The Photochemistry of 2,2-Dimethyl- and 2-Aryl-2-methylnaphthalen-1(2*H*)-ones. Substitution Requirement for the Oxadi-π-methane Rearrangement

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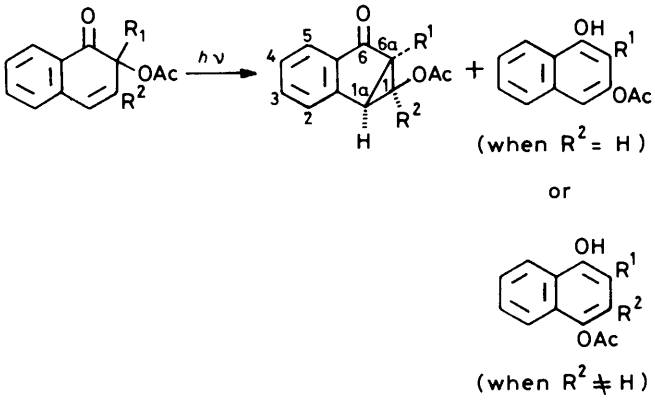
The photochemistry of 2-aryl-2-methylnaphthalen-1(2*H*)-ones (**1**) and (**2**), 2,2-dimethylnaphthalen-1(2*H*)-one (**6**), 2,2,3-trimethylnaphthalen-1(2*H*)-one (**7**), 2,2,4-trimethylnaphthalen-1(2*H*)-one (**3**), 2-(*p*-methoxyphenyl)-2,4-dimethylnaphthalen-1(2*H*)-one (**8**), and 2,2,5,7-tetramethylnaphthalen-1(2*H*)-one (**12**) has been examined. The compounds which did not contain a 4-substituent, (**1**), (**2**), (**6**), and (**7**), were virtually unchanged under conditions which caused the 4-methyl derivative (**3**) to undergo an oxadi-π-methane (ODPM) rearrangement to the 1,1a-dihydrocycloprop[*a*]indenone (**4**). Similar reactivity was shown by the 4-methyl derivative (**8**), which gave the ODPM rearrangement products (**9**) and (**10**). On further irradiation, both (**9**) and (**10**) underwent rearrangement to 4-(*p*-methoxyphenyl)-3,4-dimethylnaphthalen-1(4*H*)-one (**11**). The 4-methyl group in (**3**) and (**8**) would appear to be exerting a steric effect, since irradiation of 2,2,5,7-tetramethylnaphthalen-1(2*H*)-one (**12**) produced the 1-naphthol (**13**) and the 1-tetralone (**14**), both of which arise from further reaction of an ODPM rearrangement product. Syntheses of the naphthalen-1(2*H*)-ones (**1**), (**8**), and (**12**) are reported.

In an investigation of the photochemistry of 2-acetoxynaphthalen-1(2*H*)-ones, which is reported in the preceding paper,[1] we found that they undergo two rearrangements (see Scheme 1). In one there was a 1,2-acetoxy group migration with

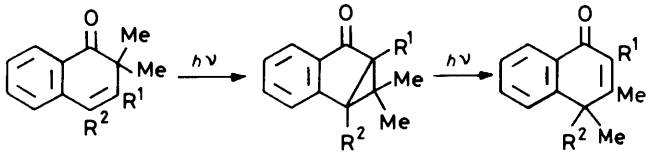


Scheme 1.

C(2)–C(4) bond formation to give a dihydrocyclopropindenone, while the other involved 1,2-acetoxy group migration with aromatisation to yield a 3-acetoxy-1-naphthol, or 1,3-acetoxy group migration to yield a 4-acetoxy-1-naphthol if the naphthalenone was substituted at C-3. We have suggested that the former rearrangement, which is stereospecific, proceeds by a concerted non-ionic mechanism, while the latter, which produces naphthols, follows an ionic pathway.

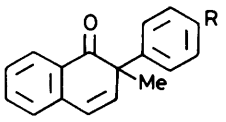
The availability of 2-aryl-2-methylnaphthalen-1(2*H*)-ones from our study of the arylation of phenols by aryl-lead triacetates[2] led us to examine their photochemistry, since it seemed likely that their behaviour may throw some light on the mechanisms of the rearrangements depicted in Scheme 1. An obvious attraction of such compounds lay in the possibility of varying the migratory aptitude of the aryl group by altering the substitution of the ring.

