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TETRAHEDRON REPORT

PHOTOENOLISATION

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1. INTRODUCTION

In 1904 Collie[1] observed that crystals of the pyrone **1** turned a brilliant yellow on exposure either to sunlight or to "light from an arc between iron poles" and that the colour faded upon melting the crystals or dissolving them in a solvent. Many years later, in the 1960s, this early report of photochromism was followed up by Ullman and his colleagues with work on some related chromone derivatives.[2] These investigations showed that irradiation could lead to a dienol species, e.g. **3** and **2**, but that the process could be reversed by a non-photochemical "dark" reaction.

The photocatalysed enolisation process is a very general phenomenon which occurs with a wide variety of substrates. In this report some of the consequences and limitations of such photoenolisation processes will be considered. In particular, evidence relating to the apparent forbidden formation of *cis*-dienols, viz. (Z)-dienols of type **4**, will be presented.

In an important paper published in 1961,[3] Yang and Rivas illustrated that the dienol intermediates obtained by the irradiation of 2-methyl- and 2-benzylbenzophenone, e.g. **6** from **5** (Scheme 1), were sufficiently long lived to allow chemical trapping, either by cycloaddition with a dienophile, quenching with oxygen, or by incorporation of deuterium into the *ortho*-alkyl substituent. Because of the importance of such trapping reactions in synthetic work the scope and application of such reactions in preparative schemes is also surveyed.

2. PHOTOCHEMICAL PROCESSES

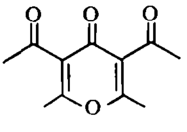
The photoreduction of benzophenone to benzopinacol in hydrogen donor solvents is one of the most highly examined photochemical reactions. The process has been shown to be initiated by abstraction of hydrogen from the solvent by the triplet $n\pi^*$ state of the carbonyl group. In propan-2-ol the quantum yield for pinacol formation, $\Phi_{\text{reduction}} = 2{\cdot}0$.[4] Introduction of *ortho*-alkyl substituents bearing α-H atoms results in a marked suppression in the pinacol forming reaction. Thus, for 2-methylbenzophenone, $\Phi_{\text{reduction}} = 0{\cdot}055$, and for 2-ethylbenzophenone, $\Phi_{\text{reduction}} = 0{\cdot}015$ in propan-2-ol. In contrast, both 4-methylbenzophenone and 2-t-butylbenzophenone showed high quantum yields, $\Phi_{\text{reduction}} = ca.\ 0{\cdot}5$. These experiments showed that the effect was neither due to adverse electronic interactions nor to any steric hindrance, but was more likely to be the result of a competitive intramolecular rearrangement involving transient formation of a photo-enol.[5] Differentiation between the two classes of aromatic ketones is also possible by ESR spectroscopy. Whereas benzophenone and 2-t-butylbenzophenone both produce strong ESR signals on flash photolysis in hydrogen donor solvents, due to formation of the ketyl radical, the signals from 2-methyl- and 2-ethylbenzophenone are very weak indeed. Intramolecular hydrogen abstraction, when possible, appears to be a more efficient process for 2-alkylbenzophenones than the intermolecular pathway.[6]

Yang and Rivas[3] had earlier demonstrated the existence of a ground state dienol species by reacting them with a variety of trapping agents, including typical Diels-Alder dienophiles. The stereospecific nature of cycloaddition products obtained from the irradiation of 2-methylbenzophenone in the presence of either maleic or fumaric acids also indicates the formation of ground state dienols.[7]

The detailed nature of the steps leading from the ground state ketone to the ground state dienol species (e.g. **5** to **6**, Scheme 1) has been the subject of several investigations involving flash photolysis experiments. Despite these some uncertainties remain. The most commonly accepted pathway is outlined in Scheme 1.

The initial process requires excitation of the carbonyl group. Direct irradiation produces an excited singlet state. For simple 2-alkylbenzophenones this state is generally of $n\pi^*$ character and it mainly decays, very rapidly, to a triplet $n\pi^*$ state by inter-system crossing. It is this triplet species which is mainly responsible for the hydrogen abstraction step (Scheme 1).[8] Detection of the triplet ketone species in a photoenolisation reaction was first claimed by Yang *et al.*[9] Irradiation of 2-benzylbenzophenone produced two species of lifetimes *ca.* 10 s and 500 μs. The longer-lived species was assigned as a dienol and the shorter-lived species as the $n\pi^*$ ketone triplet (**7**, Scheme 1). The latter assignment was subsequently discounted by Porter and Tchir[8] on the basis of known lifetimes of triplet states for benzophenone in hydrogen donating solvents. For the triplet state of 2-benzylbenzophenone the lifetime should be less than 100 ns if enolisation is to be competitive with intermolecular hydrogen abstraction.[4]

In a more extensive flash photolysis investigation, using both laser and conventional apparatus, Porter and Tchir[8,10] detected five transients from 2,4-dimethylbenzophenone **9** in cyclohexane (Scheme 2). The initial $n\pi^*$ singlet state is extremely short-lived (< 10 ns) and undergoes intersystem crossing with unit efficiency to the corresponding triplet state, **10**, lifetime <40 ns, which further decays directly into a transient of lifetime 67 ns, most probably a triplet state of the dienol, viz. **11**. This diradical transient, however, displayed some anomalous



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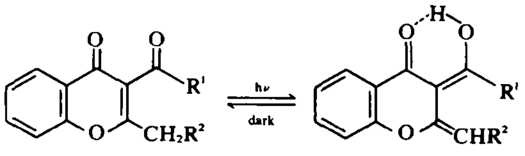
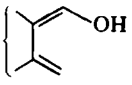


