# Photochemical Reactions. Part II.[1] Cycloaddition Reactions with Photoenols from 2-Methylbenzaldehyde and Related Systems

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On photolysis, 2-methylbenzaldehyde can form the corresponding (E)-photoenol which can be trapped with dienophiles in a highly stereoselective manner. Maleic anhydride gives a single adduct (11), the reactions of which have been studied. From trapping experiments no evidence for the formation of (Z)-photoenol intermediates could be found. Ketones which cannot form (E)-photoenols for steric reasons do not form (Z)-photoenols. Both 2-benzylbenzaldehyde and 2-methylbenzoyl cyanide can undergo photoenolisation upon irradiation.

In Part I of this series[1] a new route to substituted naphthalenes, including members of the lignan family, was described. These reactions commenced with 2-substituted benzaldehydes but no examination of the photochemistry of the basic system or of the effect of ring substituents on the course of these reactions was made. In order to reach a better understanding of the scope of this synthetic route, a parallel series of experiments was carried out using the parent compound 2-methylbenzaldehyde (1). It was anticipated that the photochemistry of 2-methylbenzaldehyde would differ from that of benzaldehyde in that the presence of the 2-methyl group would allow intramolecular hydrogen abstraction to compete with the normal intermolecular reactions.[2] For intramolecular abstraction, the excited carbonyl group (in the $n \longrightarrow \pi^*$ triplet state) would lead to the new diradical (2) (Scheme 1). Although hydrogen reversion to the starting triplet diradical is a known process,[3] collapse to ground state species can also occur.[4] Amongst the initial products expected from

this process would be the dienols [e.g. (3) and (4)] and the cyclobutenol [e.g. (5)]. The dienol species are
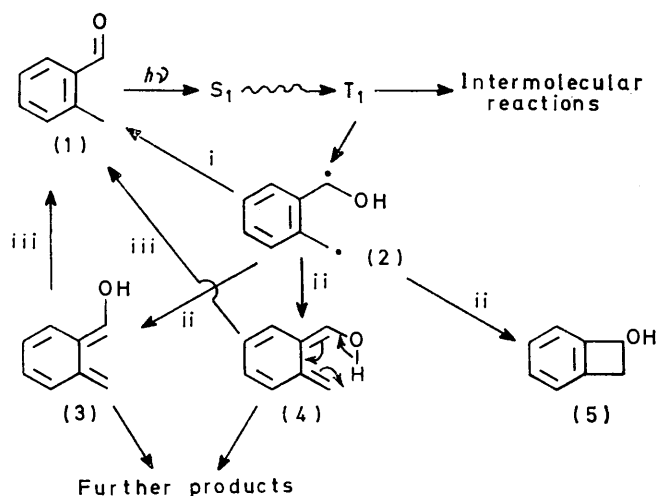
SCHEME 1 (i) Hydrogen reversion, (ii) possible biradical to ground state paths, (iii) proton transfers

[1] B. J. Arnold, S. M. Mellows, and P. G. Sammes, *J.C.S. Perkin I*, 1973, 1266.

[2] J. S. Bradshaw, R. D. Knudsen, and W. W. Parish, *J.C.S. Chem. Comm.*, 1972, 1321.

[3] P. J. Wagner, P. A. Kelso, and R. G. Zepp, *J. Amer. Chem. Soc.*, 1972, **94**, 7480; F. D. Lewis, *ibid.*, 1970, **92**, 5602.

[4] N. C. Yang and C. Rivas, *J. Amer. Chem. Soc.*, 1961, **83**, 2213; E. F. Zwicker, L. I. Grossweiner, and N. C. Yang, *ibid.*, 1963, **85**, 2671; N. D. Heindel, E. W. Sarver, and M. Pfau, *Tetrahedron Letters*, 1968, 3579.

known to be reactive towards dienophiles and such trapping reactions have been used as a chemical method for demonstrating the existence of these intermediates, especially from the photolysis of 2-substituted aromatic ketones.[4] In the absence of trapping agents the dienol species can revert to the starting carbonyl compounds by proton transfer. As a consequence of this decay process 2-alkylbenzophenones and related systems are reputed to have considerable (overall) stability towards irradiation.

In order to examine the stability of 2-methylbenzaldehyde towards irradiation it was photolysed in the absence of a dienophile. In benzene, using a quartz vessel, the aldehyde slowly disappeared with the formation of several new products. With tetrahydrofuran, or acetone, as solvent a much more rapid decay of the aldehyde was observed but in all cases the products were similar, being a mixture of dimers akin to the products obtained from the photolysis of benzaldehyde [2] and arising from intermolecular reactions. When the reaction was carried out in the presence of deuterium oxide, using acetone or benzene as solvent, and was stopped before complete disappearance of the starting aldehyde, the recovered material had not incorporated deuterium into the adjacent methyl group. Deuterium exchange would be expected if intermediate dienols present in the reaction mixture were reconverting rapidly into the starting aldehyde. This failure to observe deuterium exchange was in agreement with an earlier report [5] but does not rule out the existence of dienols under the photochemical reaction conditions since rapid, alternative fates for this species might predominate.[6] That this is the case with 2-methylbenzaldehyde was demonstrated by repeating the photolysis in the presence of a trapping agent. For example, irradiation of the aldehyde with an equimolar quantity of dimethyl butynedioate in dry benzene afforded one major, unstable product, the adduct (6), in 40% yield. The other products from this reaction consisted of dimers from the aldehyde and some non-polar polymeric material arising largely from the acetylenic ester. The structure of the adduct was proven by its ready dehydration to the naphthalene (7) by heating it in xylene in the presence of a trace of toluene-*p*-sulphonic acid. Furthermore, oxidation of the adduct (6) with manganese dioxide in benzene gave the corresponding naphthol (8). The rate of the trapping reaction, as followed by disappearance of the aldehyde, was virtually identical with the rate of reaction in the absence of the dienophile, which implies that the cycloaddition is efficient and depends on the rate of dienol formation. That the overall rate of the photochemical disappearance of the starting aldehyde was unaltered by the presence of the dienophile suggests that the latter does not interfere with the photochemical processes.

