, 730	0.73 and 1.07 (ABq, *J* 5, 2 H), 1.24 (s, 3 H), 0.6—2.3 (m, 10 H), 1.89 and 2.40 (ABq, *J* 5, 2 H), 7.1—7.4 (m, 3 H), and 7.7—8.0 (m, 1 H)
(6g-*ex*)	78—78.5	C; 78.85 H; 7.3	78.92 7.06	3 450, 1 625, 1 595, 1 345, 980, 750	0.75 and 1.14 (ABq, *J* 6, 2 H), 1.22 (s, 3 H), 1.23 (d, *J* 5, 3 H), 2.1—2.6 (m, 3 H), 7.0—7.5 (m, 3 H), and 7.6—7.9 (m, 1 H)
(6g-*en*)	134—136	C; 78.8 H; 7.25	78.92 7.06	3 400, 1 640, 1 595, 1 340, 1 250, 1 020, 980, 760	0.78 (d, *J* 7, 3 H), 1.26 (s, 3 H), 0.6—1.1 (m, 2 H), 2.1—3.0 (m, 3 H), 7.0—7.4 (m, 3 H), and 7.6—7.8 (m, 1 H)

Table 6. Physical properties of the unsaturated keto alcohols (7)

Unsaturated keto alcohol	M.p. (°C)	Elemental analysis Found (%)	Required (%)	I.r. $\nu_{max.}$ (cm^{-1}) (KBr)	^1H N.m.r. δ(p.p.m.) ($CDCl_3$) (*J* in Hz)
(7a)	87.5—88	C; 78.9 H; 7.05	78.92 7.06	3 400, 1 655, 1 600, 1 330, 1 050, 910, 730	1.15 (d, *J* 7, 2 H), 1.80 (s, 3 H), 1.93 and 2.90 (ABq, *J* 15, 2 H), 3.0 (mobile, 1 H), 4.95 (br, 2 H), 5.20 (s, 1 H), 2.13 (t, *J* 7, 1 H), 7.2—8.0 (m, 4 H)
(7b)	122—123	C; 80.3 H; 7.5	80.56 7.51	3 420, 1 660, 1 600, 1 400, 1 320, 1 300, 1 100, 1 060, 800, 740	1.05 (m, 2 H), 1.2—1.6 (m, 4 H), 1.8—2.2 (m, 5 H), 1.83 and 2.82 (ABq, *J* 14, 2 H), 4.00 (mobile, 1 H), 5.05 (s, 1 H), 5.62 (br, 1 H), and 7.2—8.0 (m, 4 H)
(7c)	109—110	C; 78.4 H; 6.45	78.48 6.59	3 370, 1 650, 1 600, 1 350, 1 060, 1 040, 810, 760	0.9—1.3 (m, 2 H), 1.9—2.3 (m, 1 H), 2.12 (dd, *J* 5 and 8, 1 H), 2.90 (dd, *J* 8 and 15, 1 H), 4.9—5.4 (m, 3 H), 5.4—6.2 (m, 1 H), and 7.1—7.9 (m, 4 H)
(7e)	Oil	C; 79.3 H; 7.75	79.31 7.49	3 400, 1 640, 1 600, 1 045, 890, 730	0.84 and 1.25 (ABq, *J* 5, 2 H), 1.47 (s, 3 H), 1.80 (s, 3 H), 2.06 and 3.01 (ABq, *J* 16, 2 H), 4.85 (s, 2 H), 5.07 (s, 1 H), and 7.0—7.9 (m, 4 H)
(7f)	Oil	C; 80.75 H; 7.75	80.81 7.85	3 350, 1 650, 1 600, 1 350, 1 050	0.70 and 1.16 (ABq, *J* 5, 2 H), 1.39 (s, 3 H), 0.7—2.9 (m, 10 H), 4.95 (br, s, 1 H), 5.59 (s, 1 H), and 7.0—7.8 (m, 4 H)
(7g)	Oil	C; 78.75 H; 7.3	78.92 7.06	3 350, 1 660, 1 600, 1 350, 980	0.86 and 1.21 (ABq, *J* 5, 2 H), 1.53 (s, 3 H), 1.8—2.3 (m, 2 H), 2.9—3.2 (m, 1 H), 4.9—5.3 (m, 2 H), 5.5—5.8 (m, 1 H), and 7.1—8.0 (m, 4 H)

7.7—7.9 (m, 1 H) (Found: C, 74.85; H, 7.35. $C_{17}H_{20}O_3$ requires C, 74.97; H, 7.40%).