2 **3**



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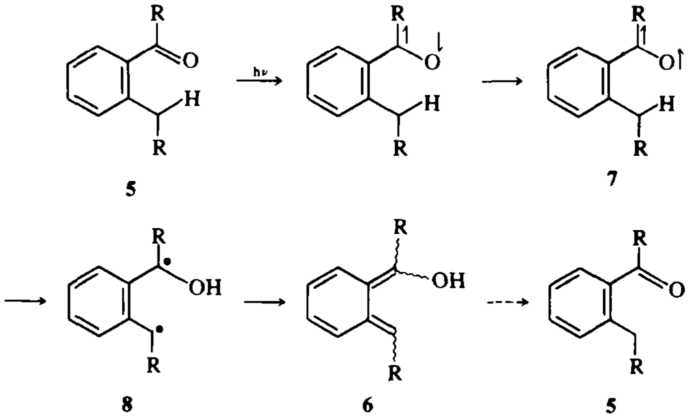
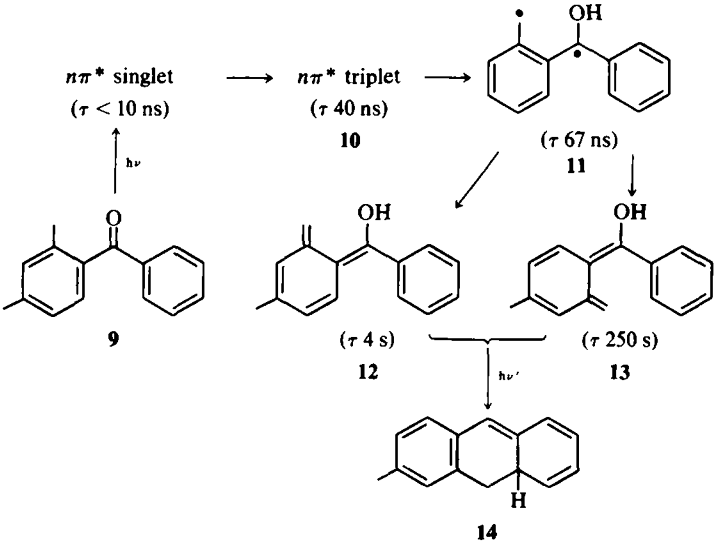


Scheme 1.



Scheme 2.

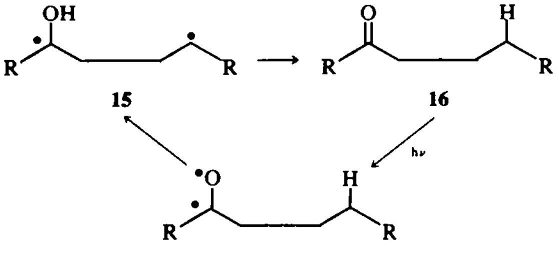
behaviour in that it was insensitive to oxygen. According to Porter this implies one of two possibilities, either (a) the triplet state is twisted or orthogonal, i.e. a 1,4-diradical, and hence only slowly reactive with oxygen, or (b) the triplet energy of this species is insufficient to sensitise oxygen and hence it remains unquenched. In either event, this species is just too short-lived to react with oxygen and, for this particular example, prefers to undergo its normal decay processes. These fates are complex since no single transient arising directly from the decay of **11** was observed. Instead it can either give rise to the next observed transients, assigned as the relatively long-lived ground state dienols **12** and **13**, or it can undergo hydrogen reversion back to the starting ketone **9**. Hydrogen reversion is a well-established process for diradicals produced from alkyl ketones (e.g. **15** to **16**, Scheme 3).[11,12]

A further complication in Scheme 2 was the observed photochemical conversion of the dienols into a dihydroanthrone species **14** by a "photo-Elbs" reaction. This overreaction product could be avoided, however, when light of longer wavelengths was filtered out.[10,13] Ullman and Huffman[14] observed the dihydroanthrone transient from 2-methylbenzophenone as a long-lived yellow species; on addition of oxygen to this intermediate, in the dark, a low yield of anthrone was obtained.

Porter and Tchir observed similar transients during the flash photolysis of 2-isopropylbenzophenone and 2-benzylbenzophenone and these results are tabulated (Table 1).[8] 2,6-Dimethylbenzophenone, however, appeared to behave differently, giving fewer transients upon flash photolysis (Section 5).

The above results suggest that for 2-alkylbenzophenones bearing α-hydrogen atoms only the $n\pi^*$ triplet state is responsible for the hydrogen abstraction step. This is not necessarily always the case. The extreme ease of intersystem crossing from the singlet to triplet state for benzophenones probably precludes participation of the singlet state in the hydrogen abstraction step but this is not always true for alkyl phenyl ketones. For these there is at least some indirect evidence that the corresponding singlet state can also participate and further, that states which are predominantly $\pi\pi^*$ in character can also participate. It should also be noted that the hydrogen abstraction step not only depends on the character of the excited state but also on the strength of the C–H bond under attack.

In a study on the photoenolisation of 2-methylacetophenone, addition of *cis*-piperylene resulted in a diffusion controlled quenching of the ketone triplet state. Formation of the corresponding dienol, however, was not completely suppressed.[18] Since *cis*-piperylene is known to be an efficient quencher of ketone triplet states, but not of singlet states,[19] it was deduced that an appreciable part of the photoenolisation process arises from the singlet excited species. Further evidence for the participation of singlet states is given by the following argument. Type II photoeliminations of alkyl phenyl ketones containing γ-H atoms on the aliphatic chain are known to arise from only the triplet state.[11] For 2-methyl substituted aryl alkyl ketones bearing γ-H atoms the efficiency of the type II photoelimination reaction is much reduced because of competing photoenolisation. Because the triplet decay rates of the 2-methyl-acetophenone and related ketones are much slower than those bearing γ-H atoms (by at least an order of magnitude[18,20]) it would be surprising if hydrogen transfer from the *ortho*-methyl group in the triplet excited ketone could compete efficiently with hydrogen transfer from a γ-C atom. That it does[21] again suggests the operation of an alternative route, that is the singlet state pathway for photoenolisation.



Scheme 3.