Of importance was the configuration of the dienol

intermediates. Photolysis of 2,4-dimethylbenzophenone is reported to produce two isomeric dienols (9; R = Me) and (10) upon flash photolysis [7] and these were distinguished by their lifetimes in aprotic and protic solvents

(6) (7)

(8) (9)

(10)
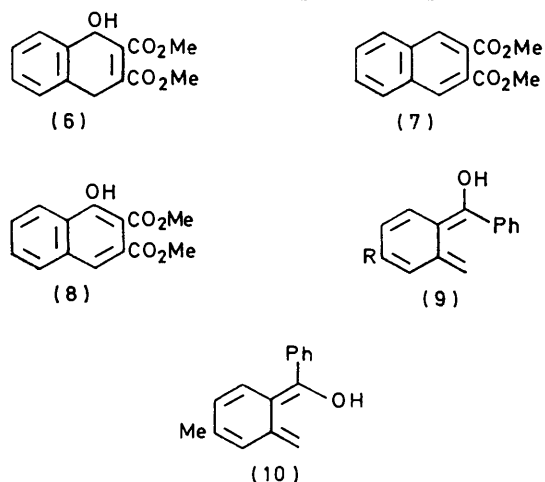
as well as by their disappearance in the presence of dimethyl butynedioate. In contrast, Nerdel and Brodowski reported [8] that only one dienol from 2-methylbenzophenone can be trapped, *viz.* the (E)-isomer (9; R = H) and, recently, Stevenson *et al.* have reported similar results using a variety of dienophiles.[9]

In order to examine the stereochemistry of the dienol species from 2-methylbenzaldehyde it was photolysed in the presence of maleic anhydride in dry acetone. One major adduct was isolated (50%) and shown to be the unstable hydroxy-anhydride (11).[10] On heating in tetrahydrofuran, either with or without a trace of sulphuric acid, the adduct isomerised into the acid lactone (12). Although a little of the acid lactone was

(11) (12)

(13) (14)
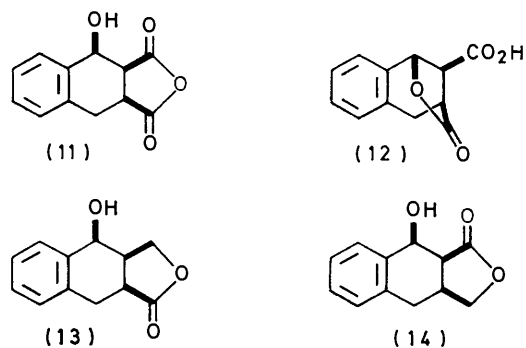
also detected amongst the photoproducts no stereoisomeric adducts could be found. The relative configuration of the initial anhydride (11) was determined as follows. Selective reduction of the acid lactone (12) with diborane [11] produced a new hydroxy-lactone (13). This was also obtained by direct reduction of the initial anhydride (11) with sodium borohydride, when (13) was produced together with the isomer (14). Since, in both

[5] G. Wettermark, *Photochem. Photobiol.*, 1965, **4**, 621.
[6] H.-D. Becker, *J. Org. Chem.*, 1967, **32**, 2140.
[7] G. Porter and M. F. Tchir, *J. Chem. Soc. (A)*, 1971, 3772.
[8] F. Nerdel and W. Brodowski, *Chem. Ber.*, 1968, **101**, 1398.
[9] E. Block and R. Stevenson, *J.C.S. Perkin I*, 1973, 308.
[10] S. M. Mellows and P. G. Sammes, *Chem. Comm.*, 1971, 21.
[11] *Cf.* G. Zweifel and H. C. Brown, *Org. Reactions*, 1963, **13**, 1.

the bicyclic lactone (12) and its reduction product (13), the hydroxy- and carboxy-groups of the lactone function must be *cis*-oriented, the initial anhydride (11) must have the stereochemistry depicted. The structures of the adduct and its transformation products were confirmed by a detailed ^{1}H n.m.r. examination. Molecular models indicate that the anhydride (11) can adopt one of two possible, preferred conformations with the alicyclic ring adopting a boat-like form, with the hydroxy-group in either a pseudo-axial or pseudo-equatorial position. Since the alcohol is intramolecularly hydrogen-bonded, probably to the adjacent carbonyl group, it is most likely in the pseudo-equatorial position. In this conformation the torsion angle between the protons at positions 1 and 2 is *ca.* 40° and would lead to an expected coupling constant of *ca.* 4 Hz, as is observed. The bicyclic lactone (12) (studied as its methyl ester) has a rigid structure in which the protons H(1),H(2) and H(2),H(3) are virtually orthogonal to one another, leading to the observed coupling constants of $J_{1,2}$ 0 and $J_{2,3}$ 0 Hz, with $J_{1,3}$ 1·5 Hz, arising from allylic (W) coupling.[12]

The ratio of the yields of the alcohols (13) and (14), arising from the reduction of the anhydride (11), varied with the reducing agent; with sodium borohydride it was 2 : 1, whilst with lithium aluminium hydride at —55° it was 1 : 2. The former lactone (13) was soluble in non-polar solvents whereas the latter isomer (14) was very insoluble in most solvents, as well as being more polar than its isomer to t.l.c. on silica gel. These effects are attributed to the presence of the intramolecular hydrogen bond in the lactone (13). The mass spectra of these two lactones also differed. The base peak of the non-polar isomer (13) occurred at *m/e* 142 [6% in (14)] corresponding to loss of water and carbon dioxide, whilst in the lactone (14) the base peak occurred at *m/e* 120 [52% in (13)] arising by a retro-Diels–Alder fragmentation of the alicyclic ring. A prominent peak at
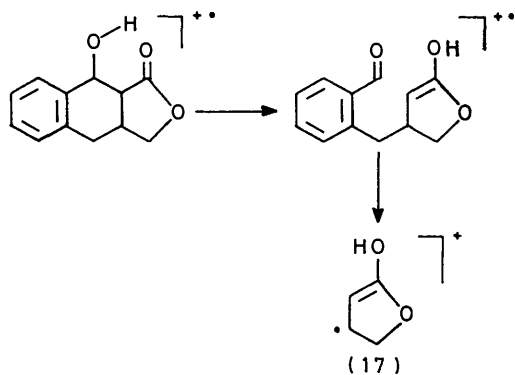
SCHEME 2

m/e 85 occurs in the spectrum from the lactone (13) (56%), assigned to the fragment (17) by the process indicated (Scheme 2), but this peak is only weak (13%) in its isomer. Both of the alcohols could be acetylated

by acetic anhydride in pyridine but oxidation with manganese dioxide was only successful for the alcohol (14) to give the keto-lactone (15).

Methylation of the lactone acid (12) with diazomethane gave the corresponding ester. In an attempt to epimerise about the methoxycarbonyl junction it was treated with 1 mol. equiv. of sodium hydride in dry tetrahydrofuran. Isolation, by acidification, did not afford the expected epimer but, instead, gave an acid shown to be the dihydronaphthoic acid (16; R = H) and formed by a β-elimination. A similar reaction occurred by using 1,5-diazabicyclonon-5-ene as base, when the corresponding ester (16; R = Me) formed.

The gross stereochemical deduction from these correlations is that the adduct (11) arises by *endo*-addition of maleic anhydride to the (*E*)-dienol (18; $R^1 = R^2 =$ H). The only alternative pathway leading to the same stereochemical result would involve the less favoured [13] *exo*-addition to the (*Z*)-dienol (4). Since only one adduct could be detected the former mode of addition is

(15)

(16)

(18)
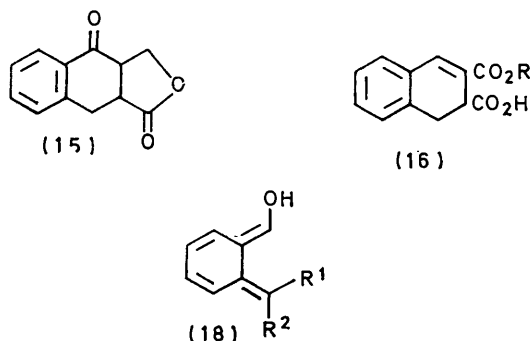
favoured. The question raised by these deductions is ' how does the (*E*)-dienol form? ' Abstraction of an internal hydrogen atom from the adjacent methyl group demands a *syn*-relationship between this group and the excited carbonyl function. Presumably a similar relationship must hold immediately after hydrogen abstraction to give the new diradical (2). Rotation about the HOCH–ring bond to produce the (*E*)-dienol (18; $R^1 = R^2 =$ H) must therefore occur either immediately prior to or *during* collapse to the ground state. The detailed mechanisms whereby excited electronic states can relax to the ground state are the subject of much attention [14] but for processes where there is spin–orbital coupling (such as in $n \longrightarrow \pi^*$ triplet processes) asymmetric rotation about bond axes has been proposed as one mechanism for travelling through the ground state and excited state energy surface. Such arguments have been used, for example, in explaining the thermal conversion of dioxetans into excited state products.[15] Ullman *et al.*[16] have studied

[12] L. M. Jackman and S. Sternhell, ' Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, Oxford, 1969, p. 334.

