The Photochemistry of 2-Acetoxynaphthalen-1(2*H*)-ones

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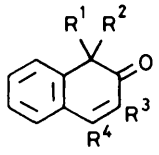
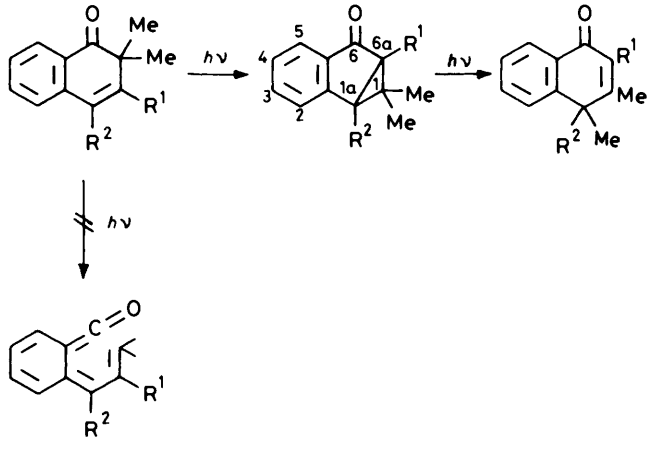
The photochemistry of the 2-acetoxynaphthalen-1(2*H*)-ones (**4**), (**13**), (**20**), and (**26**) has been examined. In each case there was rapid formation of a mixture of products, which arose either by homolytic dissociation of the C–OAc bond or by rearrangement involving acetoxy group migration. Two types of rearrangement were observed. The first involved 1,2-acetoxy group migration with C(2)–C(4) bond formation to give the dihydrocyclopropindenones (**7**), (**15**), (**22**), and (**28**). This reaction, which is stereospecific, yields the *endo*-6-acetoxy isomer only, and it is thought to proceed by a concerted non-ionic pathway. The second rearrangement, which is believed to have an ionic mechanism, resulted in formation of 3-acetoxynaphthols from naphthalenones (**4**) and (**26**), and 4-acetoxynaphthols from naphthalenones (**13**) and (**20**), in which the 3-position is substituted.

The photochemistry of cyclohex-2,4-dienones has been the subject of numerous studies[1,2a] since the pioneering work of Barton and Quinkert.[3] Despite this there has been only a small number of investigations of the effect of incorporating one of the π bonds of such a system in a benzene ring. The photochemistry of the three naphthalen-2(1*H*)-ones (**1**)—(**3**) has been exam-



(**1**) R^1 = Me, R^2 = OAc, R^3 = R^4 = H
(**2**) R^1 = R^2 = Me, R^3 = R^4 = H
(**3**) R^1 = R^2 = R^3 = R^4 = Me

ined,[4–7] and it was concluded that they behave like α,β-unsaturated ketones, since dimers were the only isolable products. On the other hand, in the most detailed study of such a system, Hart and Murray[7,8] have shown that 2,2-dimethylnaphthalen-1(2*H*)-ones undergo an oxadi-π-methane (ODPM) rearrangement to give initially tricyclic ketones, which then rearrange to naphthalen-1(4*H*)-ones (Scheme 1). No evidence



Scheme 1.

could be obtained for ring opening to a ketene, which is the common reaction of cyclohexa-2,4-dienones, and it was concluded that the products arose by a bond crossing mechanism. In a later study, 2,2,3,4-tetrachloronaphthalen-1(2*H*)-one was found to behave similarly, yielding an analogous tricyclic ketone, which was thought to arise in the same way.[9]

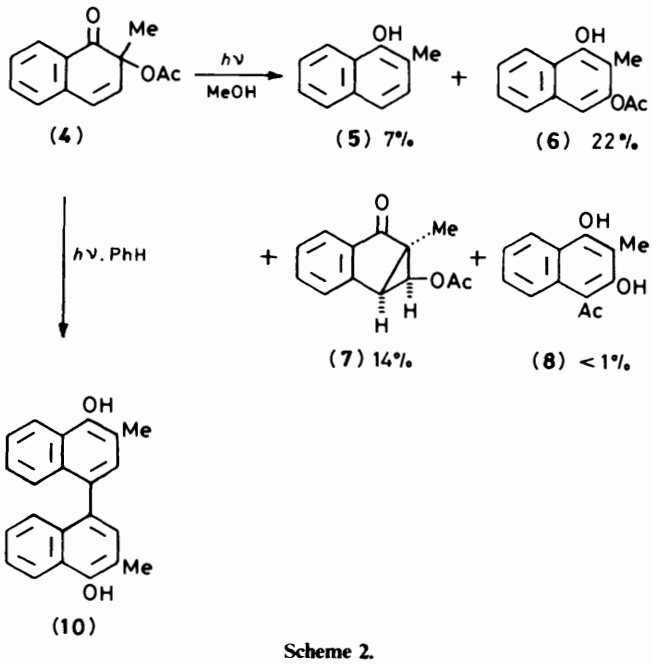
Since with highly alkylated cyclohexa-2,4-dienones ODPM-type rearrangement is increased relative to ketene formation,[2a] we decided to extend Hart's work to less substituted naphthalen-1(2*H*)-ones and 2-acetoxynaphthalen-1(2*H*)-ones in a search for ring-opened compounds. For our initial study we chose 2-acetoxy-2-methylnaphthalen-1(2*H*)-one (**4**), which is readily prepared by reaction of 2-methyl-1-naphthol (**5**) with lead tetra-acetate.[10]

Results and Discussion

Irradiation of the naphthalenone (**4**) in methanol through Pyrex led to the rapid formation of a mixture, which on silica gel chromatography yielded the naphthol (**5**), 3-acetoxy-2-methyl-1-naphthol (**6**), the dihydrocyclopropindenone (**7**), and 4-acetyl-2-methylnaphthalene-1,3-diol (**8**) (Scheme 2). When the reaction was monitored by g.l.c. it was found that yields of (**5**), (**6**), and (**7**), (see Scheme 2), were a maximum just before all the starting material had reacted. No products arising from C(1)–C(2) bond cleavage could be detected, and irradiation in the presence of cyclohexylamine, as a ketene trap, resulted in a similar product distribution. The structure of the naphthol (**6**) followed from the spectroscopic data, its conversion on acetylation into the known diacetate,[11] and its non-identity with 4-acetoxy-2-methyl-1-naphthol,[10] while the photorearrangement of (**6**) into the ketone (**8**) in a separate experiment confirmed its structural assignment, and indicated its derivation.