Hydrogen abstractions are known for systems where $n\pi^*$ excited states are impossible. For example the olefin **17** (R = H) undergoes both hydrogen scrambling,[22] between the vinylic and benzylic positions, and chemical trapping,[23] with maleic anhydride to give the adduct **18**. In this example a $\pi\pi^*$ excited state must be operative. A similar $\pi\pi^*$ state also appears to be involved in the unusual hydrogen abstraction reaction of the ketone **19**, which produces the alcohols **20** and **21** by a 7-membered transition state.[24] A triplet state mechanism was indicated by quenching experiments and the $\pi\pi^*$ character demonstrated by the small bathochromic shift for the 0–0 band in its phosphorescence spectrum on changing from a non-polar to polar solvent.[25]

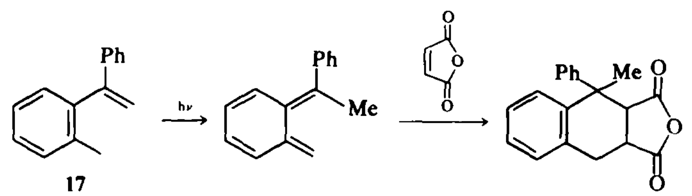
3. CHARACTERISATION AND STABILISATION OF THE DIENOLS

The dienol species (e.g. **6**, Scheme 1) produced by photoenolisation tend to be short-lived species in solutions at ambient temperatures because of further chemical reactions. The foremost of these is their reconversion to ketone tautomers by acid or base catalysed proton shifts. Protic solvents and higher temperatures favour this back reaction. The reketonisation of enols can also be photocatalysed.[26]

Because of their rather transient nature, identification of the dienols from aromatic ketones has tended to rely on a combination of spectral and chemical tests. These include absorption spectra, deuterium exchange, oxygenation and trapping with dienophiles. Although each individual method has its own intrinsic value, each test has limitations. For example, the assignment of a dienol structure to the long-lived yellow transient formed by irradiation of 2-methylbenzophenone in propan-2-ol[5] has been criticised[2] since it is more likely the corresponding dihydroanthrone. Formation of coloured species by irradiation of ketones in glass matrices at low temperatures, followed by their rapid fading on warming gives only an indication of dienol formation. Observation of incorporation of deuterium from a protic source is not necessarily a conclusive test for photoenolisation (Scheme 8), whilst the absence of incorporation does not necessarily imply lack of photoenolisation! In the case of 2-methylbenzaldehyde, for example, there is good spectral[27] and chemical[28] evidence for formation of the

Table 1. Typical flash photolysis results for benzophenones[8]

2,4-Dimethylbenzophenone	Singlet	Triplet	Diradical	Enol(s)		Dihydroanthrone
Cyclohexane	<10 ns	38 ns	67 ns	250s	3·9 s	hr
Cyclohexane/O_2	<10 ns	38 ns	67 ns	20 ms	9·5 ms	—
Ethanol	<10 ns	28 ns	1·7 μs	1·9 s	1·7 s	hr
Ethanol/O_2	<10 ns	28 ns	1·7 μs	0·3 s	0·3 s	—
2-Isopropylbenzophenone						
Cyclohexane	—	<20 ns	3·1 μs	24 s	2·0 s	hr
Ethanol	—	<20 ns	40 μs	0·7 s	0·7 s	—
Ethanol/O_2	—	<20 ns	40 μs	0·3 s	0·3 s	—
2-Benzylbenzophenone						
Cyclohexane	—	—	50 ns	7 s	520 μs	—
Cyclohexane/O_2	—	—	50 ns	2·5 s	520 μs	—
Ethanol	—	<10 ns	1·1 μs	7 s	140 μs	—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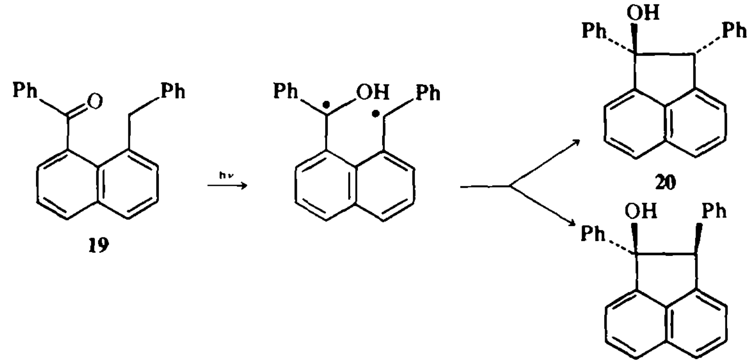
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corresponding dienol, despite lack of deuterium incorporation. Here the relatively stable dienol species behaves as a hydrogen donor, quenching other molecules of the excited aldehyde before they undergo enolisation, at a rate faster than reketonisation. The hydrogen donating properties of enols (and phenols) is well established.[29,30]

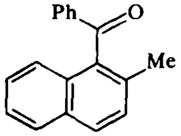
Oxygen can react with either the ground state dienol intermediate (Scheme 1, **6**)[3,6,8,31,32] or its precursors, provided they are of reasonably long existence.[33,34] Even in the use of cycloaddition reactions to trap the dienolate species, tests to check the absence of excited state or radical processes are desirable. The development of non-photochemical methods for the generation of such species has provided a means for such control and has aided their characterisation.[32,35]

Methods for stabilising enol isomers have been explored by Ullman *et al.*, their immediate aim being the development of efficient photochromic systems. Two approaches were adopted.[2] In the first, systems in which either disruption of a naphthalene nucleus occurred, rather than that in a benzene ring, using compounds such as **22** and **23**, or where extended conjugation of the derived dienol was feasible, as for the fluorene **24**. This approach was abortive since **22** and **24** did not photoenolise and the ketone **23** behaved anomalously. In contrast, the benzofurans **25** and **26** both underwent photoenolisation as evinced by formation of coloured species at −50° and the incorporation of deuterium into the benzylic positions.

