

Mechanism of Photorearrangement of 6-Hydroxybicyclo[3.3.1]nona-3,7-dien-2-ones

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The 6-hydroxybicyclo[3.3.1]nona-3,7-dien-2-ones (1) and (2) have been synthesised and irradiated. The alcohol (2) gave only isomeric 9-hydroxy-4,8,9-trimethyl-6-phenylbicyclo[3.3.1]nona-3,7-dien-2-one (6) by 1,3-rearrangement, but (1) gave, in addition to compound (7) formed by similar 1,3-rearrangement, products of dehydration and of further rearrangement. The origin of each product is established and the observed rearrangements are contrasted with the different rearrangements found with bicyclo[3.3.1]nona-3,7-diene-2,6-diones. The differences are rationalised.

WE have established¹ that bicyclo[3.3.1]nona-3,7-diene-2,6-diones undergo both 1,2- and 1,3-rearrangement from an excited triplet state to give both triasteranediones and bicyclo[3.3.1]nona-3,7-diene-2,9-diones. In contrast, 9-thiabicyclo[3.3.1]nona-3,7-diene-2,6-dione only undergoes² 1,3-rearrangement. The analysis of the influence of structural changes upon the photochemical behaviour of $\beta\gamma$ -unsaturated ketones has recently received much attention³ but explanations for the observed patterns of photoreactivity are still largely lacking. Schuster, Underwood, and Knudsen⁴ suggested that different spin density distributions in the excited singlet and triplet states lead to differing initial bonding interactions and hence to different products. However, enough exceptions are known from our own^{1,2} and other⁵ studies that this generalisation seems inadequate. Houk, Northington, and Duke⁶ proposed that the observed photochemistry was controlled by the nature of the excited singlet and triplet states. Typic-

ally, the lowest excited singlet state, an $n-\pi^*$ state, undergoes 1,3-rearrangement, but the lowest triplet state may have either $n-\pi^*$ character and then undergo reactions similar to an $n-\pi^*$ singlet state, or more usually the triplet has $\pi-\pi^*$ character and preferentially undergoes 1,2-rearrangement. This analysis suggests that triplet reactivity will depend critically upon the nature of the lowest triplet state. We have now further explored this view by examining the photochemistry of some 6-hydroxybicyclo[3.3.1]nona-3,7-dien-2-ones. These ketones were chosen in the anticipation that, as with bicyclo[3.3.1]nona-3,7-diene-2,6-diones, spin-orbit coupling between the singlet $n-\pi^*$ and triplet $\pi-\pi^*$ states would lead to high intersystem crossing efficiency but the interaction between the $\beta\gamma$ -double bond and carbonyl group would be substantially modified. This modification might be expected to lead to different photochemistry from that observed with the dione.

Ketones (1) and (2) were obtained by Grignard addition of methylmagnesium iodide to ketones (3) and

¹ P. A. Knott and J. M. Mellor, *J.C.S. Perkin I*, 1972, 1030; C. N. Lam and J. M. Mellor, *J.C.S. Perkin II*, 1974, 865.

² J. M. Mellor and C. F. Webb, *J.C.S. Perkin I*, 1972, 211.

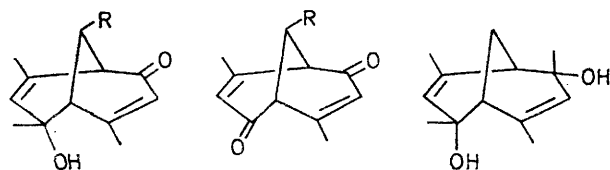
³ P. S. Engel, M. A. Schexnayder, H. Ziffer, and J. I. Seeman, *J. Amer. Chem. Soc.*, 1974, **96**, 924; S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, 1973, **73**, 531; T. R. Darling, J. Pouliquen, and N. J. Turro, *J. Amer. Chem. Soc.*, 1974, **96**, 1247.

⁴ D. I. Schuster, G. R. Underwood, and T. P. Knudsen, *J. Amer. Chem. Soc.*, 1971, **93**, 4304.