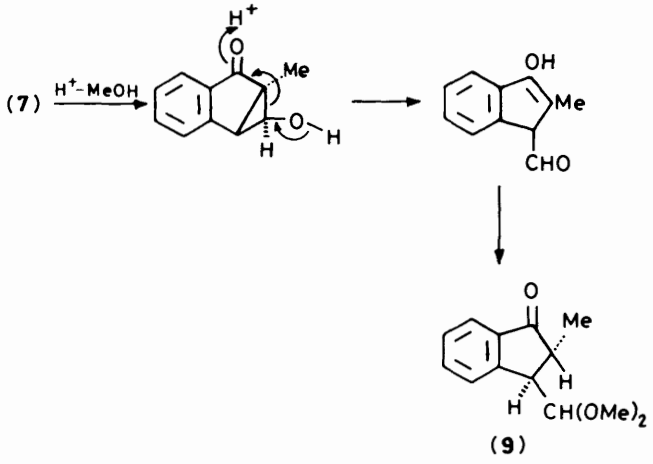
The stereochemistry assigned to the dihydrocyclopropindenone derivative (**7**) followed from the ^{1}H n.m.r. spectrum, while a careful g.l.c. and n.m.r. spectroscopic examination of the photolysis mixture showed that it was unaccompanied by the *exo*-isomer. The *cis*-disposition of the protons 1a-H and 1-H, which gave rise to doublets at δ 3.11† and 4.45 respectively, followed from the magnitude of the coupling

† Confirmation of the assignment followed from irradiation of the most downfield aromatic signal (*ortho* to C=O) which caused this doublet to sharpen ($W_{\frac{1}{2}}$ reduced by 0.3 Hz).



Scheme 2.

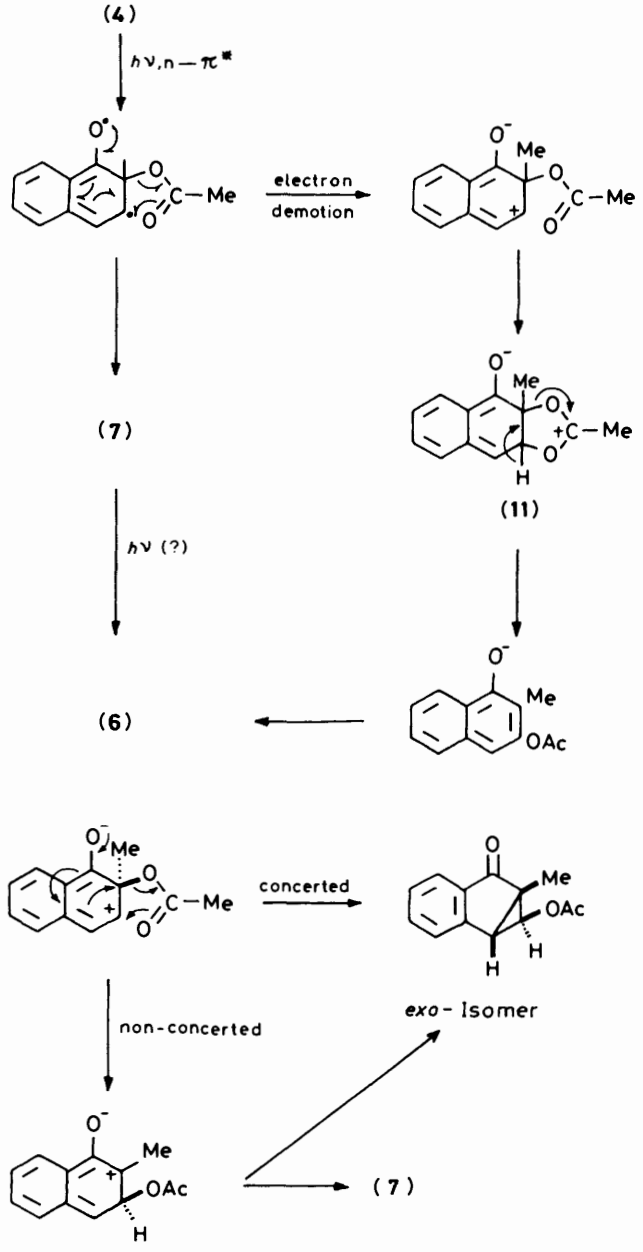
($J_{1,1a}$ 6.30 Hz).[12] The *endo*-configuration of the 1-acetoxy group is also readily assigned from the unusually high field position (δ 1.65) of its methyl signal, which requires that it lies above the benzene ring. Chemical degradation of the ketone (7) with sulphuric acid in methanol provided further



Scheme 3.

support for the proposed structure. It proceeded as expected[13] to give an indanone (Scheme 3) which, although only obtained in about 80% purity, could be assigned structure (**9**) from its spectra.*

The nature of the products obtained on irradiation of the naphthalenone (**4**) would suggest that both radical and ionic processes are operating, as in the case of 6-acetoxy-2,4,6-trimethylcyclohexa-2,4-dienone.[1] Homolysis of the C–O bond followed by hydrogen abstraction from solvent is no doubt the origin of the naphthol (**5**), and this is consistent with our finding that photolysis of (**4**) in benzene, where hydrogen abstraction



Scheme 4.

does not occur readily, resulted in formation of the 1,1′-binaphthyl (**10**), as the only isolable product.

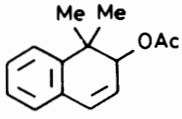
Of major interest were the mechanisms of formation of the products (**6**) and (**7**), in which acetoxy group migrations had occurred. As far as we are aware the latter type of rearrangement product has only been observed in the irradiation of 6-acetoxy-2,4,6-tri-t-butylcyclohexa-2,4-dienone,[15] while only a small number of cases of 1,2-acyloxy group migration with phenol formation has been found[15–17] since the photorearrangement of 6-acetoxy-2,4,6-trimethylcyclohexa-2,4-dienone to 3-acetoxy-2,4,6-trimethylphenol was reported in the first paper in this area.[1] For the same reasons as presented there, naphthol (**6**) cannot be arising by C–O bond homolysis followed by recombination,† and a mechanism analogous to

* The *trans* stereochemistry was tentatively assigned on the basis of a small vicinal coupling constant ($J_{2,3}$ 3.46).[14]

† The product which might be formed in such a process, 4-acetoxy-2-methyl-1-naphthol, could not be detected (g.l.c. and n.m.r.) in the irradiation mixture.

the one presented in that work is possibly operating here (Scheme 4). The fact that the phenol (**6**) was produced in methanol but not in benzene is in keeping with the proposal that an ionic process is involved in its formation. Relevant to this point, in the irradiations of two other naphthalen-1(2*H*)-ones (see later), where g.l.c. analysis of reactions in both methanol and benzene were carried out, there was also a very marked reduction in the yield in benzene of the phenolic product resulting from acetoxy group migration. The dihydrocyclopropindenone (**7**)* could be depicted as arising also from the acetoxonium ion (**11**); however, the electron displacements required, if concerted, would result in formation of the *exo*-isomer. On the other hand, a mixture of the two isomers might be expected from a stepwise ionic process, and thus we suggest that (**7**) is formed in a rearrangement occurring directly from the excited species, a process which would lead to the *endo*-isomer (Scheme 4).