[13] K. Alder and G. Stein, *Angew. Chem.*, 1937, **50**, 510; *cf.* ' The Chemistry of Alkenes,' ed. S. Patai, Interscience, New York, 1964, p. 910.

[14] L. Salem and C. Rowland, *Angew. Chem. Internat. Edn.*, 1972, **11**, 92.

[15] N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, 1973, **95**, 264.

[16] K. R. Huffman, M. Loy, and E. F. Ullman, *J. Amer. Chem. Soc.*, 1965, **87**, 5417.

the photoenolisation of the chromone (19), which produces the enol (20). They concluded that bond rotation to give the *trans*-dienol (20) occurs before

(19)   (20)
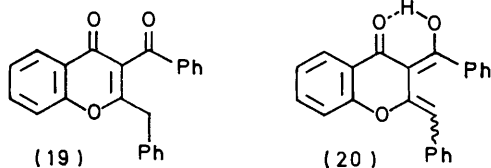
collapse to the ground state and not as a consequence of a secondary *cis*- to *trans*-isomerisation process.

Recent work [17] on the photochemistry of 1-(*o*-alkyl-phenyl)propane-1,2-diones involving chiral *o*-alkyl groups

well known route for the decay of excited state aryl alkyl ketones.[3] Explanations based on the formation of twisted ground state dienes (see Scheme 3) do not lead to the observed products if a thermal, conrotatory process is considered. For the case (Scheme 1) of the dienol biradical (2), the transient cyclobutenol (5) formed cannot undergo ring expansion but, because it is in a vibrationally hot state, could open thermally by an electrocyclic process to produce the (*E*)-dienol (3). The conrotatory ring opening of simple, monosubstituted cyclobutenes is known to produce preferentially the (*E*)-dienes.[19] Such a mechanism would also predict the formation of small quantities of benzocyclobutenol during the irradiation of 2-methylbenzaldehyde. Since
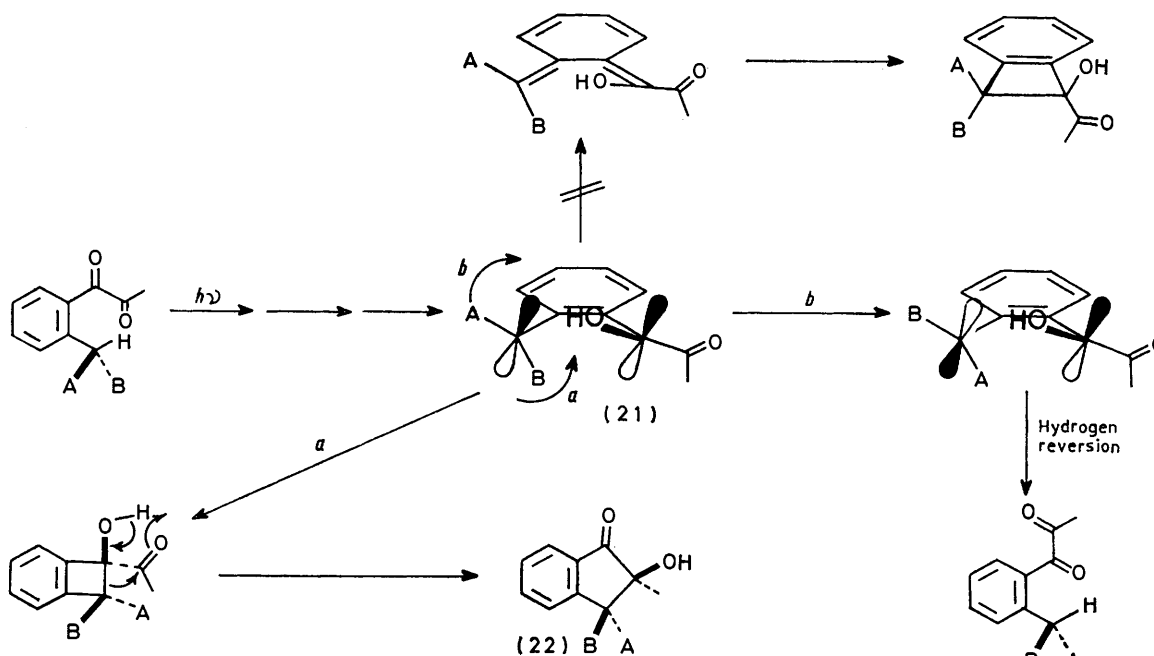
SCHEME 3

gave products with inversion of configuration about the alkyl substituent and competing racemisation of the starting material. It was suggested that the initially formed triplet biradical (21) (Scheme 3) undergoes bond rotation (*e.g. a*) about the substituent axes until a bonding configuration is attained. The first situation reached involves transient formation of a cyclobutenol intermediate. Since the system is vibrationally ' hot ' as a result of passing from an excited to a ground state, it may react further and, in this case, can undergo a concerted ring expansion to give the observed product (22) in which net inversion about the *o*-alkyl group has occurred. In the alternative rotation mode [see (21), mode *b*] the first bonding orientation reached results in hydrogen reversion, with net inversion about the alkyl group and hence racemisation of starting material.[18] The process, excited ketone to triplet biradical followed by hydrogen reversal to the ground state ketone, is a

only dimeric products could be detected under the normal (*ca.* 0·1M) conditions, photolysis of a more dilute solution (0·003M) was attempted in order to disfavour bimolecular reactions. Under these conditions small quantities of benzocyclobutenol (5) could be detected. Conducting the irradiation at −70° appeared to effect a slight increase in the yield of benzocyclobutenol probably both by increasing the viscosity of the reaction medium and by further frustrating bimolecular reactions.

The formation of benzocyclobutenols during the photolysis of aromatic ketones has been noted previously.[20] In an extensive study of 2,4,6-trialkylphenyl-ketones,[21] Kitaura and Matsuura noted that cyclo-butenol formation was often the preferred course of the reaction. Because deuterium exchange into the *ortho*-alkyl groups was noted however, they deduced that the dienols were the first species formed and that these then

[17] R. Bishop and N. K. Hamer, *J. Chem. Soc.* (*C*), 1970, 1193.
[18] N. K. Hamer and C. J. Samuel, *J.C.S. Chem. Comm.*, 1972, 470.