⁵ J. R. Williams and G. M. Sarkisian, *Chem. Comm.*, 1971, 1564; P. S. Engel and M. A. Schexnayder, *J. Amer. Chem. Soc.*, 1972, **94**, 9252.

⁶ K. N. Houk, D. J. Northington, and R. E. Duke, *J. Amer. Chem. Soc.*, 1972, **94**, 6233.

(4)⁷ respectively. With an excess of Grignard reagent, (3) gives a diol, shown by n.m.r. to have symmetry elements, but (4) only gives the keto-alcohol (2). The



symmetrical diol could be obtained by either di-*exo*- or di-*endo*-addition. In view of the complete lack of reactivity of (2) to further attack, and the known preference for *exo*-attack in related systems,⁸ we conclude that *exo*-attack upon (3) and (4) leads to (1) and (2) respectively and further attack upon (1) gives the di-*endo*-diol (5). Spectral data for (1) and (2) accord with the assigned structures.

Irradiation of (2) in benzene through Pyrex led to the formation of a single photoproduct. Mass spectroscopy showed this to be isomeric with (2) and observation of two vinyl resonances in the n.m.r. spectrum suggested a bicyclic structure. Further spectra data [λ_{\max} 247 (ϵ 9850) and 327 nm (ϵ 327); ν_{\max} 3600 and 1660 cm^{-1}] showed the retention of the chromophore of an $\alpha\beta$ -unsaturated ketone and the presence of a hydroxy-group. Hence the photoproduct must be the product (6) of 1,3-rearrangement. No change in stereochemistry is anticipated associated with either the hydroxy- or phenyl groups. This is substantiated by observation of the 4-methyl resonance at τ 9.00 as a result of anisotropic shielding by the *endo*-phenyl substituent and by lanthanide shift studies.

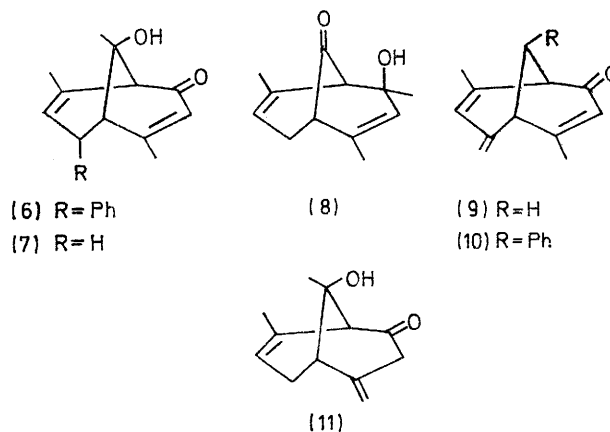
Irradiation of (1) under similar conditions gave four photoproducts. The product initially formed as the major product was (7), identified by spectroscopic analysis as described for the analogous product (6). A further minor product isolated by chromatography was shown to be isomeric by mass spectroscopy, and was shown by further spectral data to be bicyclic (vinyl resonances at τ 4.28 and 4.64) with a non-conjugated carbonyl chromophore (ν_{\max} 1700 cm^{-1}). Decoupling experiments established the relationship between vinyl and methyl resonances and the use of shift reagents revealed both further coupling relationships and the *exo*-orientation of the hydroxy-group. Hence the minor alcohol obtained by photorearrangement must be (8). Further irradiation of (1) gave, in addition to (7) and (8), another isomeric alcohol and a ketone formed by dehydration. The ketone was readily identified as (9) by spectroscopic analysis and this assignment was confirmed by an independent synthesis. The structure of the remaining alcohol was mainly determined by n.m.r. analysis. The

⁷ P. A. Knott and J. M. Mellor, *J. Chem. Soc. (C)*, 1971, 670.
⁸ J. K. MacLeod and R. J. Wells, *J. Amer. Chem. Soc.*, 1973, **95**, 2387.

⁹ C. N. Lam and J. M. Mellor, *J.C.S. Perkin I*, 1975, 80.

presence of an exocyclic methylene group was indicated by resonances at τ 5.05, in addition to a vinyl resonance at τ 4.65, and by the observation of only two methyl resonances at τ 8.35 and 8.61. Support for the assigned structure (11) was afforded by i.r. (ν_{\max} 1710 and 910 cm^{-1}) and by decoupling experiments which established allylic coupling between exocyclic protons and 3-H at τ 6.66 and 5-H at 7.56, and coupling between the protons of the 8-methyl group and 6-H.