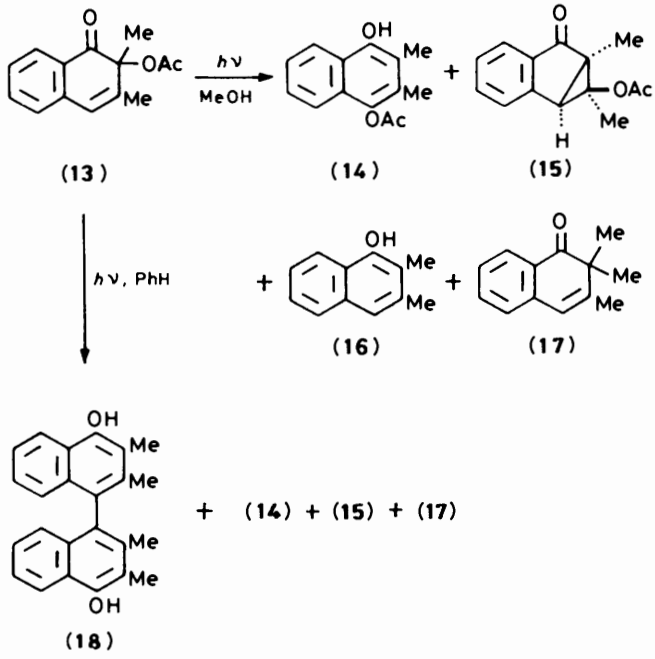
Two alternatives to the routes suggested above for the formation of compounds (**6**) and (**7**) were considered and examined briefly. The first concerned the possibility that the carbonyl group was not involved in the rearrangement producing the cyclopropane derivative (**7**), and was examined by the irradiation of 2-acetoxy-1,1-dimethyl-1,2-dihydronaphthalene (**12**). This compound was readily produced from the



(**12**)

known alcohol,[18] and was recovered unchanged after irradiations in methanol and benzene, either alone or with the triplet sensitiser, benzophenone. In the case of the phenol (**6**), the possibility of its formation from compound (**7**) by light-induced opening of the cyclopropane ring, a well-known reaction of the related bicyclo[3.1.0]hex-3-en-2-one system,[2b,19] required investigation. In fact, irradiation of the tricyclic ketone (**7**) did result in formation of the phenol (**6**); however, it was accompanied by the naphthalen-1(2*H*)-one (**4**) and the other two compounds (**5**) and (**8**), produced in the photolysis of (**4**). A g.l.c. study of the reaction showed that (**7**) was considerably less photolabile than the naphthalenone (**4**), and in view of the reversibility of the formation of (**7**) on irradiation of (**4**), we are unable at this stage to conclude whether there is a direct photochemical route from the cyclopropane derivative (**7**) to the phenol (**6**). Nevertheless, in view of the relative reactivities of (**4**) and (**7**), at the most only a small amount of (**6**) could be produced in this way on irradiation of (**4**) (see Scheme 4).

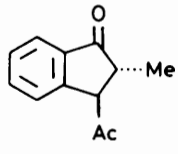
We have examined a number of other 2-acetoxynaphthalen-1(2*H*)-ones to determine the effect of substituents on their photochemistry. 2-Acetoxy-2,3-dimethylnaphthalen-1(2*H*)-one (**13**), produced by Wessely acetoxylation of 2,3-dimethyl-1-naphthol,[10] on irradiation in methanol (90% conversion) gave the phenol (**14**) and the dihydrocyclopropindenone (**15**) as the major products in yields of 42 and 24% respectively, together with small amounts of 2,3-dimethyl-1-naphthol (**16**) (5%) and the naphthalenone (**17**) (4%) (see Scheme 5). When the irradiation was conducted in benzene, the yield of the cyclopropane derivative (**15**) was only slightly lower (18%), whereas 4-acetoxy-2,3-dimethyl-1-naphthol (**14**), which we believe arises *via* an ionic process (see below) was obtained in 2—4% yield. As with the naphthalenone (**4**), the major product



Scheme 5.

(26%) was a binaphthyl (**18**), resulting from a radical coupling following C–O bond homolysis. The ketone (**17**),† which was formed (11%) in benzene also, presumably results from a coupling of the same naphthoxy radical with a methyl radical resulting from decarboxylation of an acetoxy radical, while naphthol (**16**) no doubt arises in the same way as compound (**5**) above.

The constitution of (**15**) followed from its spectra and degradation in acid or alkali to the indan-1-one (**19**) (*cf.* Scheme 3),



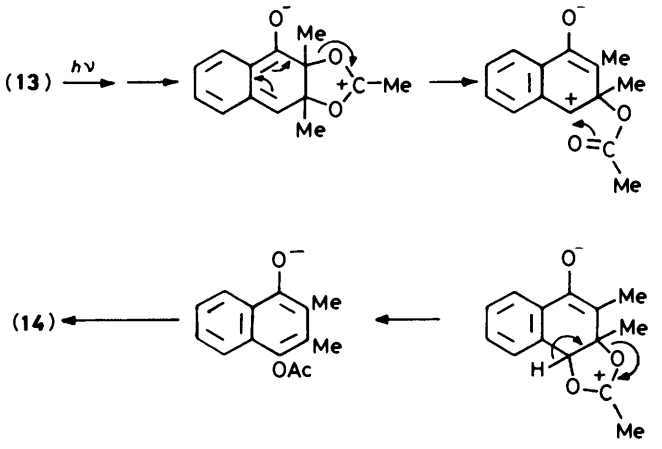
(**19**)

which was characterised as the bis-2,4-dinitrophenylhydrazone derivative and tentatively assigned the *trans*-configuration as in the case of (**9**) above. Here again, the *endo*-configuration of (**15**) was clearly indicated by the highfield position (δ 1.63) of the acetoxy methyl signal in the ^{1}H n.m.r. spectrum, and there was no evidence for the formation of the *exo*-isomer. Thus, we believe that the mechanism of formation of (**15**) is similar to that proposed above in Scheme 4 for the dihydrocyclopropindenone (**7**).

The photochemical behaviour of compound (**15**) mirrored that of (**7**); after irradiation in methanol (69% conversion), a g.l.c. analysis of the reaction mixture showed it to contain the phenols (**16**) and (**14**), and naphthalenones (**17**) and (**13**) in yields of 17, 16, 3, and < 1% respectively. Thus (**15**) is formed reversibly in the photolysis of the naphthalenone (**13**), and since the above experiment showed (**15**) was considerably less photoreactive than (**13**), it would appear that even if there is a direct pathway from the cyclopropane derivative (**15**) to the phenol (**14**), the major proportion of (**14**) formed on irradiation of naphthalenone (**13**) cannot be produced in this way. As in the formation of the phenol (**6**) (see Scheme 4), the available data

* We do not regard as significant our failure to isolate the dihydrocyclopropindenone (**7**) from the irradiation in benzene, since analogous products were shown by g.l.c. analysis to be formed in comparable yields in irradiations of two other naphthalenones in both methanol and benzene.