The second approach involved the use of hydrogen bonding to stabilise the derived dienol. Some chromones and quinolones of the types **27** and **28** were studied thus following the earlier observation of Collie with the pyrone **1**.[1] In the event, many of the compounds possessed photochromic properties, long-lived species being obtained when they were irradiated at room temperature and which had IR absorptions characteristic of an enolised β-diketone system, as required for enols such as **29** and **30**. The lifetimes of these enols were diminished by addition of bases, but enhanced by either acids or chelation to nickel salts. Irradiation in the presence of deuteriomethanol resulted in exchange of the γ-H atoms.

Certain of these chromones did not exhibit photochromism. For example, although the chromone **31** was active, the corresponding 2-methyl analogue **32** was inactive. Ullman argued that this result implies formation of an excited state dienol (viz. a diradical species) in the photoenolisation process. If not, the process can be summarised:

$$^0\text{Ketone} \rightarrow {}^1\text{Ketone} \qquad \text{(i)}$$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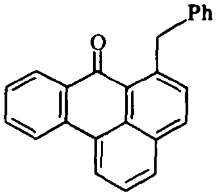
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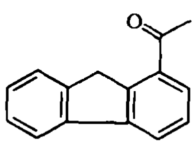
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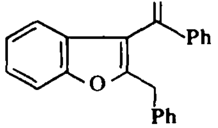
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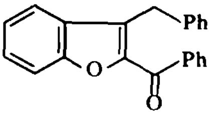
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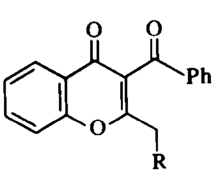

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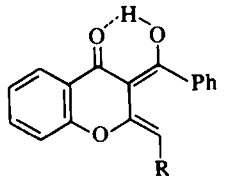
31: R = Ph
32: R = H



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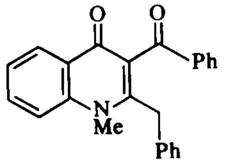

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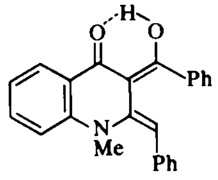

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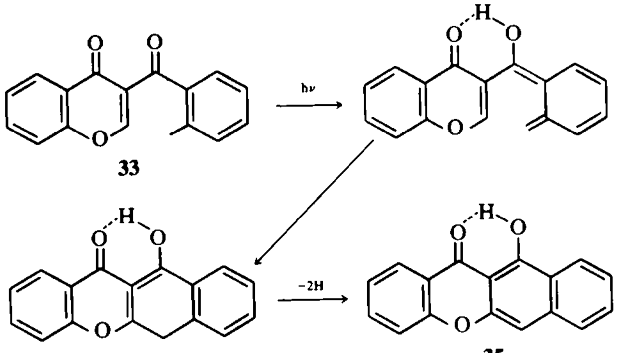


33 **34** **35**

$$^{1}\text{Ketone}\rightarrow{}^{3}\text{Ketone} \qquad \text{(ii)}$$

$$^{3}\text{Ketone}\rightarrow{}^{0}\text{Enol.} \qquad \text{(iii)}$$

Good evidence, including photosensitisation and quenching studies, showed that a triplet process was involved in step (ii). Step (iii), if it applied would be highly exothermic (excited state to ground state process). Since the chromophores of compounds 31 and 32 are almost identical, their reactivities must be controlled by the nature of the products, which, for the ground state dienols, should be of comparable character, both having energy levels lying well below the level of their triplet state precursors. On the other hand, if triplet state dienols (diradicals) were initially formed, steps (iv) and (v) need to be considered in place of step (iii):

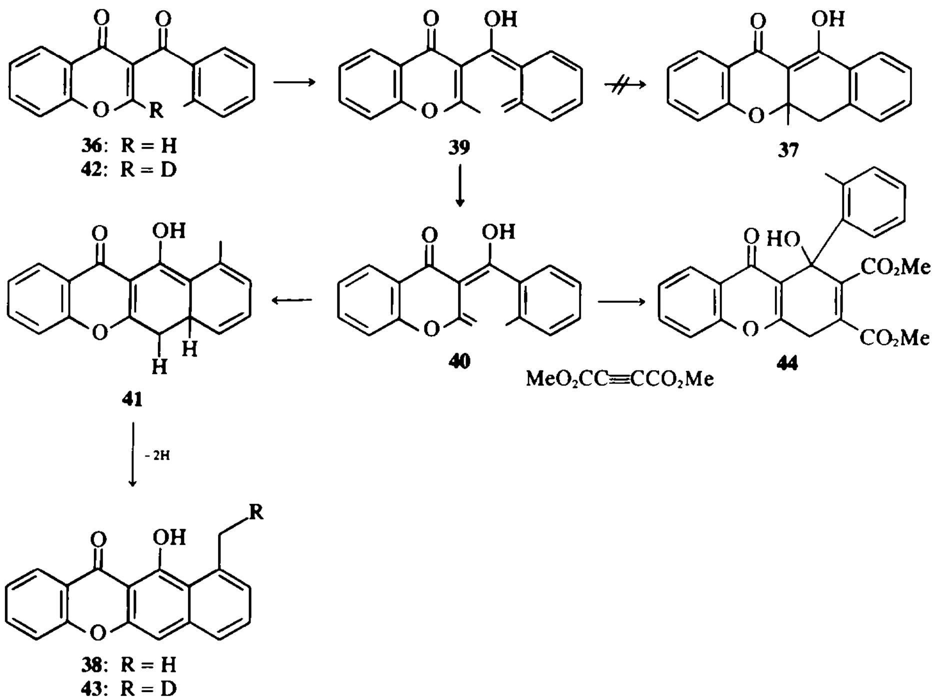
$$^{3}\text{Ketone}\rightarrow{}^{3}\text{Enol} \qquad \text{(iv)}$$