To establish the origin of the various products, each was independently irradiated. The keto-alcohol (8)



was recovered unchanged after prolonged irradiation and could be considered to be photochemically inert. Irradiation of the keto-alcohol (7) showed (see Table I)

TABLE I
Distribution of photoproducts from irradiation of (7) in benzene

Period of irradiation ^a (h)	Products (%) ^b				
	(1)	(7)	(8)	(9)	(11)
1	14.1	52.4	3.0	4.3	26.2
1.5	11.7	45.9	5.2	7.8	30.4
3	9.2	27.6	5.5	8.3	49.6
5	6.1	19.2	6.8	10.2	57.7

^a Irradiation through Pyrex using a 'merry-go-round'.
^b G.l.c. analysis on 2% QF-1 Chromosorb G AW-DMCS.

that (1) and (7) photoequilibrate. Comparison with the product distribution obtained by irradiation of (1) shows (see Table 2) that (11) is obtained as a photoproduct of (7) and the product of dehydration (9) appears to be formed more efficiently from (7) than from (1). This last point is surprising and led us to consider some aspects of the dehydration of the keto-alcohols. Although (1) and (2) undergo straightforward thermal dehydration to give (9) and (10) respectively, (6) also undergoes ready dehydration⁹ to give, *inter alia*, (12), which is known¹⁰ to photoisomerise very readily to (10). Hence photodehydration of (1) could give (9) directly, or photodehydration of (7) might give (13)

¹⁰ K. G. Hancock and R. O. Grider, *J.C.S. Chem. Comm.*, 1972, 580; G. Marsh, D. R. Kearns, and K. Schaffner, *J. Amer. Chem. Soc.*, 1971, **93**, 3129.

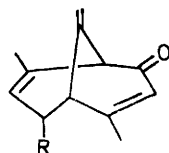
TABLE 2
Distribution of photoproducts from irradiation of (1)
in different solvents

Solvent	Period of irradiation ^a (min)	Products (%) ^b				
		(1)	(7)	(8)	(9)	(11)
C ₆ H ₆	15	58.1	35.5		1.1	5.3
	30	35.2	50.1	1.1	1.6	12.0
	45	22.3	54.9	1.4	2.8	18.6
	60	13.4	55.1	1.4	3.9	26.2
Et ₂ O	15	77.3	17.5		1.0	4.2
	30	59.8	26.6	4.4	1.6	7.6
	45	44.2	36.6	5.2	1.8	12.2
	60	32.9	42.4	5.2	2.4	17.1
MeCN	15	89.5	9.4		0.4	0.7
	30	73.8	20.2	3.6	0.6	1.8
	45	60.0	32.0	4.7	0.7	2.6
	60	46.7	41.0	6.4	1.3	4.6
MeOH	15	95.7	3.8		0.5	
	30	90.2	7.1	1.3	0.8	0.6
	45	83.0	12.0	1.9	1.1	2.0
	60	75.2	16.9	2.1	1.1	4.7

^a Irradiation through Pyrex using a 'merry-go-round'.

^b G.l.c. analysis.

which would photorearrange efficiently to (9). Our results do not permit an unequivocal conclusion but we strongly favour formation of (9) *via* (13).

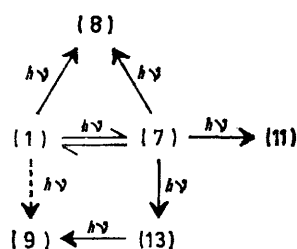


(12) R=Ph

(13) R=H

Neither can the origin of (8) be deduced unequivocally. It is formed as a minor product in irradiation of both (1) and (7) and could be formed from either by 1,3-rearrangement. The probable sequence of phototransformations is shown in the Scheme.