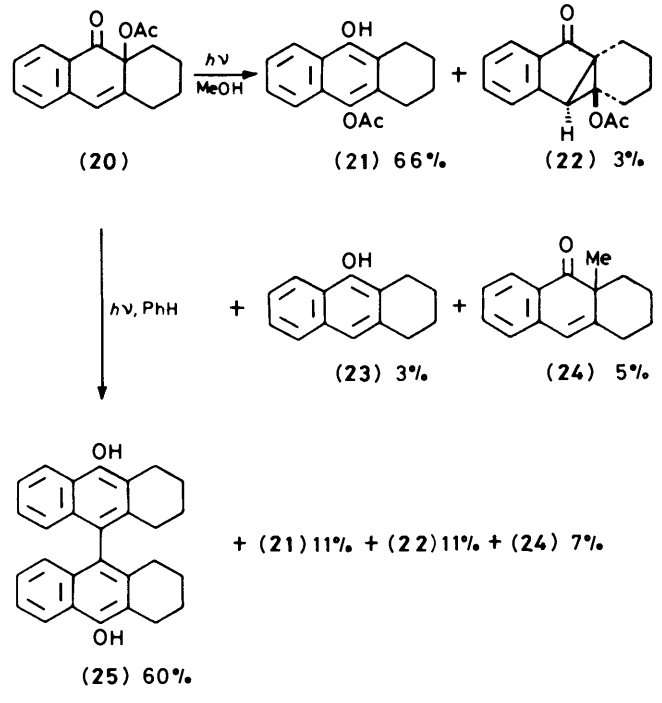
† The structure followed from the spectra which compare well with those reported for analogous 2,2-dialkylnaphthalen-1(2*H*)-ones.[7,8]



Scheme 6.

point to an ionic process, such as presented in Scheme 6, for the production of the phenol (**14**). As with the naphthalenone (**4**), irradiation of (**13**) in the presence of cyclohexylamine failed to produce any new products, and thus we conclude that ring cleavage with ketene formation does not occur in this system.

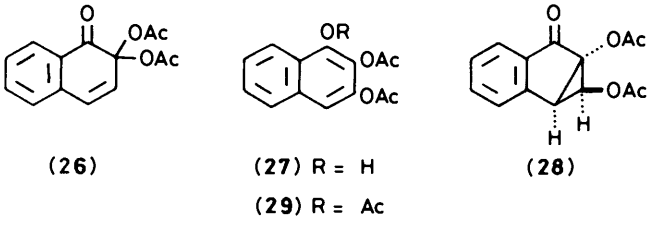
The naphthalen-1(2*H*)-one (**20**),[10] in which a fused 6-membered ring replaces the methyl groups of compound (**13**) showed similar reactivity to (**13**) on irradiation. The products and yields (Scheme 7), which are from g.l.c. studies after



Scheme 7.

irradiation times of 30 min in methanol (94% conversion) and benzene (98% conversion), are in keeping with the results obtained for (**13**). The phenol (**21**), which we believe arises by an ionic process of the type depicted in Scheme 6, was the major product in methanol and a minor product in benzene, while the binaphthyl (**25**), which results from radical coupling, was only present in the benzene reaction, where it was the major product. The naphthalenone (**24**), a product of coupling within a solvent cage of the naphthoxy radical and an acetoxy-derived methyl radical, was present in both reactions, whereas the phenol (**23**), which is produced by hydrogen abstraction from the solvent, was only formed in methanol. The rearrangement of (**20**) to the cyclopropane derivative (**22**) again proceeded stereospecifically to give the isomer with the *endo* acetoxy group, as indicated by the highfield signal (δ 1.41) for the acetoxy methyl group in the n.m.r. spectrum (see above).

2,2-Diacetoxynaphthalen-1(2*H*)-one (**26**)[10] was the final compound which we examined. Although the irradiations resulted in more complex mixtures than obtained with the previous compounds, we were able to show that similar rearrangements occurred with the isolation of 2,3-diacetoxy-1-naphthol (**27**) and the dihydrocyclopropindenone (**28**) in yields of 28 and 6% respectively from the reaction in methanol. The former compound was characterised as the acetyl derivative (**29**),* while the constitution of (**28**) rests on spectroscopic data.



(**26**) (**27**) R = H (**28**)

(**29**) R = Ac

Experimental

Irradiations were performed under nitrogen with a 125-W medium-pressure mercury arc placed inside a water-cooled Pyrex immersion well. G.l.c. was carried out on a Hewlett-Packard 402 instrument equipped with a flame ionisation detector and one of the following columns: column 1, 5% XE 60 on Gas Chromosorb Q (mesh 100—120) (1.8 m); column 2, 3% OV 17 on Gas Chromosorb Q (mesh 100—120) (1.5 m); column 3, 2.5% Carbowax 20M on Gas Chromosorb G (mesh 100—120) (0.6 m). Column chromatography was performed with Davison silica gel, and p.l.c. with Merck Kieselgel 60 $PF_{254+366}$ silica gel. U.v. and i.r. spectra were recorded on Perkin-Elmer 402 and 221 spectrophotometers respectively, n.m.r. spectra on a Varian HA 100 spectrometer, and mass spectra on a GEC-AE1 MS 902 spectrometer. M.p.s were determined on a Kofler hot-stage and are uncorrected. Analyses were performed by the Australian Microanalytical Service, Melbourne. Light petroleum refers to the fraction of b.p. 60—80 °C. The methanol and benzene employed in the photolyses was spectroscopic grade. Ether refers to diethyl ether.

Irradiation of 2-*Acetoxy*-2-*methylnaphthalen*-1(2H)-*one* (**4**).[10]—(*a*) A solution of the naphthalenone (**4**) (2.058 g) in methanol (410 ml) was irradiated as above for 70 min. The solvent was removed and the amorphous orange residue was chromatographed on a column of silica gel (80 g). Elution with light petroleum–ether (47:3) gave 2-methyl-1-naphthol (67 mg, 6%), m.p. 63.5—64.5 °C (from light petroleum) (after extraction into 3M-aqueous sodium hydroxide and acidification), identical by mixed m.p. and i.r. spectrum with authentic material.

Light petroleum–ether (9:1) eluted a yellow solid which crystallised from cyclohexane to give 4-*acetyl*-2-*methylnaphthalene*-1,3-*diol* (**8**) (6 mg, 0.4%), m.p. 121—123 °C (Found: M^+, 216.0783. $C_{13}H_{12}O_3$ requires *M*, 216.0786); $\nu_{max.}$($CHCl_3$) 3 595, 3 070, 1 630, 1 595, and 1 575 cm^{-1}; $\lambda_{max.}$(MeOH) 358sh, 352, 325, and 232 nm (ε 6 660, 7 050, 6 470, and 27 800); δ($CDCl_3$) 2.26 (3 H, s, 2-Me), 2.82 (3 H, s, Ac), 5.84 (1 H, br s, 1-OH), 7.26—

* A compound previously assigned this structure was shown to be 2,2′,3,3′,4,4′-tetra-acetoxy-1,1′-binaphthyl.[20]

7.72 (2 H, m, 6-H and 7-H), 7.96—8.26, (2 H, m, 5-H and 8-H), and 14.83 (1 H, br s, 3-OH); *m/z* 216 (62%) and 200 (100).