$$^{3}\text{Enol}\rightarrow{}^{0}\text{Enol.} \qquad \text{(v)}$$

The more conjugated excited photoenol of the benzyl derivative 31 might be expected to be more readily formed than that for the methyl analogue (32). The success of the reaction would then depend both on the energy of the enol excited state being lower than that of its precursor, the triplet excited ketone, and also on the existence of only a small activation energy in the enolisation step. That such a delicate balance pertains comes from a related study.[36] The chromone 33, which is isomeric to the unreactive compound 32, does undergo photoenolisation, the enol reacting further to give the benzoxanthenone 35 via oxidation of the dihydro-species 34. Furthermore the related 2,2′-dimethyl chromone 36 also undergoes smooth photoenolisation. In this case the product is not the dihydro-species 37 but, instead, the benzoxanthenone 38 (Scheme 4). The latter process takes place via a rapid 1,7-hydrogen shift of the initially formed ground state dienol 39 to produce the new ground-state dienol 40, which is subsequently cyclised to the dihydro-derivative 41 and then, by spontaneous oxidation by air, aromatised to the product 38. This route was established by a deuterium labelling experiment starting with the chromone 42 to produce the benzoxanthenone 43. Further evidence for formation of the intermediate dienol 40 was obtained by a trapping experiment with dimethyl butynedioate, to give the product 44.

From these observations it may be concluded that the dienol 40 must be thermodynamically more stable than its precursor 39. Despite this it is not formed directly in the photoenolisation step. This implies again that initial formation of an excited state dienol, viz. a triplet diradical, is involved. For the system involving chromone 36 the triplet diradical of the enol 40 must be inaccessible to the triplet state of the ketone.

Ullman has examined the photochemical behaviour of dienols related to the species 40.[26] Thus irradiation of the dienol 45, obtained from the chromone 31, initially gave a mixture of the dihydrobenzoxanthenones 46, a process demonstrated to proceed by a singlet excited state. Sensitised reactions, involving triplet levels, only gave rise to the starting ketone, a process which must involve the triplet diradical 47, followed by a very efficient hydrogen reversion to the starting ketone 31. Suppression



Scheme 4.

of the process **45** to **46** was achieved when filtered UV light was used ($\lambda_{max} < 410$ nm); an intense source of visible light was required to activate the dienol.

4. STEREOCHEMISTRY OF DIENOL FORMATION

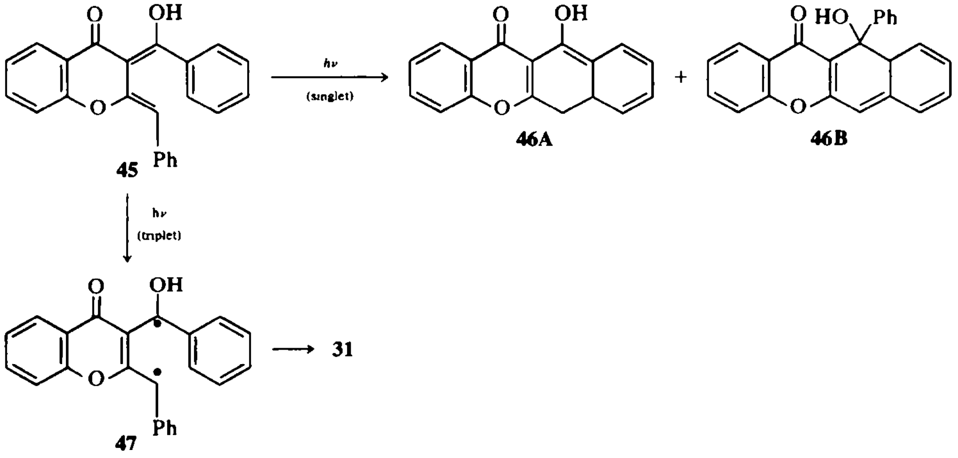
The work of Ullman's group on the chromones assumed that although intramolecular hydrogen abstraction requires a *syn*-conformation between the reacting carbonyl group and the γ-hydrogen source, collapse to the ground state dienol would somehow allow rotation about the diene system so that the (E)-dienol formed, in order to accommodate H-bonding (e.g. **48** to **49**).