The Scheme implies the possibility that (1) can undergo two different 1,3-rearrangements leading to (7)



SCHEME

and (8). Further 1,3-rearrangement occurs to the exclusion of 1,2-rearrangement. In order to account for these observations we have studied further the mechanism of photorearrangement of (1). We do not discuss here the photochemical mechanism of further transformation of (7) but note the surprisingly efficient

deconjugation to give (11). The participation of the *syn*-hydroxy-group in hydrogen abstraction seems probable.

The excited state responsible for photorearrangement of (1) was established by photosensitisation and quenching studies. Irradiation of (1) in acetone gave similar products (see Table 3) to those obtained on direct irradiation. Solvent studies showed that photorearrangement was slightly inhibited by increased solvent polarity. Again (2) was cleanly photoisomerised to (6) in acetone. Using xanthone, triphenylene, or Michler's ketone as photosensitiser in benzene, products were only obtained efficiently from (1) with xanthone as photosensitiser.

TABLE 3

Distribution of photoproducts from photosensitisation
of (1) in benzene

Photosensitiser	Period of irradiation (min)	Products (%)				
		(1)	(7)	(8)	(9)	(11)
Xanthone ^a	15	58.3	34.9		0.8	6.0
	30	33.7	53.7		1.2	11.4
Triphenylene ^b	15	89.6	8.9		1.5	
	30	77.2	20.6		1.8	0.4
Michler's ketone ^c	15	99.0	1.0			
	30	98.8	1.2			
Acetone ^d	15	83.3	12.3		0.5	3.9
	30	71.0	21.0	0.8	0.8	6.4
	45	55.3	32.6	0.8	0.8	10.5
	60	39.7	42.0	1.8	1.4	15.1

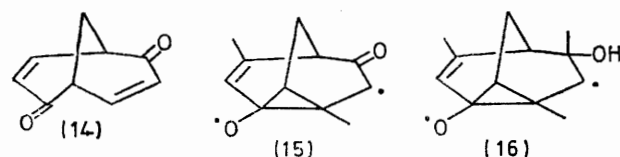
^a >99% light absorbed by xanthone. ^b >90% light absorbed by triphenylene. ^c >99% light absorbed by Michler's ketone. ^d In the absence of benzene, >99% of light absorbed by acetone.

Quenching studies with *trans*-penta-1,3-diene established a linear Stern-Volmer plot for formation of (7) with a slope of 16 l mol⁻¹. With an assumed value for k_q (10¹⁰ l mol⁻¹ s⁻¹) an effective triplet lifetime of 1.6 ns is indicated. A similar result is obtained in the quenching of the formation of (6) from (2). The quantum yields for formation of the minor products were too low to permit meaningful Stern-Volmer plots to be made. Both (1) and (2) exhibited phosphorescence in an ether-isopentane glass at 77° which was characterised by λ_{max} 447 nm showing a band progression of 1150 cm⁻¹ for (2) and 1520 cm⁻¹ for (1) with emission lifetimes of 15.4 ms for (2) and 13.2 ms for (1).

The photosensitisation and quenching studies establish that (6) and (7) are triplet-derived. As with bicyclo[3.3.1]nona-3,7-diene-2,6-diones,¹ reaction from the first excited singlet state is too inefficient to compete with the highly efficient intersystem crossing characteristic of an $\alpha\beta$ -unsaturated ketone. The triplet energy level in (1) lies between 66.6 kcal mol⁻¹ (E_T triphenylene) and 74.2 kcal mol⁻¹ (E_T xanthone). The lifetime studies indicate, by comparison with other ketones,¹⁰ that this lowest triplet state has substantial $n-\pi^*$ character, and (1) and (2) are not different in this respect from bicyclo[3.3.1]nona-3,7-diene-2,6-diones.¹

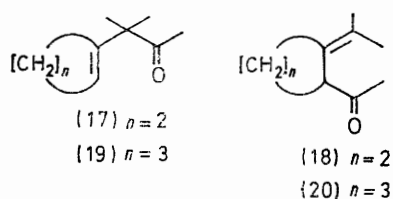
The pattern of photoreaction of alcohols (1) and (2) shows interesting differences from that of diketones