[19] *Cf.* R. E. K. Winter and M. L. Honig, *J. Amer. Chem. Soc.*, 1971, **93**, 4610.
[20] T. Matsuura and Y. Kitaura, *Tetrahedron*, 1969, **25**, 4487.
[21] Y. Kitaura and T. Matsuura, *Tetrahedron*, 1971, **27**, 1597.

underwent ring closure to give the cyclobutenols. Since this result would not explain the formation of optically active products (see above) and can be equally well explained by the reverse sequence (hot cyclobutenol to dienol) the above mechanism is still viable.

The possibility of (Z)-dienol formation in these photoreactions also has to be considered. As indicated above, no cyclo-adducts from such species have so far been isolated. It could be argued either that the 1,5-sigmatropic reaction [arrows in (4)] leading back to the starting aldehyde proceeds much faster than the rate of trapping by a dienophile, or that (Z)-dienol intermediates are highly unfavoured species. It should be noted that the thermal, electrocyclic opening of substituted benzocyclobutenols has been shown to exhibit a strong aversion to the process leading to (Z)-dienol formation.[22]

failed. An alternative structure which might explain these facts is the dihydrodibenzopyrene (26). It can be concluded from these results that more detailed work has to be carried out in order to prove, or disprove, the transient existence of (Z)-oriented dienols in these photoreactions.

Two systems in which formation of the (E)-dienol is restricted during photolysis involve the α-tetralone (27; $n = 3$) and the benzocycloheptenone (27; $n = 4$). Ring strain dictates, in these systems, that only the (Z)-dienols should be capable of existence. Photolysis of the α-tetralone (27; $n = 3$) in either benzene or ether and either alone or in the presence of maleic anhydride or dimethyl butynedioate gave, as the only isolable product, the dimer (28). When the photolysis was carried out in the presence of oxygen, the resulting mixture gave a positive peroxide test. The [1]H n.m.r.

(23)   (24)   (25)   (26)   (27)

(28)   (29)   (30)   (31)   (32)
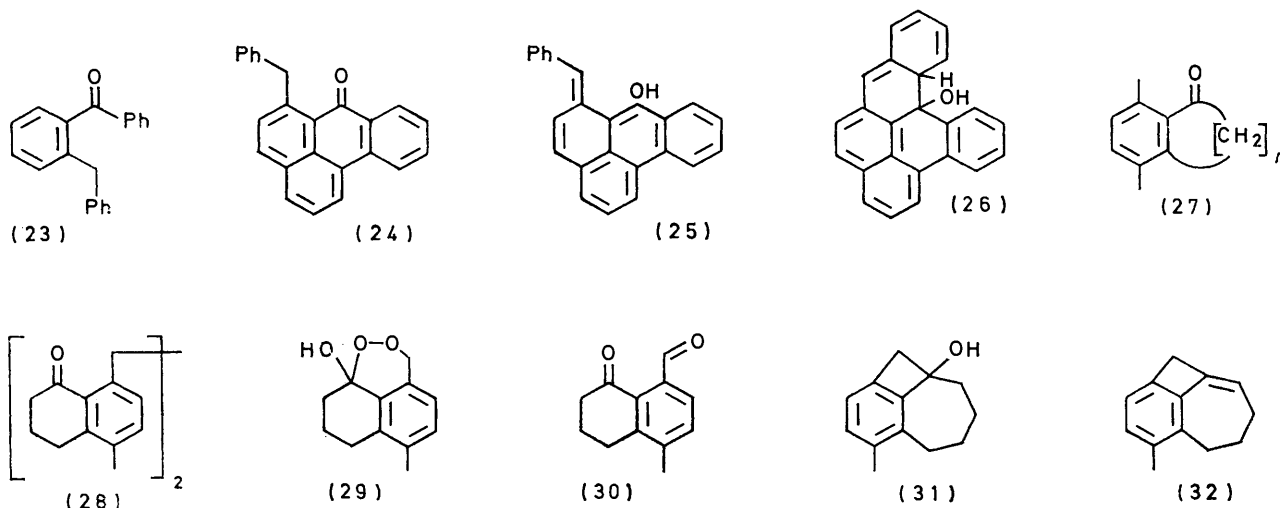
The available evidence for the formation of (Z)-dienols in photoreactions is very limited, arising mainly from flash photolysis experiments. Porter and Tchir[7] reported that 2,4-dimethylbenzophenone gave two dienols of lifetimes (cyclohexane) 250 and 4 s, corresponding to the (E)- and (Z)-dienols respectively. Since the relative rates of dienol trapping with dimethyl butynedioate were very fast compared to their estimated lifetimes, the formation of two adducts might be expected in the relevant trapping reactions. Since they are not, some doubt is thrown on the spectroscopic assignment for the (Z)-dienol. The observation that 2-benzylbenzophenone (23) only gives two dienols is to be expected if only the (E)-dienol forms; there are a total of four possible isomers from this ketone.[7] Another reaction which at first sight appears to demand the transient existence of a (Z)-dienol species involves the photolysis of 6-benzylbenzanthrone (24).[16] This compound produces a coloured transient at low temperatures and it also incorporates deuterium into the benzylic group by photolysis in the presence of deuteriomethanol. The dienol structure (25) was assigned to this intermediate but attempts to trap it in cycloaddition reactions

spectrum of the mixture revealed a signal at τ 4·50, 5·03 (ABq, J 16 Hz) which could be assigned to the arylmethylene group of the peroxide (29), or a polymer thereof. Treatment of these products with base before isolation yielded a small amount of the aldehyde (30). It can be concluded that, whilst hydrogen abstraction from the adjacent methyl group proceeds to the biradical species, which can be trapped by oxygen, it either does not collapse to the (Z)-dienol or, if it can, the ground state 1,5-hydrogen shift back to the starting ketone is extremely fast. No cyclobutenol formation was noted in this case, but it could be that the resulting product is too strained.[17] Photolysis of the benzocycloheptenone (27; $n = 4$) also proceeded smoothly but again, in the presence of dienophiles, did not lead to any adducts. Instead, the isomeric cyclobutenol (31) formed. Heating the pure alcohol in the presence of maleic anhydride at 110° for 42 h did not give an adduct. Use of higher temperatures smoothly converted it into the olefin (32). Again, therefore, no evidence for formation of the (Z)-dienol can be found.

[22] B. J. Arnold and P. G. Sammes, *J.C.S. Chem. Comm.*, 1972, 1034.

The practical consequence of the failure to trap (Z)-dienol intermediates in cycloaddition reactions is to allow stereoselective formation of products from the (E)-dienol only.