When the column was eluted with light petroleum–ether (21:4) the naphthalenone (**4**) (45 mg, 2.9%) was recovered, while elution with light petroleum–ether (4:1) afforded 3-*acetoxy*-2-*methyl*-1-*naphthol* (**6**) (177 mg, 11.6%), m.p. 119—120 °C (from cyclohexane) (Found: C, 72.5; H, 5.8. $C_{13}H_{12}O_3$ requires C, 72.2; H, 5.6%); $\nu_{max.}$(CHCl$_3$) 3 610 and 1 760 cm^{-1}; $\lambda_{max.}$(MeOH) 324sh, 299, and 231 nm (ε 2 630, 4 260, and 35 500); δ(CDCl$_3$) 2.13 (3 H, s, 2-Me), 2.35 (3 H, s, MeCO$_2$), 5.57 (1 H, s, OH), 7.11 (1 H, s, 4-H), 7.22—8.10 (4 H, m, aryl H); *m/z* 216 (*M*, 28%) and 174 (*M*–CH_2CO, 100). Acetylation of the naphthol (**6**) with acetic anhydride in pyridine yielded 1,3-diacetoxy-2-methylnaphthalene, m.p. 115—116 °C (lit.,[11] 114—116 °C); $\nu_{max.}$(CHCl$_3$) 1 770 cm^{-1}; δ(CDCl$_3$ 2.14 (3 H, s, 2-Me), 2.34 (3 H, s, Ac), 2.45 (3 H, s, Ac), and 7.18—7.92 (5 H, m, ArH).

Elution of the column with light petroleum–ether (3:1) gave material which, after being washed in ether (100 ml) with sodium hydroxide solution (3M; 50 ml), to remove a small amount of the naphthol (**6**), afforded endo-1-*acetoxy*-6a-*methyl*-1,1a-*dihydrocycloprop*[a]*inden*-6(6aH)-*one* (**7**) (107 mg, 7%) as an oil (Found: C, 72.3; H, 5.8. $C_{13}H_{12}O_3$ requires C, 72.2; H, 5.6%); $\nu_{max.}$(CHCl$_3$) 1 735 and 1 715 cm^{-1}; $\lambda_{max.}$(MeOH) 321sh, 290, and 222 nm (ε 1 220, 2 290, and 24 800); δ(CDCl$_3$) 1.57 (3 H, s, 6a-Me), 1.65 (3 H, s, Ac), 3.11 (1 H, d, $J_{1.1a}$ 6.3 Hz, 1a-H), 4.45 (1 H, d, $J_{1.1a}$ 6.3 Hz, 1-H), 7.27—7.55 (3 H, m, ArH), 7.56—7.70 (1 H, m, ArH *ortho* to C=O); *m/z* 216 (*M*, 3%) 174 (*M* – CH_2CO, 100), 146 (37), and 145 (83).

G.l.c. analysis (column 1 at 156 and 204 °C) of the crude reaction mixture from a smaller-scale irradiation of the naphthalenone (**4**) as above, showed that after 20 min (and 40 min) compounds (**4**), (**5**), (**6**), and (**7**) were present in yields of 23(7), 3(7), 9(14), and 15% (22%) respectively.

(*b*) A solution of the naphthalenone (**4**) (1.527 g) in benzene (320 ml) was irradiated as above for 65 min. Removal of the solvent gave a dark oil which was chromatographed on a column of silica gel (120 g). Starting material (**4**) was recovered from the light petroeum–ether (3:1) fraction, while elution with light petroleum–ether (3:2) gave an amorphous orange solid (155 mg). When this was fractionated by p.l.c. in light petroleum–ether (65:35) it yielded a crystalline solid (99 mg), which rapidly darkened in air. Purification of this material by vacuum sublimation at 180—200 °C gave 3,3′-*dimethyl*-1,1′-*binaphthyl*-4,4′-*diol* (**10**) as colourless crystals (becoming pink in air), m.p. 252—254.5 °C (Found: M^+, 314.130. $C_{22}H_{18}O_2$ requires *M*, 314.131); $\nu_{max.}$(Nujol) 3 280 cm^{-1}; $\lambda_{max.}$(MeOH) 329sh, 315sh, 307, and 222 nm (ε 9 940, 12 400, 12 800, and 7 300); $\lambda_{max.}$(MeOH + KOH) 347 nm (ε 13 400); δ([$^2H_6$]acetone) 2.5 (6 H, s, 2 × Me), 7.20—7.57 (8 H, m, ArH), 7.90 (2 H, s, exchangeable, 2 × OH), and 8.27—8.51 (2 H, m, 5-H and 5′-H); *m/z* 314 (100%).

Irradiation of 2-*Acetoxy*-2,3-*dimethylnaphthalen*-1(2H)-*one* (**13**).[10]—(*a*) A solution of the naphthalenone (**13**) (2.043 g) in benzene (410 ml) was irradiated as above for 30 min. Removal of the solvent and addition of acetone (20 ml) precipitated a colourless solid (0.349 g), which crystallised from acetone to give 2,2′3,3′-*tetramethyl*-1,1′-*binaphthyl*-4,4′-*diol* (**18**) as the monohydrate (0.35 g), m.p. 140—141 °C (Found: C, 80.0; H, 6.7. $C_{24}H_{22}O_2 \cdot H_2O$ requires C, 80.0; H, 6.7%); $\nu_{max.}$(Nujol) 3.590, 3 520, 1.630, and 1.595 cm^{-1}; $\lambda_{max.}$(MeOH) 342 and 252 nm (ε 12 000 and 51 500); δ([$^2H_6$]DMSO) 1.84 (6 H, s, 2 × Me), 2.40 (6 H, s, 2 × Me), 3.32 (2 H, OH), 6.73—7.61 (6 H, m, ArH 8.20—8.34 (2 H, m, 5-H and 5′-H), and 8.75 (2 H, br s, 2 × OH); *m/z* 342 (*M*, 48%), 325 (*M* – OH, 100), and 172(85).

The acetone filtrate was concentrated and the residue was chromatographed on a column of silica gel (110 g). Elution with light petroleum–ether (20:1) afforded 2,2,3-*trimethylnaphthalen*-1(2H)-*one* (**17**) (0.179 g, 10.8%) as an oil (Found: C, 83.9; H, 7.8. $C_{13}H_{14}O$ requires C, 83.7; H, 7.5%); $\nu_{max.}$(CHCl$_3$) 1 670, 1 645, and 1 595 cm^{-1}; $\lambda_{max.}$(MeOH) 340, 282sh, 272, 265, and 235 nm (ε 1 770, 2 600, 4 380, 4 600, and 34 700); δ(CDCl$_3$) 1.27 (6 H, s, 2 × Me), 1.99 (3 H, d, $J_{4.Me}$ 1.45 Hz, 3-Me), 6.34 (1H, dq, $J_{4.Me}$ 1.45, $J_{4.8}$ 0.8, 4-H), 7.1—7.6 (3 H, m, 5-H, 6-H, and 7-H), and 8.0 (1 H, m, 8-H); *m/z* 186 (*M*, 26%) and 171 (*M* – CH_3, 24).