(3), (4), and (14). The diketones undergo both 1,2- and 1,3-rearrangement from a triplet state, but with (1) and (2) only 1,3-rearrangement is observed. This



suggests that in the lowest triplet state the bonding interaction between the carbonyl group and the β -carbon, which leads to 1,2-rearrangement, is less well developed in the alcohols relative to the diones, or alternatively that the bonding interaction between carbonyl group and γ -carbon, which leads to 1,3-rearrangement is better developed in the alcohols. The observed rearrangements may be explained on this basis. 1,2-Rearrangement proceeds by an oxa-di- π -methane route³ and requires β -bonding to give a species of type (15) or (16). Of these, (15) is particularly stabilised and hence 1,2-rearrangement with diones (3) or (4) is expected. 1,3-Rearrangement occurs with a development of diradical character by stretching of the α -bond. Facility for 1,3-rearrangement will therefore be influenced by the degree of stabilisation of a radical centre as the α -bond stretches. In this respect 1,3-rearrangement will be favoured in (1) and (2) by better allylic stabilisation, and in 9-thiabicyclo[3,3,1]nona-3,7-diene-2,6-dione by stabilisation by sulphur.

Observation of 1,3-rearrangement from the triplet state of a $\beta\gamma$ -unsaturated ketone is unusual but has a recent precedent: Engel and Schexnayder⁵ showed that (17) on irradiation in acetone gave some compound (18), and similarly (19) gave (20) inefficiently. The nature of the triplet state may, however, afford a distinction between (17) and (19), and alcohols (1) and (2) and ketones (3) and (4). The nature of the lowest triplet state in (17) and (19) has not been defined but is



probably π - π^* , whereas phosphorescence studies suggest that (1) and (2), and (3) and (4), may have a lowest triplet state with substantial n - π^* character.

In conclusion, the nature of the photorearrangements observed with diones (3) and (4) are different from those of alcohols (1) and (2) and these differences are adequately explained by analysis of stabilising features of species along the reaction co-ordinates.

EXPERIMENTAL

I.r. spectra were measured for chloroform solutions with a Unicam SP 200 spectrophotometer. N.m.r. spectra

were measured for deuteriochloroform solutions with a Varian HA 100 spectrometer. U.v. spectra were measured for solutions in ethanol or n-hexane with a Unicam SP 800 spectrophotometer. Mass spectra were measured with an A.E.I. MS12 spectrometer. Photochemical studies were conducted, unless otherwise stated, by irradiation through Pyrex under nitrogen with a 125 W medium pressure mercury lamp. G.l.c. analyses were carried out using a 4 m column of 2% QF-1 on Chromosorb GAW-DMCS 100–200 mesh.

6-Hydroxy-4,6,8-trimethylbicyclo[3.3.1]nona-3,7-dien-2-one (1).—An ethereal solution of dione (3) (1.8 g) was heated under reflux with methylmagnesium iodide [from magnesium (0.4 g)] for 2 h. The solution was added with stirring to 0.5N-hydrochloric acid, the products were extracted with ether, and the ether layer was washed successively with sodium hydrogen carbonate and sodium hydrogen sulphite solutions and with water. Removal of the solvent from the dried ethereal layer and chromatography over silica gel afforded the following fractions: in 40% ether–light petroleum, unchanged dione (3) (0.51 g); in 60% ether–light petroleum the *dienone* (1) (0.62 g), m.p. 112–113° [from ethyl acetate–light petroleum (b.p. 60–80°)] (Found: C, 75.0; H, 8.5. $C_{12}H_{16}O_2$ requires C, 74.95; H, 8.4%); ν_{\max} 3630, 3600, and 1670 cm^{-1} ; λ_{\max} 248.3 (ϵ 10,460) and 335 nm (307); τ 4.27 (1H, m, 3-H), 4.72 (1H, m, 7-H), 6.73 (2H, m, 1- and 5-H), 7.80 (2H, q, $J_{1,9} = J_{5,9}$ 3.3 Hz, 9-H), 7.90 (3H, d, J 1.4 Hz, 4-Me), 8.30 (3H, d, J 1.4 Hz, 8-Me), and 8.51 (3H, s, 6-Me); M^+ 192; and finally 2,4,6,8-tetramethylbicyclo[3.3.1]nona-3,7-diene-2,6-diol (5) (0.1 g), m.p. 156–157° (from ethyl acetate) (Found: C, 74.85; H, 9.45. $C_{18}H_{20}O_2$ requires C, 74.95; H, 9.7%); ν_{\max} 3600 cm^{-1} ; λ_{\max} 243 nm (ϵ 126); M^+ $-H_2O$ 190; τ 4.50 (2H, m, 3- and 7-H), 7.80 (2H, t, $J_{1,5} J_{5,9}$ 3.4 Hz, 1- and 5-H), 7.95 (6H, d, J 1.5 Hz, 4- and 8-Me), 8.14 (2H, t, $J_{1,5} = J_{5,9}$ 3.4 Hz, 9-H), and 8.56 (6H, s, 2- and 6-Me).