(33)   (34)

Two further systems have been irradiated. A brief examination of the products from the cycloaddition of

maleic anhydride, using benzene as solvent, afforded an unstable adduct, probably as (37). Since cyanohydrin derivatives of α-tetralones are known to be unstable, the crude photolysis product was immediately treated with aqueous sodium hydrogen carbonate to give a base-soluble product. Re-acidification yielded the carboxylic acid (38). Presumably liberation of the ketone is accompanied by hydrolysis of the anhydride group and subsequent decarboxylation of the β-keto-acid. The acid (38) must arise as a result of photoenolisation and trapping of the starting benzoyl cyanide (36). The
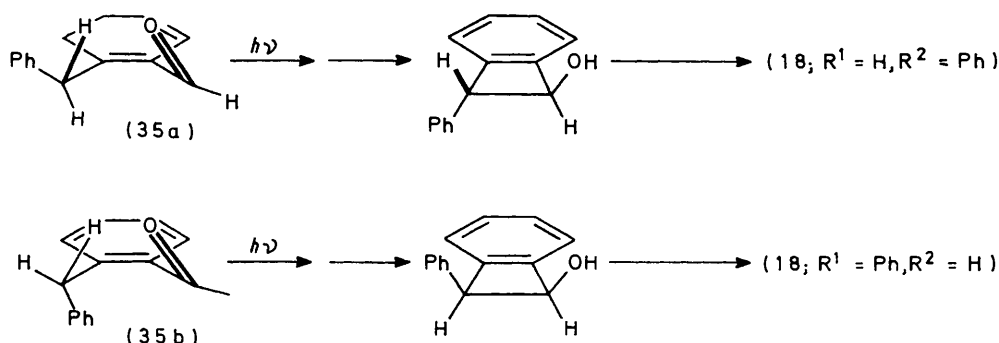

SCHEME 4

the photoenols from 2-benzylbenzaldehyde and maleic anhydride has been made. In acetone, photolysis proceeded rapidly to give a mixture of two isomeric hydroxy-anhydride adducts. In order to separate these unstable compounds they were heated in toluene, when they were converted into the corresponding lactone acids (33; R = H) and (34; R = H) and then methylated with diazomethane to give the esters (33; R = Me) and (34; R = Me). The ratio was 4 : 1. The lactonisation step confirms the cis-disposition about positions 1 and 3. A careful ^{1}H n.m.r. examination allowed tentative structural assignments to be given to the products. The adducts must arise by endo-addition of maleic anhydride to the dienols (18; R^1 = H, R^2 = Ph) and (18; R^1 = Ph; R^2 = H). The ratio of the two adducts must reflect the relative populations of the ground state conformations at which hydrogen transfer to the excited carbonyl group occurs. In this case these can be represented by the structures (35a) and (35b) (and their mirror images) leading to the dienols (18; R^1 = H; R^2 = Ph) and (18; R^1 = Ph, R^2 = H), respectively, possibly via their transient cyclobutenol counterparts (Scheme 4) (cf. Scheme 3).

Finally, the photochemistry of 2-methylbenzoyl cyanide (36) has been examined. The ketone was obtained by oxidation of the cyanohydrin derived from 2-methylbenzaldehyde, using manganese dioxide in benzene as oxidant. It was anticipated that if photo-enolisation occurred from this species, subsequent cyclo-additions would lead to a cyanohydrin and hence, by hydrolysis, to the corresponding ketone. In the event, photolysis of the aroyl cyanide (36) in the presence of

electronic effect of the nitrile group on the photochemical behaviour of the adjacent ketone group is of interest and is comparable to photoenolisation studies made with α-diketones [17] and phenylglyoxylates.[23]

(36)   (37)   (38)
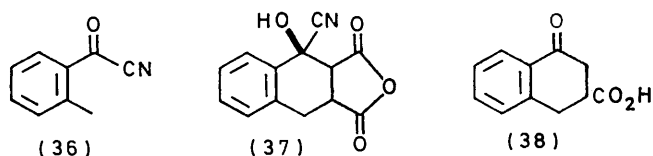
EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. I.r. spectra were recorded on a Unicam SP200 spectrophotometer and u.v. spectra with a Unicam SP800 instrument, using ethanolic solutions. ^{1}H N.m.r. spectra were determined on either a Varian A60 or T60 instrument, generally for solutions in [^{2}H]chloroform containing tetramethylsilane as internal reference. Solvents were distilled and dried before use. Anhydrous sodium sulphate was used to dry extracts. T.l.c. was carried out on silica gel GF$_{254}$, normally using benzene, ethyl acetate, or acetone mixtures. Irradiations were carried out using medium pressure mercury lamps (450 or 125 W) and quartz or Pyrex reaction vessels. Solutions were purged with nitrogen before and during photolysis.

Irradiation of 2-Methylbenzaldehyde with Dimethyl Butynedioate.—The aldehyde (2·4 g) in benzene (100 ml) containing dimethyl butynedioate (2·8 g) was irradiated with the 450 W lamp in a quartz vessel for 3 h. The solvent was removed *in vacuo* and the residue crystallised from 1 : 1 benzene–light petroleum to give needles of *dimethyl 1,4-dihydro-1-hydroxynaphthalene-2,3-dicarboxylate* (6) (2·0 g, 40%), m.p. 114—115°, ν$_{max.}$ (Nujol) 3400 and 1720 cm^{-1}, λ$_{max.}$ (cyclohexane) 231 nm (ε 5000), τ 2·4—2·9 (4H, m, aromatic), 4·51 (1H, m, ArCHO), 6·17 and 6·51 (2H, distorted ABq, coupled to the proton at 4·51, ArCH_2),

[23] S. P. Pappas, B. C. Pappas, and J. E. Blackwell, *J. Org. Chem.*, 1967, **32**, 3066.

6·22 and 6·25 (2 × MeO), and 7·16br (1H, exchanged with D_2O, HO) (Found: C, 64·2; H, 5·3. $C_{14}H_{14}O_5$ requires C, 64·1; H, 5·4%).

Heating the alcohol (6) (0·10 g) in dry xylene (2 ml) containing a few mg of toluene-p-sulphonic acid, for 6 h gave a new product, characterised as the diester (7) (0·06 g, 60%), m.p. 49—50° (lit.,[24] 47°), $v_{max.}$ 1720 and 1710 cm^{-1}.

Oxidation of the crude reaction product, obtained from irradiation of the aldehyde (0·23 g) and the acetylene (0·28 g), using freshly dried manganese dioxide (1·0 g) in benzene at room temperature for 12 h gave, by p.l.c., two products. The less polar compound was the naphthalene (6) (0·23 g, 40%) whilst the more polar product was *dimethyl* 1-*hydroxynaphthalene*-2,3-*dicarboxylate* (8) (0·10 g, 20%), m.p. 145—160° (decomp.), $v_{max.}$ (Nujol) 3400—3200br,w, 1730, and 1665 cm^{-1}, $\lambda_{max.}$ (cyclohexane) 238sh, 252 (ε 25,000), 260 (25,000), 289 (4000), 297 (4000), 310 (4000), 333sh, 347 (5000), and 355 nm (5600), τ 1·5—1·6 (1H, m, aromatic), 2·4—2·8 (4H, m, aromatic), 6·16 and 6·70 (2 × MeO), −2·23 (1H, exch. with D_2O) (Found: C, 64·8; H, 4·7. $C_{14}H_{12}O_5$ requires C, 64·6; H, 4·65%).

Irradiation of 2-Methylbenzaldehyde in the Absence of Dienophiles.—(a) *In acetone.* The aldehyde (0·4 g) in acetone (40 ml) containing deuterium oxide (5 ml) was irradiated in a quartz vessel, aliquot portions being withdrawn at intervals. After 90 min all the aldehyde had disappeared. N.m.r. examination of the recovered aldehyde from the aliquot portions showed no deuterium incorporation.