Our initial study was carried out with 2-(*p*-methylphenyl)-2-methylnaphthalen-1(2*H*)-one (**1**), the synthesis of which is described later, and 2-(*p*-methoxyphenyl)-2-methylnaphthalen-1(2*H*)-one (**2**).[2] Irradiation of compounds (**1**) and (**2**) under conditions which caused isomerisation of 2-acetoxy-2-alkylnaphthalen-1(2*H*)-ones,[1] failed to induce any reaction. Even prolonged irradiation (12 h) in benzene had no effect, while similar treatment in methanol caused only a small reduction in the concentration of (**1**) and (**2**), with no evidence from spectra for the formation of rearranged products. Although the failure of compounds (**1**) and (**2**) to undergo rearrangements of the type shown in Scheme 1, could be ascribed to differences in the nature of the migrating groups, the absence of the alternative oxadi-π-methane (ODPM) rearrangement[3] was not readily rationalised in the light of the work of Hart and Murray.[4,5] These workers found that irradiation of 4-alkyl-2,2-dimethylnaphthalen-1(2*H*)-ones, under conditions similar to those of the present work, led to C(1)–C(2) bond cleavage with formation of a dihydrocyclopropindenone. The latter compounds, on further irradiation, underwent cyclopropane ring-opening and 1,2-methyl group migration to yield 4-alkyl-4-methylnaphthalen-1(4*H*)-ones (see Scheme 2).



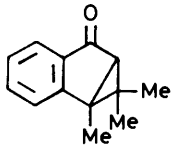
Scheme 2.

Since C(1)–C(2) bond homolysis might be expected to be a more facile process in 2-aryl-2-methylnaphthalen-1(2*H*)-ones than in the 2,2-dimethyl derivatives, we first wished to determine whether our conditions would reproduce the results of Hart and Murray. Irradiation of 2,2,4-trimethylnaphthalen-1(2*H*)-one (**3**) in methanol did, in fact, proceed as reported[5] to give 3,4,4-trimethylnaphthalen-1(4*H*)-one (**5**), together with its precursor, the trimethyldihydrocyclopropindenone (**4**) which we were able to isolate and characterise. The starting material (**3**) appeared to be the only other compound present in the mixture. A possible explanation for the failure of the 2-arylnaphthalenones (**1**) and (**2**) to undergo the rearrangement outlined in Scheme 2 was the absence of 4-

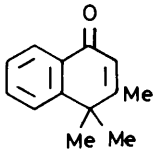


(1) R = Me
(2) R = OMe

(3) R^1 = H, R^2 = Me
(6) R^1 = R^2 = H
(7) R^1 = Me, R^2 = H



(4)



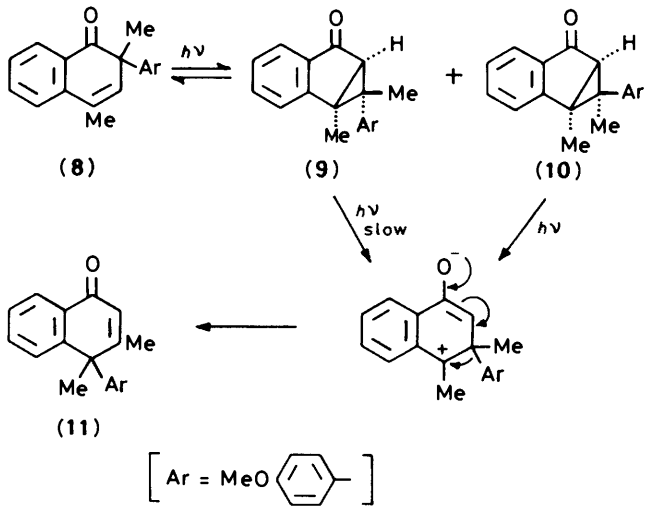
(5)

substitution, which was present in the three photoreactive 2,2-dimethylnaphthalen-1(2*H*)-ones.[4,5] This possibility was reinforced by our finding that 2,2-dimethylnaphthalen-1(2*H*)-one (**6**)[6] and 2,2,3-trimethylnaphthalen-1(2*H*)-one (**7**)[1] were both unaffected on irradiation.

To investigate this hypothesis, 2-(*p*-methoxyphenyl)-2,4-dimethylnaphthalen-1(2*H*)-one (**8**) was synthesized (see later) and subjected to the same irradiations conditions. Photolysis of (**8**) in methanol proceeded rapidly to yield three products (t.l.c. and n.m.r. spectrum), which were separated by p.l.c. (82% recovery) and shown to be the isomeric dihydrocyclopropindenones (**9**) (43%), and (**10**) (12%), and the naphthalenone (**11**) (27%). The structures of (**9**), (**10**), and (**11**) followed readily from their spectra, while the configuration at C-1 in (**9**) and (**10**) could be assigned on the basis of n.m.r. chemical shift results. In the *endo*-aryl isomer (**10**), in which there is mutual shielding of the aromatic protons, there is an upfield shift of *ca.* 0.3 p.p.m. for the entire aromatic region, with respect to the corresponding signals observed for the *exo*-isomer (**9**). In addition, the signal for the protons of the methoxy group of (**10**) is 0.2 p.p.m. upfield from the corresponding signal for the isomer (**9**).