6-Hydroxy-4,6,8-trimethyl-9-phenylbicyclo[3.3.1]nona-3,7-dien-2-one (2).—An ethereal solution of the dione (4) (10 g) was heated under reflux with methylmagnesium iodide [from magnesium (9.6 g)] for 24 h. Work-up gave a yellow solid (10.5 g) and recrystallisation from chloroform–light petroleum (b.p. 60–80°) gave the *dienone* (2), m.p. 119–120° (Found: C, 80.2; H, 7.4. $C_{18}H_{20}O_2$ requires C, 80.4; H, 7.5%); ν_{\max} 3650, 3500, and 1670 cm^{-1} ; λ_{\max} 251 (ϵ 6860) and 337 nm (318); M^+ 268; τ 2.7–3.0 (5H, m, 9- C_6H_5), 4.25 (1H, m, 3-H), 4.64 (1H, m, 7-H), 6.45 (1H, t, $J_{1,9} = J_{5,9}$ 2.2 Hz, 9-H), 6.96 (1H, m, 1- or 5-H), 7.07 (1H, m, 1- or 5-H), 7.99 (3H, d, J 1.3 Hz, 4-Me), 8.21 (3H, d, J 1.4 Hz, 8-Me), and 8.39 (3H, s, 6-Me).

Irradiation of the Dienone (2).—The ketone (2) (3.4 g) in benzene (300 ml) was irradiated for 4 h. Removal of the solvent under reduced pressure and chromatography of the residue over silica gel (150 g) afforded the following fractions. 30% Ether–benzene eluted unchanged starting material (0.5 g) and 40% ether–benzene gave 9-hydroxy-4,8,9-trimethyl-6-phenylbicyclo[3.3.1]nona-3,7-dien-2-one (6) (2.3 g), m.p. 165–166° [from chloroform–light petroleum (b.p. 60–80°)] (Found: C, 80.3; H, 7.5. $C_{18}H_{20}O_2$ requires C, 80.4; H, 7.5%); ν_{\max} 3600, 3400, and 1660 cm^{-1} ; λ_{\max} 247 (ϵ 9850) and 327 nm (327); M^+ 268; τ 2.7–3.0 (5H, m, 6- C_6H_5), 4.14 (1H, m, 3-H), 4.53 (1H, m, 7-H), 6.13 (1H, m, 6-H), 7.32 (1H, s, 1-H), 7.35 (1H, d, $J_{5,6}$ 6.6 Hz, 5-H), 8.17 (3H, q, J 1.6 and 2.5 Hz, 8-Me), 8.54 (3H, s, 9-Me), and 9.00 (3H, d, J 1.6 Hz, 4-Me). Decoupling

experiments established the relationship between resonances at τ 4.14 and 9.00, at 4.53 and 8.17, and at 6.13 and 8.17. On addition of a shift reagent, 3-H experienced substantially larger induced shifts than 7-H.