(b) *In benzene.* The aldehyde (1·0 g) in benzene (100 ml) saturated with deuterium oxide was irradiated in both quartz and Pyrex vessels. In neither case was incorporation of deuterium into the methyl group observed. The reaction was repeated in the absence of deuterium oxide and the products isolated by preparative t.l.c. Three compounds were isolated and briefly examined. The most polar material had $v_{max.}$ (CHCl$_3$) 3500, 1690, and 1610 cm^{-1}, τ 2·4—3·2 (*ca.* 8H, m, aromatic), 4·89 (1H, s), 5·12 (1H, s), 7·89 (3H, s), 8·38 (3H, s), and an exchangeable proton at 6·5—8·0, m/e 239, 221, 195, 178, 121, 119, and 91. The next compound had $v_{max.}$ (CHCl$_3$) 3500, 1690, 1605, and 1580 cm^{-1}, τ −0·2 (1H, s, aldehyde), 2·0—3·0 (8H, m, aromatic), 5·39 (2H, s, ArCH_2), and 7·55 (3H, s), m/e 238, 221, 178, 119, and 91. The least polar product had $v_{max.}$ (CHCl$_3$) 1680, 1605, and 1580 cm^{-1}, τ 2·2—2·9 (8H, m, aromatic) and 7·32 (6H, s, Me), m/e 238, 119, and 91. All three products are therefore dimers, the latter being compatible with 2,2′-dimethylbenzil.

(c) *In dilute solution.* The aldehyde (60 mg) in benzene (200 ml) was irradiated with the 450 W lamp at room temperature for 35 min. The solvent was evaporated off to yield a viscous oil. Comparison with an authentic sample of 1,2-dihydrobenzocyclobuten-1-ol [25] (5) on t.l.c. indicated a component of the same R_F. N.m.r. examination of the products showed the presence of the characteristic pattern due to the alcohol [τ 4·87 (1H, dd, J 2 and 5 Hz), 6·4 (1H, dd, J 2 and 14 Hz), and 7·1 (1H, dd, J 5 and 14 Hz)]. Isolation of the material corresponding to the alcohol and treatment with 0·25N-sodium hydroxide at room temperature for 1 h [26] gave the characteristic odour of the aldehyde, previously absent. An estimated 10% of the benzocyclobutenol had formed.

Repetition of the photolysis, at the same concentration

but using acetone as solvent and at −60 to −70° gave a similar result, the estimated yield of the alcohol being *ca.* 15%.

Irradiation of 2-Methylbenzaldehyde with Maleic Anhydride.—Freshly sublimed maleic anhydride (2·5 g) and 2-methylbenzaldehyde (3·0 g) in dry acetone (100 ml) contained in a quartz vessel were irradiated with a medium pressure mercury lamp (125 W) for 8 h. The acetone was removed *in vacuo* and the residue triturated with dichloromethane to give a white precipitate. The solid was collected and recrystallised from benzene–ethanol to give white needles of 1,2,3,4-*tetrahydro*-c-1-*hydroxynaphthalene*-r-2,c-3-*dicarboxylic anhydride* (11) (2·6 g, 50%), m.p. 118—135° (decomp.), $v_{max.}$ (Nujol) 3500—3000, 1840, and 1760 cm^{-1}, τ [CDCl$_3$ containing a few drops of (CD$_3$)$_2$SO] 2·67 (4H, aromatic), 4·80 (1H, d after D_2O exchange, J 4 Hz, ArCHO), 5·1 (1H, exchanged with D_2O, HO), and 6·6 (4H, m, bridge and benzylic protons) (Found: C, 66·2; H, 4·7. $C_{12}H_{10}O_4$ requires C, 66·05; H, 4·6%).

Heating the anhydride (11) (0·50 g) in tetrahydrofuran (6 ml), either with or without added 2N-sulphuric acid (2 ml) rapidly gave an isomeric product. Ether extraction of the solution, using aqueous washings, followed by drying and evaporation afforded a pale yellow oil. Trituration with dichloromethane and recrystallisation of the solid from benzene–ethanol gave 1,2,3,4-*tetrahydro*-c-1-*hydroxynaphthalene*-r-2,c-3-*dicarboxylic acid* 3,1-*lactone* (12) (0·40 g, 80%), m.p. 160—164°, $v_{max.}$ 3500—2500, 1780, and 1720 cm^{-1}, τ −0·50 to 2·0br (1H, exchangeable, CO$_2$H), 2·7 (4H, m, aromatic), 4·4br (1H, s), and 6·75 (4H, m). This acid was characterised as its *methyl ester*, obtained by methylation with an excess of diazomethane in ether, m.p. 91—92°, $v_{max.}$ (CHCl$_3$) 1780 and 1735 cm^{-1}, τ 2·8 (4H, m, aromatic), 4·54 (1H, d, J 1·5 Hz, 1-H), 6·24 (3H, s, MeO), 6·66 (1H, m, 3-H), and 6·68 (3H, m, 2-H and 4-H$_2$), τ (C$_6$D$_6$) 3·0—3·4 (4H, m, aromatic), 4·83 (1H, d, J 1·5 Hz, 1-H), 6·7 (3H, s, MeO), 6·97 (1H, m, 3-H), 7·35 (2H, m, 4-H$_2$), and 7·48 (1H, s, 2-H). Decoupling experiments showed $J_{1,2}$ 0, $J_{2,3}$ 0, and $J_{1,3}$ 1·5 Hz (Found: C, 67·0; H, 5·5. $C_{13}H_{12}O_4$ requires C, 67·2; H, 5·2%).

Reduction of the Acid Lactone (12).—Diborane (1·33 mmol), prepared from sodium borohydride and boron trifluoride–ether, was distilled into tetrahydrofuran (THF) (10 ml) containing the acid lactone (12) (0·12 g, 1 mmol) at 0°. After 2 h, 2N-sulphuric acid was added, and the solution was stirred for a further 1 h at 0° before addition of ether and extraction, using water for the washing. The dried ether extract was evaporated to give 3aα,4,9,9aα-*tetrahydro*-4β-*hydroxynaphtho*[2,3-c]*furan*-1(3H)-*one* (13) (0·05 g, 40% *ex* p.l.c.), m.p. 172—177°, $v_{max.}$ (Nujol) 3500—3400, 1760, and 1740 cm^{-1}, τ [(CD$_3$)$_2$SO] 2·4—2·9 (4H, m, aromatic), 5·2br (1H, d, J 4 Hz, 1-H), 5·7 and 5·9 (2H, m, CH·CH_2·O), 6·7 (2H, m), and 7·0 (2H, m, 4-H$_2$), m/e 204 (M^+), 186, 142, 129, 120, 119, 91, and 85 (Found: C, 70·6; H, 6·1. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%).