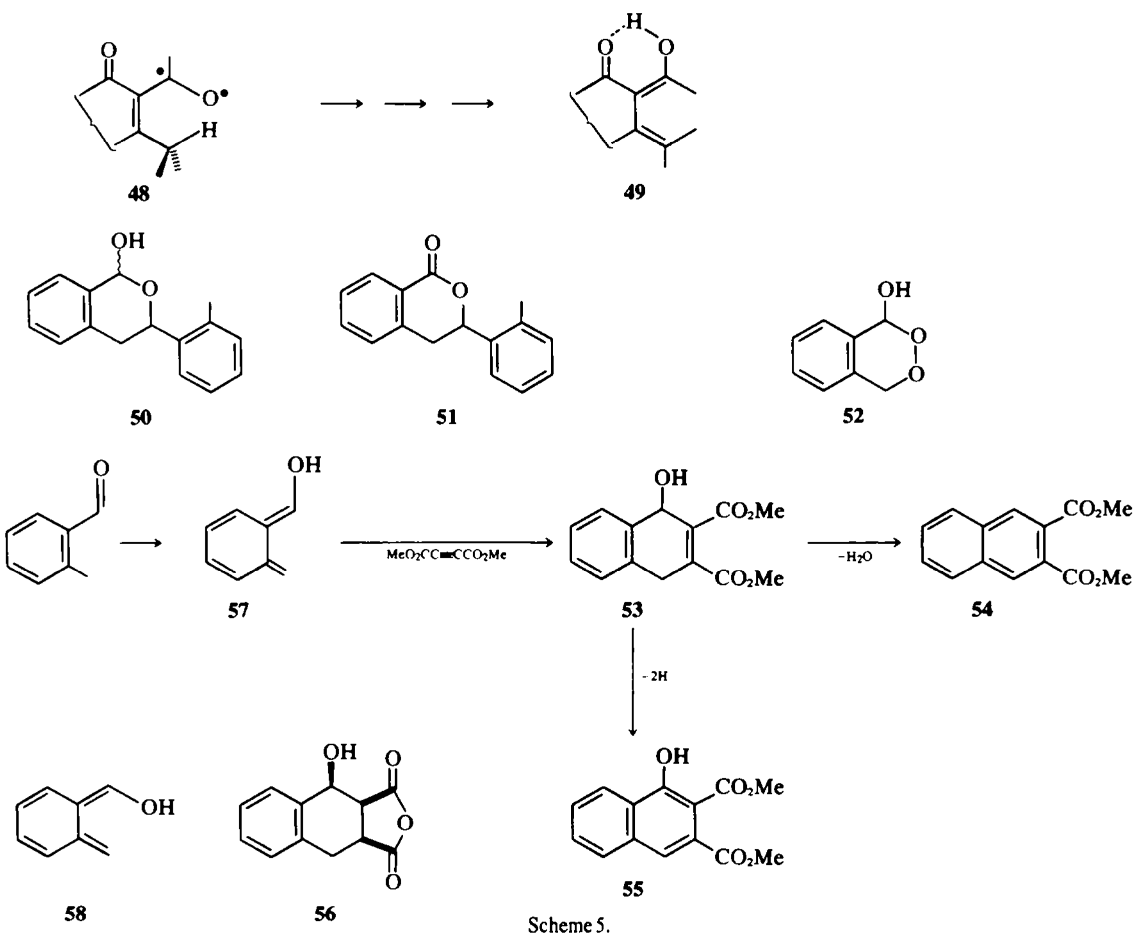
Rotation was assumed to occur during the enolisation process. Since the quantum yield for photoenolisation was not intensity dependent only one quantum of light energy is involved, thus ruling out a second-step *cis-trans*-isomerisation. The electronic state of the dienol which could undergo bond rotation was assumed to be the recognised triplet enol.[2]

Further evidence for the (E)-dienol intermediate was obtained from an examination of the photochemical behaviour of 2-methylbenzaldehyde.[28] In the absence of trapping agents, products of intermolecular reactions formed, akin to the dimers produced from benzaldehyde.[37] Amongst products isolated are a hemiacetal, **50**, and, in the presence of air, the lactone **51** and peroxide **52**.[38]

Dienol formation does occur, however, since, in the presence of suitable dienophiles, cycloaddition occurs remarkably efficiently. As discussed above, therefore, the formation of products of the type **50** to **52** can be explained by postulating a relatively long-lived dienol intermediate which has time to interact either with other excited molecules of 2-methylbenzaldehyde, for example as a hydrogen donor, or, even more efficiently, with suitable dienophiles before collapse to the starting ketone.

Irradiation of the aldehyde with dimethyl butynedioate gave one major, but unstable, product, which was the adduct **53** (Scheme 5). This could either be dehydrated, by heating it in an inert solvent with a trace of acid, to give

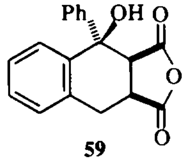




Scheme 5.

the naphthalene **54**, or be oxidised with manganese dioxide to give the naphthol **55**. The overall rate of disappearance of the aldehyde was unaltered by the presence of the dienophile suggesting that, in this case, the latter does not interfere with the initial photochemical processes. This is not necessarily the case. In the presence of 2,3-dimethylbut-2-ene, for example, the normal course of the reaction is completely diverted to the formation of oxetanes.[39]

Returning to the question of dienol configuration, trapping of the dienol from 2-methylbenzaldehyde with maleic anhydride gave one adduct, shown to be the unstable, but all-*cis* hydroxyanhydride **56** (Scheme 5).[40] Since no other epimeric adduct was detected amongst the reaction products only one gross stereochemical deduction can be formed. The adduct **56** must arise by *endo*-addition of maleic anhydride to the (E)-dienol **57**. The only alternative pathway leading to the same stereochemical result would involve the less favoured[41] *exo*-addition to the (Z)-dienol **58**. (E)-Dienol formation is consistent with the observations of Ullman on the chromone systems and with the results of Nerdel and Brodowski, who found that 2-methylbenzophenone reacts with maleic anhydride to produce the all-*cis*-adduct **59** in high yield. The latter result is particularly pertinent in light of the flash photolysis results with 2,4-dimethylbenzophenone.[8] Assignments to two transients as dienols were made, dienols **12** and **13**, both of which appeared to be quenched by dimethyl butynedioate. The rates of quenching indicated that the (Z)-dienol reacted at least twice as fast as the (E)-isomer and at a rate considerably faster than that of its natural decay. (Incidentally, these rates of reaction with the dienophile were in the order of 10^5–10^6 times faster than that for reaction of the related species 2-phenylfuran![42]) Hence two isomeric adducts would be expected corresponding to trapping of both dienol isomers. That they are not both observed can only be explained by either (i) very low absolute concentrations of the (Z)-isomer compared to that of the (E)-isomer, or (ii) a wrong assignment to the flash photolysis transients. To date, the report of Porter and Tchir is the only one where evidence for the formation of two isomeric dienols has been presented. Other flash photolysis studies have either reached alternative conclusions[9] or have only detected the one dienol transient.[27] The failure to observe more than one dienol, however, is not proof that only one exists. It would be expected that the spectral differences between a pair of isomeric dienols would be minimal and hence differentiation almost impossible without the aid of either kinetic measurements or chemical trapping methods.