Small-scale irradiations of the naphthalenone (**8**) in benzene and ether also resulted in formation of the same three products (t.l.c. and n.m.r. spectroscopy), but at a considerably slower rate, while the reactions were unaffected in the presence of cyclohexylamine, introduced as a ketene trap. It was possible to outline the course of the reaction by monitoring (n.m.r. spectroscopy) an irradiation of (**8**) in benzene. After 75% reaction (1.25 h), only a small amount of the naphthalen-1(4*H*)-one (**11**) had been formed; the major products were the isomers (**9**) and (**10**), which were present in approximately equal amounts. Further irradiation of this mixture resulted in a continued increase in the concentration of (**11**), and a corresponding decrease in the concentrations of (**8**), (**9**), and (**10**). Although the above experiment indicated that the isomers (**9**) and (**10**) were probably intermediates in the formation of the naphthalen-1(4*H*)-one (**11**), as would be expected from the earlier work,[5] separate irradiations of (**9**) and (**10**) in benzene did not resolve this point, since both reactions produced mixtures containing the four compounds (**8**), (**9**), (**10**), and (**11**). We therefore conclude that the ODPM rearrangement in this case is reversible under the above conditions. Analogous retro-ODPM reactions have been reported for a bicyclo-[3.1.0]hex-3-en-2-one derivative of a steroid,[7] and for 4,6,6-trimethylbicyclo[3.1.0]hex-3-en-2-one.[8] For the latter compound, the reaction has been shown to proceed through a diene ketene, a pathway which is not operating in the case of compounds (**9**) and (**10**) as indicated earlier.

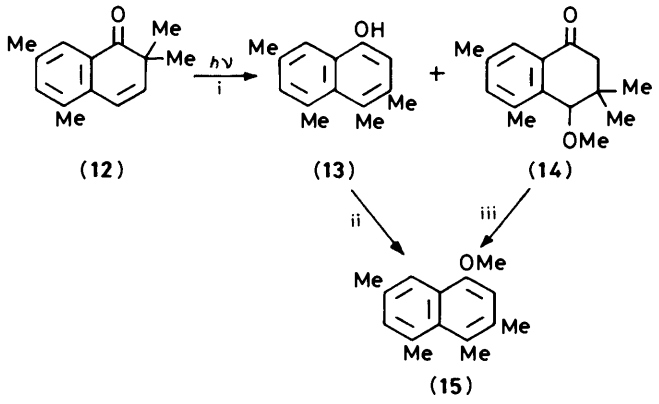
In an attempt to account for the relative reaction rates of the naphthalenone (**8**) in methanol and benzene, the isomers (**9**) and (**10**) were irradiated separately in methanol. There was no evidence for the reversibility observed in benzene since only one product, naphthalen-1(4*H*)-one (**11**), was formed in each case. However, the reactivities of the two compounds were very different. The *endo*-isomer (**10**) was completely converted into (**11**) in 4 h, whereas in a comparable experiment there was only 20% conversion of the *exo*-isomer (**9**) after 10 h irradiation. This greater reactivity of the *endo*-isomer, which had also been noted during the photolyses of (**8**) in benzene and ether, is possibly due to a greater relief of strain on fragmentation of the C(1)–C(2) bond in this compound. Migration of the *p*-methoxyphenyl group to C-4 to produce (**11**) could be occurring in a diradical resulting from homolysis of this bond; however, there is good evidence that zwitterion intermediates are involved in analogous rearrangements of some 6-arylbicyclo[3.1.0]hex-3-en-2-ones[9] at room temperature, and we favour such a mechanism here (see Scheme 3), in view of the greater speed of the reaction in methanol.



Scheme 3.

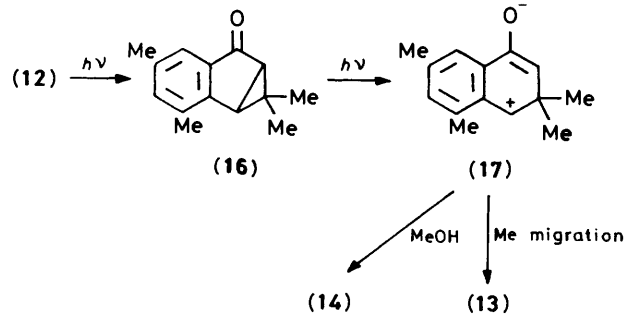
Since in all the naphthalen-1(2*H*)-ones, which had been found to undergo the ODPM rearrangement, a 4-substituent had been present, it appeared that the *peri* interaction rather than electronic factors may be the driving force. To examine this possibility we synthesized 2,2,5,7-tetramethylnaphthalen-1(2*H*)-one (**12**) (see later). When (**12**) was irradiated in methanol two major products were produced (t.l.c.), and these were shown to be 3,4,5,7-tetramethyl-1-naphthol (**13**) and 4-methoxy-3,3,5,7-tetramethyl-3,4-dihydronaphthalen-1(2*H*)-one (**14**) (Scheme 4). The latter compound (**14**), the structure of which followed from its spectra, was readily converted in almost quantitative yield into 1-methoxy-3,4,5,7-tetramethylnaphthalene (**15**) on treatment with methanol and hydrochloric acid. By use of this compound (**15**) as a g.l.c. standard we were able to obtain quantitative data for the photolysis of (**12**). On completion of the irradiation in methanol, dimethyl sulphate and potassium carbonate were introduced, and the mixture heated under nitrogen. Analysis of the mixture by g.l.c. showed the major product (47%) to be the methyl ether (**15**), while the tetralone (**14**) was present in 13% yield, before and after the methylation.