Reduction of the Hydroxy-anhydride (11).—(a) *With lithium aluminium hydride.* A solution of the anhydride (0·20 g) in dry THF (8 ml) was added to a suspension of lithium aluminium hydride (0·06 g) in THF (2 ml) at −55° with stirring. The mixture was allowed to warm to room temperature over 1 h before adding 2N-H$_2$SO$_4$ until the solution was just acidic. After a further 1 h ether was

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[26] R. G. Kadesch, *J. Amer. Chem. Soc.*, 1944, **66**, 1207.

added and the organic phase separated and washed with water, dried, and evaporated to dryness. The products were separated by p.l.c. to give two products. The major, less polar compound was 3aα,4,9,9aα-*tetrahydro*-9β-*hydroxynaphtho*[2,3-c]*furan*-1(3H)-*one* (14) (0·06 g, 30%), m.p. 128—129°, $\nu_{max.}$ (Nujol) 3480 and 1740 cm^{-1}, τ 2·7—3·0 (4H, m, aromatic), 5·1 (1H, m, 1-H), 5·5 and 6·2 (2H, two m), 6·28 (1H, d, J 5 Hz, OH), 6·8 (2H, m), and 7·3 (2H, m), τ (C_6D_6) 2·9 (4H, m, aromatic), 5·45 (1H, m, 1-H), 6·3 and 6·7 (2H, m, $-CH_2O-$), 7·5 (1H, m, 2-H), 7·9 (1H, m, 3-H), and 8·0br (2H, s, 4-H$_2$), m/e 204 (M^+), 186, 145, 144, 142, 141, 129, 128, 120, 119, and 85 (Found: C, 70·7; H, 6·0. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%).

The more polar product from the t.l.c. separation was the isomeric lactone (13) (0·03 g, 15%), m.p. 172—177°.

(b) *With sodium borohydride.* The anhydride (11) (0·20 g) in dry THF (10 ml) and dry propan-2-ol (4 ml) was stirred with sodium borohydride (0·06 g) at room temperature overnight before adding 2N-H$_2$SO$_4$ and working up as above. P.l.c. afforded the lactones (13) (0·075 g, 35%) and (14) (0·05 g, 25%).

Acetylation of the Lactones (13) *and* (14).—The lactones were separately acetylated in benzene (3 ml) containing acetic anhydride (0·5 ml) and pyridine (0·5 ml) using 0·1 g amounts. After 48 h at room temperature the mixtures were worked up in the normal manner and the esters recrystallised from benzene–light petroleum. The *acetate* from the lactone (13) had m.p. 141—145° (Found: C, 68·15; H, 5·8. $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·7%). The *isomeric acetate*, derived from the lactone (14), had m.p. 146—148° (Found: C, 68·2; H, 5·8%).

Oxidation of the Lactone (13).—The lactone (0·5 g) was dissolved in benzene (10 ml) and the minimum of dimethylformamide (to obtain homogeneity) and the mixture was refluxed in the presence of manganese dioxide (0·3 g) for 2 h. The solids were then removed by filtration and the filtrate evaporated *in vacuo* to afford a yellow solid, which crystallised from benzene–ethanol as colourless needles of 3,3aα,9,9aα-*tetrahydronaphtho*[2,3-c]*furan*-1,4-*dione* (15) (0·26 g, 55%), m.p. 146—147°, $\nu_{max.}$ (Nujol) 1760 and 1685 cm^{-1}, τ 2·1—2·7 (4H, m, aromatic), 5·3 and 5·7 (2H, m, $-CH_2O-$), and 6·7 (4H, m) (Found: C, 71·2; H, 5·1. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·0%).

Basic Treatment of the Methyl Ester from the Acid (12).— The lactone ester (0·05 g) in dry THF (5 ml) was treated at room temperature with sodium hydride (25 mg). After 3 h the mixture was poured into water, extracted with ether, acidified and the aqueous layer re-extracted with ether to afford an acid. This material was not fully characterised but it showed τ 2·8 (5H, m, aromatic and vinylic H), 7·0 (1H, m, CH·CO$_2$H), and 7·5 (2H, m, Ar·CH$_2$) consistent with structure (16; R = H), M^+ 218.

When the reaction was repeated, using diazabicyclononene as the base, a different acid formed, shown, by n.m.r. analysis to be the methyl ester (16; R = Me).

Irradiation of 5,8-*Dimethyl*-1-*tetralone* (27; $n = 3$).— Freshly prepared tetralone [26] was irradiated under the following conditons: (a) *In ether.* The ketone (380 mg) in ether (40 ml) was irradiated in Pyrex, using a 450 W medium pressure lamp, for 2 h. The solution was evaporated and the residue triturated with ether–light petroleum to give 3,3',4,4'-*tetrahydro*-5,5'-*dimethyl*-8,8'-*ethylenedinaphthalen*-1(2H)-*one* (28) (50 mg), m.p. (CHCl$_3$–hexane) 251— 252°, $\nu_{max.}$ (Nujol) 1670, 1575, 1330, 1280, and 855 cm^{-1}, $\lambda_{max.}$ 217, 254, and 309 (ε 42,600, 15,800, and 5400), τ 2·56br

(4H, s, aromatic), 6·74 (4H, s, ArCH$_2$), 6·9—7·5 (8H, m), 7·6—8·1 (4H, m), and 7·69 (6H, s, Me), m/e 346 (M^+) and 173 (base peak) (Found: C, 82·9; H, 7·4. $C_{24}H_{26}O_2$ requires C, 83·2; H, 7·6%). The residue from the reaction mixture showed the presence of starting material and traces of more polar components.

(b) *In benzene.* Under similar conditions, but using benzene as solvent a similar result was obtained. When the irradiation of the ketone (308 mg) in benzene (40 ml) was carried out in the presence of dimethyl butynedioate (330 mg, 2·3 equiv.) only the dimer could be detected and no adducts were isolated by p.l.c.

(c) *In benzene with oxygen.* The tetralone (140 mg) was irradiated in benzene solution (40 ml) whilst passing a stream of pure oxygen through the solution. After 1·5 h a precipitate formed which was collected and found to give a positive starch–iodide test. The solid was unstable to p.l.c. but ^{1}H n.m.r. analysis showed the presence of an AB quartet, τ 4·50 and 5·03 (J 16 Hz). In a repeat of this reaction (360 mg scale), the products were treated with 2N-NaOH (25 ml) and EtOH (15 ml) at room temperature for 1 h. After acidification with dilute HCl, the organic material was extracted with ether. Separation of the products by p.l.c. afforded 5,6,7,8-tetrahydro-4-methyl-8-oxo-1-naphthaldehyde (30) (27 mg, 7%), as an oil, τ —0·53 (1H, s, ArCHO), m/e 188, 187, 160, 145, 132, 128, 118, 104, and 94 (base peak). The material rapidly oxidised in air.