Photochemical Reaction of the Keto Ester (11a).—A solution of the keto ester (11a) (100 mg) in benzene–Bu^{t}OH (1 : 1) (30 ml) was irradiated under nitrogen for 2 h. After removal of the solvent, products were separated by column chromatography to give the cyclobutanol (12a) (80 mg, 80%) and the unsaturated ester (13a) (16 mg, 16%). Similarly irradiation of (11a) (100 mg) in methanol (30 ml) gave the same products (12a) (72 mg, 72%) and (13a) (11 mg, 11%). 4α-*Acetoxy*-8bα-*hydroxy*-1,1-*dimethyl*-1,2,3,3a,4,8b-*hexahydrocyclopropa*[b]*cyclobuta*[c]*naphthalene* (12a), m.p. 136—137 °C; $\nu_{max.}$ (KBr) 3 500, 2 940, 1 715, 1 260, 1 100, 1 070, and 755 cm^{-1}; δ($CDCl_3$) 0.65 (m, 2 H), 0.80 (s, 3 H), 1.26 (s, 3 H), 1.55 and 2.50 (ABq, *J* 10 Hz, 2 H), 1.9 (m, 1 H), 2.08 (s, OCOMe), 6.19 (d, *J* 7 Hz, 1 H), and 7.1—7.3 (m, 4 H) (Found: C, 74.7; H, 7.25. $C_{17}H_{20}O_3$ requires C, 74.97; H, 7.40%). 7β-*Acetoxy*-1a-(2-*methylprop*-2-*enyl*)-1a,2,7,7a-*tetrahydro*-1H-*cyclopropa*[b]*naphthalen*-2β-*ol* (13a), colourless oil; $\nu_{max.}$ (CCl_4) 3 400, 1 730, and 1 600 cm^{-1}; δ(CCl_4) 0.3—0.5 (m, 2 H), 1.80 (C=CMe), 2.16 (s, OCOMe), 4.80 (br s, 1 H), 4.90 (br s,

Table 7. Physical properties of the bicyclic diketones (16) and the alkylidene phthalides (17)

Compound	M.p. (°C)	Elemental analysis Found (%)	Required (%)	I.r. $\nu_{max.}$ (cm^{-1}) (KBr)	^1H N.m.r. δ(p.p.m.) ($CDCl_3$) (*J* in Hz)
(16e)	53—54	C; 79.45 H; 7.65	79.31 7.49	1 680, 1 660, 1 595, 1 180, 880, 750	0.98 (s, 3 H), 1.07 (s, 3 H), 1.23 (s, 3 H), 1.6—2.4 (m, 4 H), 3.4 (m, 1 H), 7.6—7.7 (m, 2 H), and 8.0—8.2 (m, 2 H)
(16f)	Oil	C; 80.95 H; 8.0	80.81 7.85	1 680, 1 660, 1 590, 1 450, 1 260, 880	1.24 (s, 3 H), 0.9—1.8 (m, 12 H), 2.1—2.7 (m, 2 H), 3.1—3.4 (m, 1 H), 7.4—7.6 (m, 2 H), and 7.7—8.1 (m, 2 H)
(16h)	192—193	C; 85.05 H; 6.0	85.21 6.05	1 695, 1 665, 1 595, 1 450, 1 295, 1 275, 760, and 715	1.18 (s, 3 H), 2.28 (d, *J* 15, 1 H), 2.60 (dd, *J* 8 and 15, 1 H), 2.88 (dd, *J* 4 and 16, 1 H), 3.42 (dd, *J* 10 and 16, 1 H), 3.62 (m, 1 H), 6.8—7.3 (m, 13 H), and 7.5—7.7 (m, 1 H)
(17e)	38—39	C; 79.55 H; 7.75	79.31 7.49	1 770, 1 690, 1 480, 1 060, 985, 760, 690	1.13 (s, 6 H), 1.77 (s, 3 H), 2.51 (d, *J* 8, 2 H), 4.70 (s, 2 H), 5.32 (t, *J* 8, 1 H), and 7.3—7.8 (m, 4 H)
(17f)	88—88.5	C; 80.75 H; 7.65	80.81 7.85	1 775, 1 595, 1 280, 980, 910, 770	1.1—1.8 (m, 10 H), 2.50 (d, *J* 8, 2 H), 4.75 (br s, 1 H), 4.95 (br, s, 1 H), 5.48 (t, *J* 8, 1 H), 7.3—7.6 (m, 3 H), and 7.7—7.9 (m, 1 H)

1 H), 4.90 (br s, 1 H), 6.13 (d, *J* 4 Hz, 1 H), 1.50 (m, 1 H), 1.85 and 2.83 (ABq, *J* 14 Hz, 2 H), and 7.0—7.4 (m, 4 H) (Found: C, 74.75; H, 7.45. $C_{17}H_{20}O_3$ requires C, 74.97; H, 7.40%).

A solution of the cyclobutanol (12a) (50 mg) in benzene (30 ml) or benzene–Bu^tOH (1 : 1) (30 ml) was irradiated for 10 h, but the cyclobutanol (12a) was recovered quantitatively in both solvents.

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