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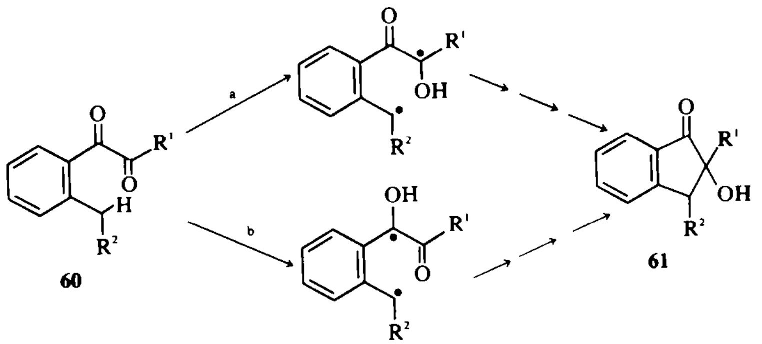
It may be concluded from the above results that, whereas there is excellent chemical and spectroscopic evidence for the existence of the (E)-dienols from aromatic ketones or aldehydes, there is very little



Scheme 6.

evidence for the formation of the (Z)-isomer. This theme is further developed in the subsequent discussion.

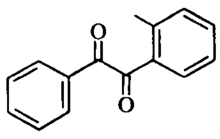
5. CYCLOBUTENOL FORMATION AND NON-ENOLISABLE SYSTEMS

In producing (E)-dienols the photoenolisation process demands rotation about the bond between the oxygen bearing atom and the aryl ring in the diradical (e.g. **8**, Scheme 1). This movement must occur either immediately prior to or during collapse to the ground state. The detailed mechanisms whereby excited states can relax to the ground are the subject of much current attention[43–45] but for processes where there is spin-orbital coupling (as in $n\pi^*$ to ground state transformations) asymmetric rotation about bond axes has been proposed as one method for travelling through the excited state to ground state energy surfaces.[46] Ullman's work gives credence to this idea (see **48** to **49**). There is also another possible reaction course. This involves the actual or incipient formation of a benzocyclobutene by collapse of the dienol diradical by ring-formation, followed by its re-opening, by a thermal process, to give the (E)-dienol. Some related work on the photochemistry of certain aromatic α-diketones bearing *ortho*-alkyl substituents (e.g. **60**) is relevant in this context. Such compounds react photochemically to form hydroxyindanones (e.g. **61**). These products could arise by a direct 1,7-hydrogen abstraction reaction (Scheme 6, path a) but this path is less favoured than the much more common 1,6-abstraction pathway (Scheme 6, path b) involving the nearer carbonyl group. For the diketone **62**, Burkoth and Ullman suggested that the dienols **63** and **64** might be intermediates.[47] On conducting the photoreaction in deuteriomethanol, however, no incorporation of the label was observed in either the starting material or product. This observation was explained by assuming that any (Z)-dienol that formed would revert very rapidly back to the starting ketone by a 1,5-hydrogen shift before deuterium exchange could occur and that the (E)-dienol would lead directly to product **65** by a facile intramolecular cyclisation at a rate faster than intermolecular hydrogen exchange.

In contrast, Hamer[48–51] rules out the existence of the ground state dienols **63** and **64** because of evidence obtained with 1-(2-alkylphenyl)-propane-1,2-diones bearing chiral *ortho*-alkyl groups. Products with *inversion* of configuration about the alkyl substituent were obtained together with a competing racemisation of the starting material. It was suggested that the initially formed triplet diradicals **67A** and its conformer **67B** (Scheme 7) undergo bond rotation about the substituent axes until a bonding configuration is attained (e.g. direction a). 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 state to a ground state, it may react further and, in this case, undergo a concerted ring expansion to give the observed optically active products **68** and **69**, in which the required net inversion about the alkyl group has occurred. In the alternative rotation mode (Scheme 7, direction b) the first bonding orientation reached results in hydrogen reversion with net inversion of configuration about the alkyl group and hence racemisation of the starting material.

Explanations of reaction based on the formation of a twisted ground state (Z)-dienol (Scheme 7, path c) do not lead to the observed products if a thermal conrotatory process is considered. The ratio of the products **68** and **69** appears to be controlled by the conformational distribution in the starting material and that hydrogen abstraction takes place in two modes, viz. to give **67A** and **67B**.

The formation of the optically active indanones **68** and **69** from the optically active diketone **66**, together with the lack of deuterium incorporation and the failure of maleic anhydride to trap any intermediates was cited as evidence for the absence of ground state dienol species. Recently however, Ogata and Takagi found that a chemical trapping reaction using an excess of dimethyl butynedioate whilst irradiating 1-(*o*-tolyl)propane-1,2-dione, **70**, gave the adduct **71**, albeit in low yields.[52] This result illustrates the difficulty of selecting an unambiguous trapping reagent. It could be that the acetylenic ester is in this instance acting as a diradical trap, i.e. as a diylophile for the dienol triplet intermediates, rather than as a dienophile, although it is reputedly poor in this capacity.[53] Alternatively a small amount of the reaction profile may



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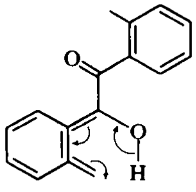

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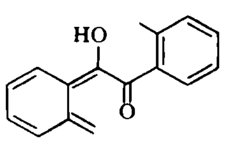