Irradiation of 6,7,8,9-*Tetrahydro*-1,4-*dimethylbenzocyclohepten*-5-*one* (27; $n = 4$).—The benzocycloheptenone [26] (144 mg) was irradiated in benzene (40 ml) for 30 h using the 450 W light source and a Pyrex reactor. Some starting material (27 mg, 15%) remained after this time, but the major product, isolated by p.l.c., was 1,5,6,7,8,8a-*hexahydro*-4-*methylcyclobuta*[de]*benzocyclohepten*-8a-*ol* (31) (55 mg, 40%), m.p. 75—78°, $\nu_{max.}$ (Nujol) 3300, 1200, 1185, 1120, 1010, 895, 880, 800, 785, and 720 cm^{-1}, $\lambda_{max.}$ 215, 273, and 278 nm (ε 11,250, 1000, and 1000), τ 3·28 and 3·33 (2H, ABq, J 8 Hz, aromatic), 6·96br (2H, s), 7·39 (2H, m), 7·84 (3H, s, Me), and 7·7—9·0 (7H, m, one exchangeable H with D$_2$O); addition of the shift reagent Eu([^{2}H$_9$]fod)$_3$ to the n.m.r. sample caused the signal at τ 6·96 to move rapidly downfield and to develop into an AB quartet, J 14 Hz, assigned to the cyclobutene CH$_2$ group; M^+ 188 (Found: C, 83·1; H, 8·8. $C_{13}H_{16}O$ requires C, 82·9; H, 8·6%).

When the benzocycloheptenone was irradiated in benzene containing dimethyl butynedioate, no adduct formation could be detected and only formation of the alcohol (31) and traces of polar materials was observed.

Reactions of the Alcohol (31).—(a) *Dehydration.* The alcohol (22 mg) was heated for 2 h in hexane (10 ml) containing toluene-*p*-sulphonic acid (5 mg). The solution was cooled and the non-polar product isolated by p.l.c. to give 1,5,6,7-tetrahydro-4-methylcyclobuta[*de*]benzocycloheptene (32) (18 mg) as an oil, τ 3·10 (2H, s, aromatic), 4·47 (1H, t, vinylic H), 6·37 (2H, s, cyclobutene CH$_2$), 6·9—8·1 (6H, m), and 7·78 (3H, s, Me).

(b) *Reaction with base.* The alcohol (16 mg) was heated in ethanolic sodium hydroxide (10%; 10 ml) at reflux for 17 h. After addition of dilute HCl and ether extraction the benzocycloheptenone was identified [(12 mg, 75%), identical in its properties with an authentic sample of the ketone (27; $n = 4$)].

(c) *Action of heat.* The alcohol was unaffected by heating at 110° in toluene for 140 h. When the alcohol was heated in xylene, at 140°, for 15 h it was converted into

the olefin (32). No benzocycloheptenone (27; $n = 4$) formed under these conditions.

(d) *Heating with maleic anhydride.* The alcohol (27 mg) was heated in toluene (10 ml) at 110° in the presence of maleic anhydride (70 mg) for 42 h. No reaction was observed.

Under similar conditions, 1-ethyl-1,2-dihydrobenzocyclo-buten-1-ol did react with maleic anhydride.[27]

Preparation and Irradiation of 2-Benzylbenzaldehyde.—The Grignard reagent from bromophenyl(phenyl)methane (4·0 g) in dry ether (20 ml) was treated with triethyl orthoformate (2·0 g) at 40° for 30 min, followed by evaporation of the ether under reduced pressure then heating to 120° under dry nitrogen. A vigorous reaction ensued and the mixture became semi-solid. After a further 1 h at 100° the flask was cooled, the contents diluted with ether, and the products extracted in the usual manner. The crude acetal produced was hydrolysed by dissolving in ether (100 ml) and stirring with $2N$-H_2SO_4 at room temperature overnight. The aldehyde produced was purified by means of its bisulphite addition complex. The recovered aldehyde (0·65 g, 20%) had ν_{max} (film) 1680 cm^{-1}, τ -0.33 (1H, s, CHO), 2·0—2·85 (9H, m, aromatic), and 5·57 (2H, s, Ar_2CH_2).

Irradiation of the aldehyde (0·44 g) and maleic anhydride (0·22 g) in dry acetone (100 ml) for 3 h was followed by evaporation to afford a pale yellow gum. On heating this in toluene at 110° for 1 h, followed by methylation with diazomethane, two methyl esters were produced. These were separated by p.l.c. to give, as the major isomer, c-1-*hydroxy*-c-2-*methoxycarbonyl*-c-4-*phenyl*-1,2,3,4-*tetra-hydronaphthalene*-r-3-*carboxylic acid* 3,1-*lactone* (33; R = Me) (0·24 g, 40%), as an oil, ν_{max} (CCl$_4$) 1790 and 1740 cm^{-1}, τ 2·7—3·2 (9H, m, aromatic), 4·49 (1H, s), 5·42 (1H, d, J 5 Hz), 6·28 (3H, s, MeO), and 6·67 (2H, m) (Found: C, 73·8; H, 5·1. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%), M^+, 308.

The minor, less polar isomer, was tentatively assigned as c-1-*hydroxy*-c-2-*methoxycarbonyl*-t-4-*phenyl*-1,2,3,4-*tetra-*

hydronaphthalene-r-3-*carboxylic acid* 3,1-*lactone* (34) (0·06 g, 10%), obtained as an oil, ν_{max} (CCl$_4$) 1790 and 1740 cm^{-1}, τ 2·7—7·2 (9H, m, aromatic), 4·50 (1H, s), 5·37br (1H, s), 6·33 (3H, s, MeO), and 6·67 (2H, m) (Found: M^+, 308·1040. $C_{19}H_{16}O_4$ requires M, 308·1049).

Preparation and Irradiation of 2-Methylbenzoyl Cyanide.— The bisulphite addition complex of 2-methylbenzaldehyde (1·3 g) was treated with potassium cyanide (0·26 g) in water (6 ml) at 10° with stirring. After 5 min the emulsion was extracted with ether, dried, and the solvent removed by careful evaporation to afford a yellow oil. Some residual aldehyde was removed by stirring the product, in more ether, with some aqueous sodium hydrogen sulphite solution. Separation and drying, followed by evaporation afforded fairly pure cyanohydrin (0·5 g). This oil was dissolved in benzene (50 ml) and then oxidised with freshly dried manganese dioxide (5 g) at room temperature for 2 h. The mixture was filtered and evaporated to leave the 2-methylbenzoylcyanide as an oil (0·45 g, 90%), ν_{max} (film) 2250 and 1680 cm^{-1}, τ 1·7 (1H, m, aromatic), 2·5—2·7 (3H, m, aromatic), and 7·40 (3H, s, Me). The nitrile was rapidly hydrolysed on exposure to air.

The nitrile (0·10 g) and maleic anhydride (0·07 g) in dry benzene (40 ml) were irradiated for 1 h in a Pyrex vessel. Evaporation afforded an oily residue which was dissolved in dichloromethane, washed with saturated sodium hydrogen carbonate solution, and then water. Apart from a small amount of unchanged starting material all the products were soluble in the base. Reacidification of the aqueous phase with $2N$-HCl and ether extraction gave 1,2,3,4-tetrahydro-4-oxonaphthalene-2-carboxylic acid (38) (0·06 g, 45%), m.p. 146—148° (lit.,[28] 145—147°), ν_{max} 3400—2500 and 1700 cm^{-1}, τ 1·9 (1H, m, aromatic), 2·4— 2·8 (3H, m, aromatic), 6·6—7·4 (5H, m, aliphatic), and 0·97 (1H, exchanged with D_2O),

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