We therefore conclude that the naphthalenone (**12**) behaves like the 4-alkylnaphthalenones on irradiation to yield the ODPM rearrangement product, the dihydrocyclopropindene



Scheme 4. *Reagents and conditions:* i, MeOH; ii, Me_2SO_4–K_2CO_3; iii, MeOH–HCl

(**16**). This is not isolated owing to its photochemical conversion into a zwitterion (**17**), which reacts with methanol to yield the tetralone (**14**), or undergoes a methyl migration to produce the naphthol (**13**) (see Scheme 5). Since ODPM rearrangement is observed with both 4- and 5-alkylated naphthalen-1(2*H*)-ones, it would appear that the effect of these substituents is steric rather than electronic.

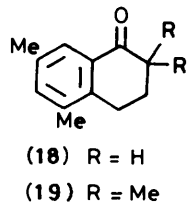


Scheme 5.

Our failure to isolate tricyclic ketone (**16**) from the above irradiation would indicate that it is more reactive than related compounds (**4**), (**9**), and (**10**). The reason for this increased photolability is possibly due to the reactivity of the corresponding zwitterion. That from the ketone (**16**), as depicted in (**17**), bears a positive charge on a secondary carbon, whereas the corresponding valence bond structures for the zwitterions from (**4**), (**9**), and (**10**) it is tertiary.

Synthesis of Naphthalen-1(2H)-*ones* (**1**), (**8**), *and* (**12**).—Our method for the arylation of phenols[2] with aryl-lead triacetates[10] was used to obtain the naphthalen-1(2*H*)-ones (**1**) and (**8**). Treatment of 2-methyl-1-naphthol with *p*-tolyl-lead triacetate at room temperature in chloroform containing pyridine produced compound (**1**) (51%), while reaction of 2,4-dimethyl-1-naphthol[11] with *p*-methoxyphenyl-lead triacetate under the same conditions gave naphthalenone (**8**) in good yield (68%). It is of interest, with regard to our study of the reactions of phenols with aryl-lead triacetates, that the latter reaction yielded none of the other possible product, 4-(*p*-methoxyphenyl)-2,4-dimethylnaphthalen-1(4*H*)-one.

The route used in the synthesis of 2,2,5,7-tetramethylnaphthalen-1(2*H*)-one (**12**) involved the known 5,7-dimethyl-



3,4-dihydronaphthalen-1(2*H*)-one (**18**).[12] Methylation of this compound with methyl iodide and sodium hydride afforded the 2,2-dimethylated ketone (**19**), which was converted into the naphthalen-1(2*H*)-one (**12**) by monobromination at C-4 with *N*-bromosuccinimde followed by dehydrobromination.

Experimental

For the general experimental procedures see the preceding paper.[1] 2,2-Dimethylnaphthalen-1(2*H*)-one[6] (**6**), 2,2,3-trimethylnaphthalen-1(2*H*)-one[1] (**7**), 2,2,4-trimethylnaphthalen-1(2*H*)-one (**3**),[5] and 2-(*p*-methoxyphenyl)-2-methylnaphthalen-1(2*H*)-one[2] (**2**) were prepared as previously reported in the literature. Irradiations were conducted under nitrogen with a 125-W medium-pressure mercury arc placed in a water-cooled Pyrex immersion well.

2-*Methyl*-2-(p-*tolyl*)*naphthalen*-1(2H)-*one* (**1**).—2-Methyl-1-naphthol (1.2 g, 7.6 mmol) was added to a solution of *p*-tolyl-lead triacetate[13] (4.0 g, 8.3 mmol) and pyridine (0.6 g, 7.6 mmol) in chloroform (40 ml) and the mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the product was isolated by means of ether. Purification by p.l.c. in light petroleum–ether (3:1) afforded 2-*methyl*-2-(p-*tolyl*)*naphthalen*-1(2H)-*one* (**1**) (0.99 g, 50%), m.p. 90—92 °C (from ethanol) (Found: C, 87.0; H, 6.3. $C_{18}H_{16}O$ requires C, 87.1; H, 6.5%); $\nu_{max.}$($CHCl_3$) 1 660 cm^{-1}; $\lambda_{max.}$(MeOH) 238 nm (ε 44 300); δ($CDCl_3$) 1.69 (3 H, s, 2-Me), 2.26 (3 H, s, 4′-Me), 6.26 (1 H, d, *J* 10.0 Hz, 3-H), 6.73 (1 H, d, *J* 10.0 Hz, 4-H), 6.78—7.67 (7 H, m, aryl H), and 7.92—8.15 (1 H, m, 8-H).