Irradiation of the Dienone (1).—The ketone (1) (4 g) in benzene (250 ml) was irradiated for 12 h. Removal of the solvent under reduced pressure gave partially crystalline material which on chromatography on silica gel (200 g) afforded the following fractions. 5% Ether-benzene eluted 4-hydroxy-2,4,6-trimethylbicyclo[3.3.1]nona-2,6-dien-9-one (8) (150 mg) as an oil, ν_{\max} 3500 and 1700 cm^{-1} ; λ_{\max} 229 (ϵ 6110) and 315 nm (177); M^+ 192; τ 4.28 (1H, m, 3-H), 4.64 (1H, m, 7-H), 7.4–8.4 (4H, m, 1-, 5-, and 8-H), 8.07 (3H, d, J 1.5 Hz, 2-Me), 8.42 (3H, m, 6-Me), and 8.65 (3H, s, 4-Me). Decoupling experiments established the relationship between resonances at τ 4.28 and 8.07 and at 4.64 and 8.42. Addition of $\text{Eu}(\text{fod})_3$ revealed $J_{1,8}$ 4.4 Hz and showed substantial shifts for the resonances of 3-H, 4-Me and *exo*-8-H; 40% ether-benzene afforded unchanged starting material (2.2 g), and ether eluted 9-hydroxy-4,8,9-trimethylbicyclo[3.3.1]nona-3,7-dien-2-one (7) (860 mg), m.p. 136° (from chloroform-n-pentane) (Found: C, 74.8; H, 8.4. $\text{C}_{12}\text{H}_{16}\text{O}_2$ requires C, 75.0; H, 8.4%); ν_{\max} 3570, 3390, and 1670 cm^{-1} ; λ_{\max} 237 (ϵ 9410) and 325 nm (488); M^+ 192; τ 4.27 (1H, m, 3-H), 4.80 (1H, m, 7-H), 7.44 (1H, m, 1-H), 7.82 (1H, m, 5-H), 7.67 (1H, m, 6-H), 7.88 (1H, m, 6-H), 8.08 (3H, d, J 1.2 Hz, 4-Me), 8.38 (3H, d, J 1.6 Hz, 8-Me), and 8.75 (3H, s, 9-Me).

In a further experiment monitored by g.l.c., the ketone (1) (350 mg) in benzene (250 ml) was irradiated for 40 h and the crude reaction mixture was separated by preparative t.l.c. In addition to (7) and (8) and starting material, two other products were isolated. The less polar com-

ponent was ketone (9), identified by comparison with an authentic sample.¹ The further component, 9-hydroxy-8,9-dimethyl-4-methylenebicyclo[3.3.1]non-7-en-2-one (11), had ν_{\max} 1710 and 910 cm^{-1} ; λ_{\max} 300 nm (ϵ ca. 50); M^+ 192; τ 4.65 (1H, m, 7-H), 5.05 (2H, m, 4-H), 6.66 (2H, m, 3-H), 7.56 (1H, t, J 6.5 Hz, 5-H), 7.81 (2H, m, 6-H), 7.84 (1H, m, 1-H), 8.35 (3H, m, 8-Me), and 8.61 (3H, s, 9-Me). Decoupling experiments established the relationship between resonances at τ 4.65 and 8.35, at 5.05 and 6.66, and at 5.05 and 7.56.

Photosensitisation, Quenching, and Solvent Studies with Alcohols (1), (7), and (8).—Irradiations were conducted in a 'merry-go-round' apparatus through Pyrex using a 400 W lamp and analysis was made by g.l.c. Results are shown in Tables 1–3. In sensitisation experiments compound (1) (10 mg) in benzene (15 ml) was irradiated in the presence of added xanthone (30 mg), triphenylene (30 mg), or Michler's ketone (100 mg) so that the photosensitiser absorbed >99, >90, and >99% of the light respectively. In solvent studies, the appropriate alcohol (10 mg) in solvent (15 ml) was irradiated.

In quenching experiments compound (1) (100 mg) was irradiated in benzene (10 ml) in the presence of added *trans*-penta-1,3-diene (0–0.4M). Using *n*-octadecane as internal standard for g.l.c. analysis, a linear Stern–Volmer plot was obtained. Similarly, n.m.r. analysis gave a linear Stern–Volmer plot in photorearrangement of (2)–(6).

Irradiation of alcohol (8) for 60 h gave no low molecular weight products. N.m.r. analysis after 12 h showed that (8) was unchanged.

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