Light petroleum–ether (4 : 1) eluted a viscous yellow oil (0.501 g) which crystallised from light petroleum to give endo-1-*acetoxy*-1,6a-*dimethyl*-1,1a-*dihydrocycloprop*[a]*inden*-6(6aH)-*one* (**15**) (0.422 g, 20.7%), m.p. 56—58 °C (Found: C, 73.1; H, 6.2. $C_{14}H_{14}O_3$ requires C, 73.1; H, 6.1%); $\nu_{max.}$(CHCl$_3$) 1 745 and 1 710 cm^{-1}; $\lambda_{max.}$(MeOH) 326sh, 297, 256sh, and 235 nm (ε 805, 2 040, 5 250, and 14 900); δ(CDCl$_3$) 1.40 (3 H, s, 1-Me), 1.48 (3 H, s, 6a-Me), 1.63 (3 H, s, Ac), and 2.80 (1 H, s, 1a-H) which sharpened ($W_{\frac{1}{2}}$ reduced by 0.3 Hz) on irradiation of the most downfield aromatic proton signal, 7.20—7.52 (3 H, m, ArH), and 7.53—7.66 (1 H, m, ArH *ortho* to C=O). On elution of the column with light petroleum–ether (5:3) a further quantity of binaphthyl (**18**) (52 mg, total yield 26.8%), m.p. and mixed m.p. 140—140 °C, was obtained.

G.l.c. analysis (column 1 at 183 and 225 °C) of the crude reaction mixture from a smaller-scale irradiation of naphthalenone (**13**) as above, showed that after 15 min (and 30 min) compounds (**13**), (**14**), (**15**), (**17**), and (**18**) were present in yields of 57 (1), 4 (2), 8 (18), 4 (11), and 9% (26%) respectively.

(*b*) A solution of naphthalenone (**13**) (1.915 g) in methanol (380 ml) was irradiated as above for 30 min, and the product was chromatographed on a column of silica gel (90 g). Light petroleum–ether (10:1) eluted 2,2,3-trimethylnaphthalen-1(2*H*)-one (**17**), identical (i.r. and n.m.r. spectra) with material obtained above, light petroleum–ether (17:3) eluted 2,3-dimethyl-1-naphthol (27 mg, 1.8%), m.p. 82.5—84.5 °C (from light petroleum) (lit.,[21] 84—85.5 °C), identical (mixed m.p. and i.r. spectrum) with authentic material, and light petroleum–ether (3:1) afforded the starting naphthalenone (**13**) (0.434 g, 22.6%). Elution of the column with light petroleum–ether (7:3) yielded 4-acetoxy-2,3-dimethyl-1-naphthol (**14**) (0.484 g, 25.3%), m.p. and mixed m.p. 153—154 °C (lit.,[22] 153—154 °C). Although the dihydrocyclopropindenone (**15**) was not isolated in this chromatography, g.l.c. analysis (column 1 at 183 °C) of the crude mixture showed it to be present in 10% yield.

G.l.c. monitoring (column 1 at 183 °C) of a smaller scale irradiation under the above conditions showed that after 15 min (and 22 min) compounds (**13**), (**14**), (**15**), (**16**), and (**17**) were present in yields of 32 (10), 30 (42), 16 (24), and 2% (4%) respectively.

Irradiation of 9a-*Acetoxy*-1,2,3,4-*tetrahydroanthracen*-9-(9aH)-*one* (**20**).[10]—(*a*) A solution of the anthracenone (**20**) (2.0 g) in benzene (400 ml) was irradiated as above for 40 min. Removal of the solvent and addition of acetone (10 ml) deposited a solid which crystallised from benzene to yield 1,1′,2,2′,3,3′,4,4′-*octahydro*-9,9′-*bianthracene*-10,10′-*diol* (**25**) (0.248 g), m.p. 148.5—150 °C (Found: C, 85.3; H, 6.7. $C_{28}H_{26}O_2$ requires C, 85.3; H, 6.6%); $\nu_{max.}$(Nujol) 3 400, 1 640, and 1 595 cm^{-1}; $\lambda_{max.}$(MeOH) 294sh, 260, and 238 nm (ε 1 610, 16 900, and 35 200); $\lambda_{max.}$(MeOH + KOH) 341 and 253 nm (ε 9 050 and 55 300); δ([$^2H_6$]DMSO) 1.28—3.27 (16 H, m, aliphatic H), 6.72—7.51 (6 H, m, ArH), 8.18—8.43 (2 H, m, 5-H and 5′-H), 8.84 (2 H, br s, exchangeable, 2 × OH); *m/z* 198 (*M*/2 + 1, 7%).

The solvent was removed from the combined acetone and benzene filtrates, and the residue was chromatographed on a column of silica gel (110 g). Elution with light petroleum–ether (19:1) yielded a pale yellow oil (0.226 g), which was fractionated by p.l.c. in light petroleum–ether (9:1) to give 9a-*methyl*-1,2,3,4-*tetrahydroanthracen*-9(9aH)-*one* (**24**) (0.20 g, 12.0%) as an oil (Found: C, 84.8; H, 7.6. $C_{15}H_{16}O$ requires C, 84.9; H, 7.5%);

$\nu_{max.}$($CHCl_3$) 1 670, 1 650, and 1 595 cm^{-1}; $\lambda_{max.}$(MeOH) 344, 285sh, 275sh, and 237 nm (ε 1 140, 1 790, 2 740, and 21 800); δ($CDCl_3$) 1.30 (3 H, s, 9a-Me), 1.19—2.53 (8 H, m, aliphatic H), 6.31 (1 H, m, $J_{8,10}$ 0.72 Hz, confirmed by decoupling, 10-H), 7.16 (1 H, m, 5-H), 7.26 (1 H, m, 7-H), 7.42 (1 H, m, 6-H), and 8.04 (1 H, m, 8-H); *m/z* 212 (*M*, 100%) and 197 (*M* − CH_3, 39).