2-(p-*Methoxyphenyl*)-2,4-*dimethylnaphthalen*-1(2H)-*one* (**8**).—2,4-Dimethyl-1-naphthol[11] (2.0 g, 12 mmol) was added to a solution of *p*-methoxyphenyl-lead triacetate[13] (6.88 g, 14 mmol) and pyridine (0.92 g, 12 mmol) in chloroform (60 ml), and the mixture was stirred at room temperature for 5 h. The reaction was worked up as in the synthesis of (**1**) above to yield 2-(p-*methoxyphenyl*)-2,4-*dimethylnaphthalen*-1(2H)-*one* (**8**) (2.20 g, 68%), m.p. 61—62 °C (from methanol) (Found: C, 81.8; H, 6.7. $C_{19}H_{18}O_2$ requires C, 82.0; H, 6.5%); $\nu_{max.}$($CHCl_3$) 1 675 and 1 600 cm^{-1}; $\lambda_{max.}$ 238, 258, 265, and 273 nm (ε 32 500, 5 800, 5 600, and 4 000); δ($CDCl_3$) 1.67 (3 H, s, 2-Me), 2.24 (3 H, d, $J_{allylic}$ 1.4 Hz, 4-Me), 3.72 (3 H, s, MeO), 6.07 (1 H, q, $J_{allylic}$ 1.4 Hz, 3-H), 6.81 and 7.32 (4 H, AA′BB′, 3′-H, 5′-H and 2′-H, 6′-H respectively), 7.35—7.48 (2 H, m, 6-H and 7-H), 7.48—7.71 (1 H, m, 5-H), and 8.00 (1 H, m, 8-H); *m*/*z* 278 (*M*, 100%) and 263 (*M* − CH_3, 88).

2,2,5,7-*Tetramethylnaphthalen*-1(2H)-*one* (**12**).—A mixture of 4-(2,4-dimethylphenyl)butanoic acid[12] (30.0 g) and polyphosphoric acid (180 g) was heated on a steam-bath for 4 h, and then poured into ice and water (500 ml). The product was isolated by ether extraction and distilled to afford 5,7-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one (**18**) (18.3 g, 64%), b.p. 142—144 °C at 2.6 mmHg (lit.,[12] m.p. 50 °C); δ($CDCl_3$) 2.10 (2 H, m, 2 × 3-H), 2.26 (3 H, s, Me), 2.30 (3 H, s, Me), 2.58 (2 H, m,

2 × 2-H), 2.81 (2 H, m, 2 × 4-H), 7.09 (1 H, m, 6-H), and 7.36 (1 H, m, 8-H).

The ketone (**19**) (9.2 g) was added to a stirred suspension of sodium hydride (3.0 g) in dimethylformamide (50 ml) at −5 °C, and methyl iodide (20 g) was added dropwise with stirring so that the temperature remained below 30 °C. The mixture was stirred at room temperature for 0.5 h, and then worked up with ether and water to give a yellow oil, which on distillation afforded 2,2,5,7-*tetramethyl*-3,4-*dihydronaphthalen*-1(2H)-*one* (**19**) (8.4 g, 67%) as a colourless oil, b.p. 138—144 °C at 1.8 mmHg (Found: C, 83.0; H, 9.0. $C_{14}H_{18}O$ requires C, 82.8; H, 8.9%); $\nu_{max.}$($CHCl_3$) 1 680 and 1 605 cm^{-1}; $\lambda_{max.}$(MeOH) 232, 257, and 303 nm (ε 52 600, 10 300, and 2 070); δ($CDCl_3$) 1.18 (6 H, s, Me_2C), 1.97 (2 H, m, 2 × 3-H), 2.25 (3 H, s, ArMe), 2.31 (3 H, s, ArMe), 2.82 (2 H, m, 2 × 4-H), 7.17 (1 H, m, 6-H), and 7.73 (1 H, m, 8-H); *m/z* 202 (*M*, 44%), 187 (*M* − CH_3, 37), 159 (*M* − CH_3CO, 40), and 146 (*M* − C_4H_8, 100).