Elution with light petroleum–ether (17:3) yielded a mixture of two compounds which were separated by p.l.c. in light petroleum–ether (3:2). The more polar material was the starting material (**20**) (51 mg, 2.5%), while the less polar fraction crystallised from light petroleum to afford endo-4a-*acetoxy*-1,2,3,4,4a,10-*hexahydro*-9a,10-*cycloanthracen*-9(9aH)-*one* (**22**) (117 mg, 5.9%), m.p. 103.5—105 °C (Found: C, 74.8; H, 6.2. $C_{16}H_{16}O_3$ requires C, 75.0; H, 6.2%); $\nu_{max.}$($CHCl_3$) 1 748, 1 710, and 1 608 cm^{-1}; $\lambda_{max.}$(MeOH) 348sh, 228sh, 298, 259sh, and 237 nm (ε 365, 975, 2 100, 5 640, and 14 750); δ($CDCl_3$) 1.16—2.95 (8 H, m, cyclohexyl H), 1.41 (1 H, s, $MeCO_2$), 3.07 (1 H, s, 10-H) which sharpened ($W_{\frac{1}{2}}$ reduced by 0.3 Hz) on irradiation of the signal due to 8-H, 7.17—7.51 (3 H, m, 5-H, 6-H, and 7-H), and 7.54—7.69 (1 H, m, 8-H); *m/z* 256 (*M*, 3%), 214 (*M* − CH_2CO, 100), 196 (*M* − CH_3CO_2H, 36), 186 (72), and 185 (93). On elution of the column with light petroleum–ether (1:1) a further quantity of the octahydrobianthracene (**25**) (0.106 g, total yield 23.0%), m.p. 148.5—150 °C, was obtained. Although 10-acetoxy-1,2,3,4-tetrahydro-9-anthrol (**21**)[10] was not isolated in a pure state in this chromatography, g.l.c. analysis (column 2, 205 °C) of the crude reaction product showed it to be present in 10.5% yield.

G.l.c. monitoring [column, 2, 144 °C for compounds (**20**), (**22**), (**24**), and (**25**), and 205 °C for compound (**21**)] of a smaller scale irradiation under the above conditions showed that after 15 min (and 30 min) compounds (**20**), (**21**), (**22**), (**24**), and (**25**) were present in yields of 46 (2), 9 (11), 7 (11), 4 (7), and 33% (60%) respectively.

(*b*) A solution of the anthracenone (**20**) (0.50 g) in methanol (100 ml) was irradiated as above and the composition of the mixture was determined by g.l.c. analysis after various reaction times as in (*a*) above. The analysis for 1,2,3,4-tetrahydro-9-anthrol (**23**) was performed with column 2 at 172 °C. After 17 min (and 30 min) irradiation compounds (**20**), (**21**), (**22**), (**23**), and (**24**) were present in yields of 21 (6), 45 (66), 2(3), 3 (3), and 2% (5%) respectively.

Irradiation of 2,2-*Diacetoxynaphthalen*-1(2H)-*one* (**26**).[10]—A solution of the naphthalenone (**26**) (1.95 g) in methanol (390 ml) was irradiated as above for 1 h, and the product obtained on removal of the solvent was chromatographed on a column of silica gel (100 g). Elution with light petroleum–ether (3:2) gave a red viscous oil which was fractionated by p.l.c. in light petroleum–ether (7:3) to yield two fractions. The less polar material was purified by p.l,c, in the same solvent to yield endo-1,6a-*diacetoxy*-1,1a-*dihydrocycloprop*[a]*inden*-6(6aH)-*one* (**28**) (117 mg, 5.9%) as an oil (Found: *M* − CH_2CO, 218.057.* $C_{14}H_{12}O_5$ requires *M* − CH_2CO, 218.058); $\lambda_{max.}$(MeOH) 327, 297, and 256 (ε 885, 1 890, and 7 450); δ($CDCl_3$) 1.66 (3 H, s, 1-Ac), 2.17 (3 H, s, 6a-Ac), 3.48 (1 H, br d, $J_{1,1a}$ 7.4 Hz, 1a-H) which gave a sharp doublet ($W_{\frac{1}{2}}$ reduced by 0.5 Hz) on irradiation of the most downfield aromatic signal, 4.92 (1 H, d, $J_{1,1a}$ 7.4 Hz, 1-H), 7.26—7.58 (3 H, m, ArH), and 7.60—7.76 (1 H, m, ArH *ortho* to C=O); *m/z* 260 (*M*, 0.2%), 218 (*M* − CH_2CO, 20), and 176 (*M* − 2 × CH_2CO, 79).

The more polar fraction (0.553 g) from the p.l.c., a phenolic amorphous solid, was acetylated with acetic anhydride in pyridine and the product was purified by p.l.c. in light petroleum–ether (7:3). It crystallised from methanol to yield 1,2,3-*triacetoxynaphthalene* (0.395, 17.2%), m.p. 110.5—111 °C (Found: C, 63.2; H, 4.8. $C_{16}H_{14}O_6$ requires C, 63.6; H, 4.6%); $\nu_{max.}$($CHCl_3$) 1 780 and 1 605 cm^{-1}; $\lambda_{max.}$(MeOH) 288, 279, 267, 260sh, and 225 nm (ε 3 700, 5 480, 5 070, 3 700, and 78 000); δ($CDCl_3$) 2.33 (6 H, s, 2-Ac and 3-Ac), 2.43 (3 H, s, 1-OAc), 7.40—7.62 (2 H, m, 6-H and 7-H), 7.66 (1 H, d, $J_{4,8}$ 0.9 Hz, 4-H) which collapsed to a singlet on irradiation of the signal due to 8-H, and 7.72—7.92 (2 H, m, 5-H and 8-H); *m/z* 302 (*M*, 4%), 260 (*M* − CH_2CO, 8), 218 (*M* − 2 × CH_2CO, 36), and 176 (*M* − 3 × CH_2CO, 100).

Acid Catalysed Degradation of Dihydrocyclopropindenone (**7**).—A solution of the dihydrocyclopropindenone (**7**) (34 mg) in methanol and sulphuric acid (1.5M; 5.0 ml) was stirred at room temperature for 48 h, and the resulting yellow solution was worked up to give an orange oil (35 mg), which by t.l.c. and the n.m.r. spectrum was a mixture of two compounds. The major constituent (*ca.* 85%) was assigned the structure *trans*-2-methyl-3-(dimethoxymethyl)indan-1-one (**9**); δ($CDCl_3$) 1.35 (3 H, d, *J* 7.5 Hz, 2-Me), 2.62 (1 H, dq, $J_{2,3}$ 3.5 Hz, $J_{2,Me}$ 7.5 Hz, 2-H), 3.24 (1 H, dd, $J_{2,3}$ 3.5 Hz, *J* 6.3 Hz, 3-H), 3.44 (3 H, s, OMe), 3.49 (3 H, s, OMe), 4.44 (1 H, d, *J* 6.3 Hz, acetal H), and 7.12—8.14 (4 H, m, aryl H). The minor component of the mixture was, on the grounds of the n.m.r. spectrum, the corresponding aldehyde, 3-formyl-2-methylindan-1-one, δ 1.28 (d, 2-Me) and 9.82 (d, CHO) with integrals in ratio of 3:1.