A mixture of the ketone (**19**) (7.3 g, 0.03 mol), *N*-bromosuccinimide (7.1 g, 0.04 mol), and benzoyl peroxide (0.8 g) in carbon tetrachloride was heated at reflux for 1 h. The mixture was filtered and the residue was washed with chloroform. The solvent was removed from the filtrate, and the residue was heated at reflux for 0.5 h in a 10% solution of potassium hydroxide in ethanol. The mixture was cooled, diluted with water, and the product isolated by means of ether. The oily residue (7.5 g) was distilled through a spinning band column (0.5 m) to give 2,2,5,7-*tetramethylnaphthalen*-1(2H)-*one* (**12**) (1.8 g, 26%), b.p. 133—138 °C at 1.8 mmHg (Found: C, 84.5; H, 8.1. $C_{14}H_{16}O$ requires C, 84.0; H, 8.0%); $\nu_{max.}$($CHCl_3$) 1 675, 1 640, and 1 602 cm^{-1}; $\lambda_{max.}$(MeOH) 233, 242, 314, and 345 nm (ε 20 100, 20 400, 1 330, and 1 140); δ($CDCl_3$) 1.26 (6 H, s, Me_2C), 2.35 (3 H, s, ArMe), 2.39 (3 H, s, ArMe), 6.08 (1 H, d, $J_{3,4}$ 9.9 Hz, 3-H), 6.69 (1 H, dd, $J_{3,4}$ 9.9 Hz, $J_{4,8}$ 0.8 Hz, 4-H), 7.12 (1 H, m, 6-H), 7.74 (1 H, m, 8-H); *m/z* 200 (*M*, 100%) and 185 (*M* − CH_3, 57).

Irradiation of 2,2,4-*Trimethylnaphthalen*-1(2H)-*one* (**3**).—A solution of the naphthalenone (**3**) (273 mg) in methanol (32 ml) was irradiated as described above for 18 h. The solvent was removed to yield an orange coloured oil, which was separated by p.l.c. in light petroleum–ether (9:1) into three fractions, the least polar of which was starting material (**3**). The second fraction, after further purification by p.l.c. in light petroleum–ether (17:3), afforded 1,1,1a-*trimethyl*-1,1a-*dihydrocycloprop*[a]*inden*-6(6aH)-*one* (**4**), as an oil (23 mg, 8.4%) (Found: M^+, 186.1042. $C_{13}H_{14}O$ requires *M*, 186.1044); $\nu_{max.}$($CHCl_3$) 1 695 and 1 604 cm^{-1}; $\lambda_{max.}$(MeOH) 226, 298, 310sh, and 350 nm (ε 16 000, 1 760, 1 380, and 386); δ($CDCl_3$) 0.81 (3 H, s, *endo*-1-Me), 1.28 (3 H, s, *exo*-1-Me), 1.71 (3 H, s, 1a-Me), 1.97 (1 H, s, 6a-H), and 7.22—7.76 (4 H, m, ArH); *m/z* 186 (*M*, 84%), 171 (*M* − CH_3, 100), and 143 (*M* − CH_3CO, 60).

The most polar fraction, 3,4,4-trimethylnaphthalen-1(4*H*)-one[5] (**5**), was obtained as an oil (55 mg, 20%); $\nu_{max.}$($CHCl_3$) 1 655, 1 625, and 1 600 cm^{-1}; $\lambda_{max.}$(MeOH) 254 and 291sh nm (ε 12 500 and 3 080); δ($CDCl_3$) 1.50 (6 H, s, 2 × 4-Me), 2.13 (3 H, d, $J_{allylic}$ 1.5 Hz, 3-Me, 6.34 (1 H, q, $J_{allylic}$ 1.5 Hz, 2-H), 7.21—7.76 (3 H, m, 5-H, 6-H, 7-H), and 8.02—8.33 (1 H, m, 8-H).

Irradiation of 2-(p-*Methoxyphenyl*)-2,4-*dimethylnaphthalen*-1(2H)-*one* (**8**).—A solution of the naphthalenone (**8**) (1.0 g) in methanol (100 ml) was irradiated for 1.75 h under the above conditions. The solvent was removed and the residual oil was fractionated by p.l.c. in light petroleum–ethyl acetate (4:1). The least polar material was further purified by p.l.c. in the same solvent system to yield exo-1-(p-*methoxyphenyl*)-1,1a-*dimethyl*-1,1a-*dihydrocycloprop*[a]*inden*-6(6aH)-*one* (**9**) (0.43 g, 43%) as colourless needles, m.p. 112—123 °C (from methanol) (Found: C, 81.8; H, 6.5. $C_{19}H_{18}O_2$ requires C, 82.0; H, 6.5%); $\nu_{max.}$ 1 705 and 1 605 cm^{-1}; $\lambda_{max.}$(MeOH) 231, 255sh, and 304sh nm (ε 30 500, 7 700, and 1 900); δ($CDCl_3$) 1.08 (3 H, s, 1-Me), 1.41 (3 H, s, 1a-Me), 2.64 (1 H, s, 6a-H), 3.81 (3 H, s, MeO), 6.88 and 7.21 (4 H, AA′BB′, 3′-H, 5′-H and 2′-H and 6′-H respectively), and 7.22—7.73 (4 H, m, ArH); *m/z* 278 (*M*, 100%), 263 (*M* − CH_3, 99), and 133(59).

Further purification of the second fraction by p.l.c. in the above solvent system afforded endo-1-(p-*methoxyphenyl*)-1,1a-*dimethyl*-1,1a-*dihydrocycloprop*[a]*inden*-6(6aH)-*one* (**10**) (0.12 g, 12%) as colourless prisms, m.p. 131—132 °C (from methanol) (Found: C, 81.7; H, 6.5. $C_{19}H_{18}O_2$ requires C, 82.0; H, 6.5%); $\nu_{max.}$($CHCl_3$) 1 705 and 1 605 cm^{-1}; $\lambda_{max.}$(MeOH) 225, 257sh, and 308sh nm (ε 26 100, 8 800, and 1 500); δ($CDCl_3$) 1.51 (3 H, s, 1-Me), 1.88 (3 H, s, 1a-Me), 2.36 (1 H, s, 6a-H), 3.61 (3 H, s, MeO), 6.51 and 6.87 (4 H, AA′BB′, 3′-H, 5′-H and 2′-H, 6′-H respectively), and 6.96—7.48 (4 H, m, ArH); *m/z* 278 (*M*, 100%), 263 (*M* − CH_3, 98), and 133(60).

The most polar material was purified by p.l.c. in the same solvent system as above to give 4-(p-*methoxyphenyl*)-3,4-*dimethylnaphthalen*-1(4H)-*one* (**11**) (0.27 g, 27%) as colourless prisms, m.p. 95—96 °C (from methanol) (Found: C, 82.2; H, 6.8. $C_{19}H_{18}O_2$ requires C, 82.0; H, 6.5%); $\nu_{max.}$($CHCl_3$) 1 655, 1 620, and 1 595 cm^{-1}; $\lambda_{max.}$(MeOH) 237 and 269sh nm (ε 22 100 and 12 000); δ($CDCl_3$) 1.78 (3 H, d, $J_{allylic}$ 1.3 Hz, 3-Me), 1.82 (3 H, s, 4-Me), 3.77 (3 H, s, MeO), 6.40 (1 H, q, $J_{allylic}$ 1.3 Hz, 2-H), 6.83 and 7.12 (4 H, AA′BB′, 3′-H, 5′-H and 2′-H, 6′-H respectively), 6.98—7.48 (3 H, m, 5-H, 6-H, 7-H), 8.18 (1 H, m, 8-H); *m/z* 278 (*M*, 100%), 263 (*M* − CH_3, 95), and 235 (*M* − CH_3CO, 22).

Irradiation of the Ketones (**9**) *and* (**10**).—(*a*) A solution of the *exo*-isomer (**9**) (65 mg) in methanol (10 ml) was irradiated as above for 10 h. The solvent was removed, and analysis of the residue by n.m.r. spectroscopy showed the presence of starting material (**9**) (80%) and naphthalen-1(4*H*)-one (**11**) (20%).

(*b*) A solution of *endo*-isomer (**10**) (55 mg) in methanol (10 ml) was irradiated as above for 4 h. The solvent was removed to yield the naphthalenone (**11**) (identical by t.l.c., and i.r. and n.m.r. spectra).

Irradiation of 2,2,5,7-*Tetramethylnaphthalen*-1(2H)-*one* (**12**).—(*a*) A solution of the naphthalenone (**12**) (0.70 g) in methanol (70 ml) was irradiated as above for 21 h. The solvent was removed to give an oily solid which was fractionated by p.l.c. in light petroleum–ether (22:3). The most polar material was further purified by p.l.c. in the same solvent system to yield 4-*methoxy*-3,3,5,7-*tetramethyl*-3,4-*dihydronaphthalen*-1(2H)-*one* (**14**) (0.167 g, 20%) as an oil (Found: M^+, 232.1458. $C_{15}H_{20}O_2$ requires *M*, 232.1463); $\nu_{max.}$(film) 1 680 and 1 605 cm^{-1}; $\lambda_{max.}$(MeOH) 262 and 306 nm (ε 9 360 and 1 900); δ($CDCl_3$) 0.78 (3 H, br s, axial 3-Me), 1.22 (3 H, s, equatorial 3-Me), 2.21 (1 H, dd, J_{gem} 17.7 Hz, $J_{2,4}$ 1.2 Hz, equatorial 2-H) 2.34 (3 H, br s, 7-Me, confirmed by irradiation of 6-H and 8-H), 2.44 (3 H, br s, 5-Me, confirmed by irradiation of 6-H and 8-H), 2.93 (1 H, dd, J_{gem} 17.7 Hz, $J_{axial\ 3\text{-}Me}$ 0.88 Hz, confirmed by decoupling, axial 2-H), 3.31 (3 H, s, MeO), 4.17 (1 H, dd, $J_{2,4}$ 1.2 Hz, $J_{4,8}$ 0.6 Hz, confirmed by decoupling, equatorial 4-H), 7.22 (1 H, br d, $J_{6,8}$ 1.95 Hz, 6-H), and 7.72 (1 H, br d, $J_{6,8}$ 1.95 Hz, coupling to 7-Me and 4-H confirmed by multiple irradiations, 8-H); *m/z* 232 (*M*, 47%), 217 (*M* − CH_3, 14), 177 (*M* − C_4H_7, 13), 176 (*M* − C_4H_8, 9), 161 (176 − CH_3, 100), and 133 (*M* − $C_6H_{11}O$, 68).