Hydrolysis of the Dihydrocyclopropindenone (**15**).—(*a*) A solution of sodium hydroxide (3M; 30 ml) was added rapidly to a solution of the dihydrocyclopropindenone (**15**) (0.237 g) in methanol (50 ml), which had been thoroughly flushed with nitrogen, and the mixture was stirred at room temperature under nitrogen for 4 h. Acidification with dilute sulphuric acid (3M; 30 ml), followed by extraction with ether (2 × 50 ml) gave a dark oil (0.154 g), which was fractionated by p.l.c. in light petroleum–ether (11:9) to yield trans-3-*acetyl*-2-*methylindan*-1-*one* (**19**) (68 mg, 35%) as an oil (Found: M^+, 188.083. $C_{12}H_{12}O_2$ requires *M*, 188.084); $\nu_{max.}$($CHCl_3$) 1 715 and 1 600 cm^{-1}; $\lambda_{max.}$(MeOH) 284, 245, and 226sh nm (ε 1 470, 8 860, and 9 550); δ($CDCl_3$) 1.3 (3 H, d, *J* 7.2 Hz, 2-Me), 2.14 (3 H, s, Ac), 2.77 (1 H, dq, $J_{2,3}$ 4.2 Hz, $J_{2,Me}$ 7.2 Hz, 2-H), 3.80 (1 H, d, $J_{2,3}$ 4.2 Hz, 3-H), and 7.26—7.76 (4 H, m, 4 × ArH); *m/z* 188 (100%), 146 (*M* − CH_2CO, 100), and 145 (*M* − CH_3CO, 32). The *bis*(2,4-*dinitrophenylhydrazone*) *derivative* of the indanone (**19**), was obtained as red crystals, m.p. 208—210 °C (from ethyl acetate) (Found: C, 52.5; H, 3.9. $C_{24}H_{20}N_8O_8$ requires C, 52.5; H, 3.6%); $\lambda_{max.}$(MeOH) 374 and 223sh nm (ε 22 600 and 16 000); δ([$^2H_6$]acetone) 1.53 (3 H, d, $J_{2,Me}$ 7.3 Hz, 2-Me), 1.94 (3 H, s, Me), 3.59 (1 H, dq, $J_{2,3}$ 1.7 Hz, $J_{2,Me}$ 7.3 Hz, 2-H), 4.10 (1 H, d, $J_{2,3}$ 1.7 Hz, 3-H), 7.38—8.44 (8 H, m, ArH), 8.96—9.09 (2 H, m, ArH), 10.93 (1 H, s, NH), and 11.36 (1 H, s, NH); *m/z* 548 (*M*, 5%).

(*b*) A solution of dihydrocyclopropindenone (**15**) (43 mg) in methanol (15 ml) and sulphuric acid (1.5M; 10 ml) was kept at room temperature for 24 h. Addition of water and ether extraction afforded a yellow oil (37 mg) which, from an analysis of the n.m.r. spectrum, was a mixture of the indanone (**19**) and the starting material (**15**) in an approximate ratio of 1:1.

Irradiation of the Dihydrocyclopropindenone (**7**) *and* (**15**).—(*a*) A solution of the dihydrocyclopropindenone (**7**) (113 mg) in methanol (22 ml) was irradiated in the manner outlined earlier. G.l.c. analysis (column 1 at 156 and 204 °C) of the crude reaction mixture after 5 h indicated that 60% of (**7**) had been converted into a complex mixture which contained 2-acetoxy-2-methylnaphthalen-1(2*H*)-one (**4**), 2-methyl-1-naphthol (**5**), 3-acetoxy-2-methyl-1-naphthol (**6**), and 4-acetyl-2-methylnaphthalene-1,3-diol (**8**).

* Metastable refocussing demonstrated the ion *m/z* 218 was a daughter ion of ion *m/z* 260.

(*b*) A solution of the dihydrocyclopropindenone (**15**) (38 mg) in methanol (10 ml) was irradiated as in (*a*) above, and the reaction was monitored by g.l.c. analysis (column 1 at 183 and 225 °C). After 30 min (and 60 min) irradiation compounds (**13**), (**14**), (**15**), (**16**), and (**17**) were present in yields of <1 (<1), 27 (16), 55 (31), 10 (17), and 1% (3%) respectively.

2-Acetoxy-1,1-dimethyl-1,2-dihydronaphthalene (**12**).—A solution of 1,1-dimethylnaphthalen-2(1*H*)-one[23] (5.9 g) in dry ether (30 ml) was added with stirring to a suspension of lithium aluminium hydride (2.64 g) in dry ether, and the mixture was stirred at room temperature for 5 min. Ethyl acetate (20 ml) was added, and the reaction was worked up by means of dilute hydrochloric acid and ether to yield 1,1-dimethyl-1,2-dihydronaphthalen-2-ol as a colourless oil (5.8 g, 98%) (lit.,[18] 59—61 °C) (Found: M^+, 174.1048. Calc. for $C_{12}H_{14}O$: *M*, 174.1045); $\nu_{max.}$($CHCl_3$) 3 480—3 350, 1 650, and 1 600 cm^{-1}; $\lambda_{max.}$(MeOH) 264 and 224sh nm (ε 7 680 and 14 300); δ($CDCl_3$) 1.24 (3 H, s, Me), 1.40 (3 H, s, Me), 2.2 (1 H, br s, exchangeable, OH), 3.97 (1 H, dd, $J_{2,3}$ 4.6 Hz, $J_{2,4}$ 0.8 Hz, 2-H), 6.06 (1 H, dd, $J_{2,3}$ 4.6 Hz, $J_{3,4}$ 9.7 Hz, 3-H), 6.55 (1 H, ddd, $J_{2,4}$ 0.8 Hz, $J_{3,4}$ 9.7 Hz, $J_{4,8}$ 0.4 Hz, 4-H), and 7.02—7.47 (4 H, m, ArH); *m*/*z* 174 (*M*, 5%) and 156 (*M* − CH_3, 100). Treatment of this material with acetic anhydride in pyridine afforded *2-acetoxy-1,1-dimethyl-1,2-dihydronaphthalene* (**12**) (92%) as an oil (Found: C, 78.0; H, 7.4. $C_{14}H_{16}O_2$ requires C, 77.8; H, 7.4%); $\nu_{max.}$($CHCl_3$) 1 730 cm^{-1}; $\lambda_{max.}$(MeOH) 264 and 233 nm (ε 10 500 and 21 000); δ($CDCl_3$) 1.22 (3 H, s, Me), 1.38 (3 H, s, Me), 1.97 (3 H, s, Ac), 5.26 (1 H, dd, $J_{2,3}$ 4.8 Hz, $J_{2,4}$ 0.5 Hz, 2-H), 6.02 (1 H, dd, $J_{2,3}$ 4.8 Hz, $J_{3,4}$ 9.7 Hz, 3-H), 6.65 (1 H, br dd, $J_{3,4}$ 9.7 Hz, $J_{2,4}$ 0.5 Hz, 4-H), and 7.04—7.47 (4 H, m, ArH); *m*/*z* 216 (*M*, 2%), 156 (*M* − CH_3CO_2H, 100), and 141 (156 − CH_3, 76).

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