A solution of the tetralone (**14**) (108 mg) in methanol (5 ml) was treated under nitrogen with hydrochloric acid (10M; 15 ml) and the mixture was stirred at room temperature overnight. Dilution with water and extraction with chloroform afforded 1-*methoxy*-3,4,5,7-*tetramethylnaphthalene* (**15**) (87 mg, 89%), m.p. 97—98 °C (from methanol) (Found: C, 83.7; H, 8.5. $C_{15}H_{18}O$ requires C, 84.1; H, 8.4%); $\lambda_{max.}$(MeOH) 231, 240sh, 303, 322, and 337 nm (ε 38 600, 37 500, 6 320, 3 520, and 2 950);

$\delta(CDCl_3)$ 2.42 (6 H, s, 2 × Me), 2.66 (3 H, s, Me), 2.86 (3 H, s, Me), 3.96 (3 H, s, MeO), 6.60 (1 H, s, 2-H), 7.09 (1 H, br s, 6-H), and 7.91 (1 H, s, 8-H); *m/z* 214 (*M*, 100%) and 199 ($M - CH_3$, 59).

(*b*) A solution of the naphthalenone (**12**) (150 mg) in dry methanol (15 ml) was irradiated as above for 17 h. Potassium carbonate (70 mg) and dimethyl sulphate (250 mg) were added, and the mixture heated at reflux under nitrogen for 6 h. The solvent was removed under reduced pressure and ether (20 ml) was added. The solution was washed with water (10 ml), concentrated ammonia solution (10 ml), and finally with water (10 ml). Analysis of the product remaining on removal of the ether by n.m.r. spectroscopy, with methylene bromide as internal standard, showed it to contain the naphthalene (**15**) (47%) and the tetralone (**14**) (23%).

Acknowledgements

We acknowledge support from the A.R.G.S.

References

1 H. Greenland, J. T. Pinhey, and S. Sternhell, *J. Chem. Soc., Perkin Trans. 1*, 1986, 1789.
2 H. C. Bell, G. L. May, J. T. Pinhey, and S. Sternhell, *Tetrahedron Lett.*, 1976, 4303; H. C. Bell, J. T. Pinhey, and S. Sternhell, *Aust. J. Chem.*, 1979, **32**, 1551.
3 D. I. Schuster in 'Rearrangements in Ground and Excited States,' ed. P. de Mayo, Academic Press, New York, 1980, vol. 3, p. 255.
4 H. Hart and R. K. Murray, *J. Org. Chem.*, 1967, **32**, 2448.
5 H. Hart and R. K. Murray, *J. Org. Chem.*, 1970, **35**, 1535.
6 E. N. Marvel and A. O. Geiszler, *J. Am. Chem. Soc.*, 1952, **74**, 1259.
7 J. Frei, C. Ganter, K. Kägi, K. Kocsiś, M. Miljković, R. Siewinski, R. Wenger, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 1966, **49**, 1049.
8 O. L. Chapman, J. C. Clardy, T. L. McDowell, and H. E. Wright, *J. Am. Chem. Soc.*, 1973, **95**, 5086.
9 K. Schaffner and M. Demuth in 'Rearrangements in Ground and Excited States,' ed. P. de Mayo, Academic Press, New York, 1980, vol. 3, p. 290.
10 R. P. Kozyrod, J. Morgan, and J. T. Pinhey, *Aust. J. Chem.*, 1985, **38**, 1147, and references therein.
11 N. P. Buu-Hoi and D. Lavit, *J. Chem. Soc.*, 1955, 2776.
12 E. de Barry Barnett and F. G. Sanders, *J. Chem. Soc.*, 1933, 434.
13 H. C. Bell, J. R. Kalman, J. T. Pinhey, and S. Sternhell, *Aust. J. Chem.*, 1979, **32**, 1521.

Received 4th December 1985; *Paper* 5/2118