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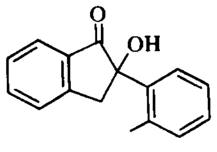
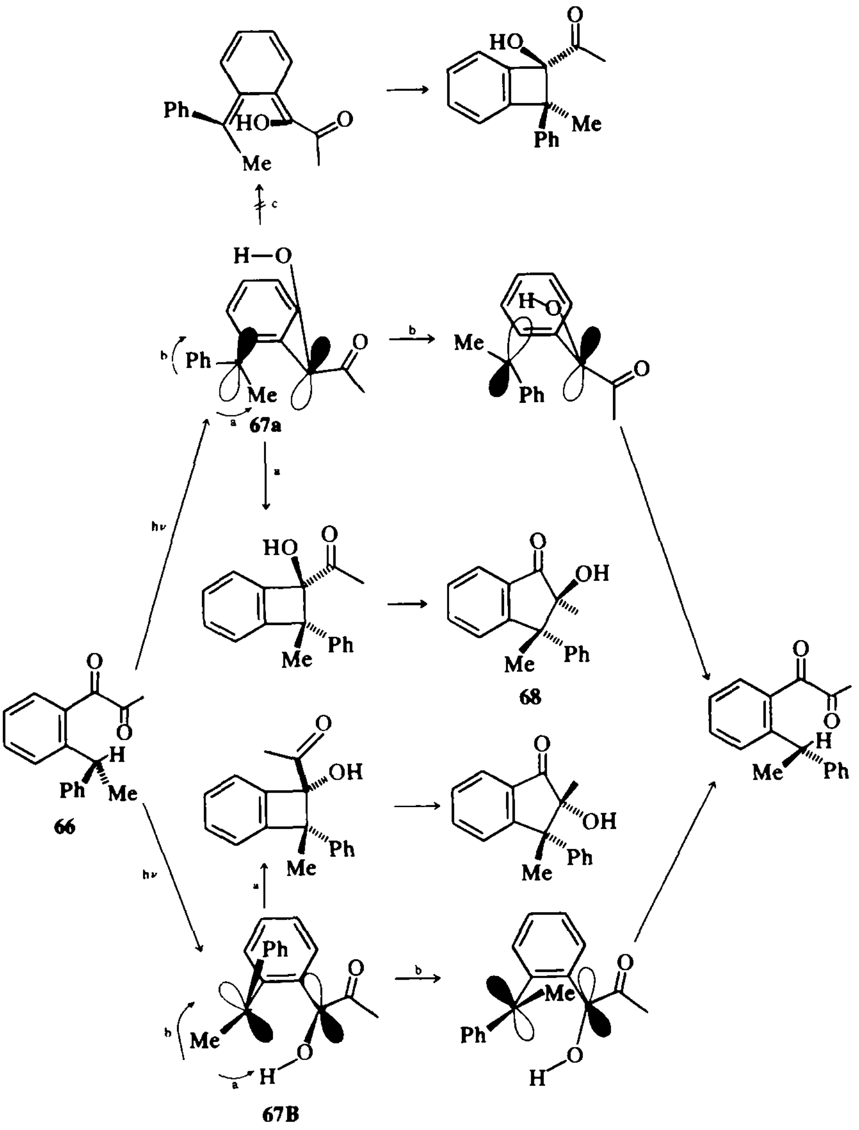


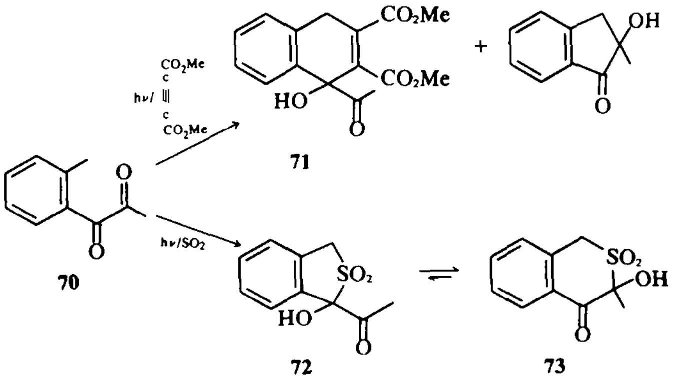
65



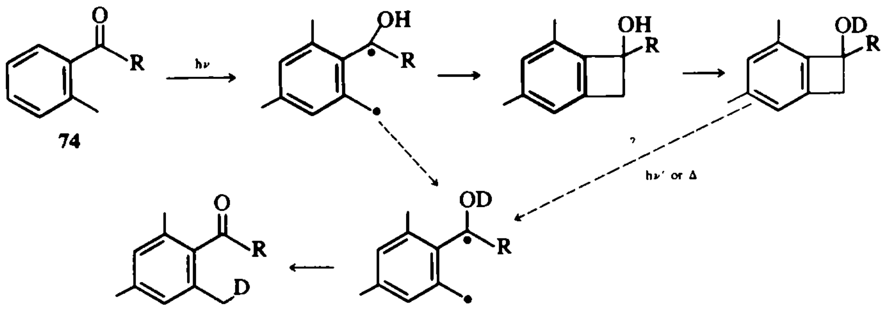
Scheme 7.

lead through to the dienol which is then trapped. That the reaction does proceed via a diradical intermediate is indicated by trapping with the more efficient diylophile sulphur dioxide.[54] With the diketone 70 the adduct 73 formed in high yield;[55] the adduct 73 and its isomer 72 are in rapid equilibrium (Scheme 8), which, in this series, highly favours the 6-membered cyclic sulphone.

A similar argument involving transient formation of benzocyclobutenols may also be applied to the fate of simpler ketones. For these the transient cyclobutenols, if



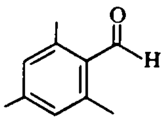
Scheme 8.



Scheme 9.

formed, cannot undergo ring expansion but, because they are in a vibrationally hot state, pass on thermally, by an electrocyclic process, to give the (E)-dienol. The conrotatory ring opening of simple monosubstituted cyclobutenes is known to preferentially produce (E)-dienes.[56] This mechanism would also predict the formation of small quantities of benzocyclobutenols during the irradiation of 2-alkylaromatic ketones. Such a result is obtained with 2-methylbenzaldehyde. Photolysis under dilute conditions, (0·003 M) to disfavour bimolecular reactions, gave a small quantity of benzocyclobutenol.[28]

The formation of benzocyclobutenols during the photolysis of aromatic ketones has other precedents, particularly for hindered ketones. In an extensive study of 2,4,6-trialkylphenylketones, Kitaura and Matsuura[57] noted that cyclobutenol formation was often the preferred course of reaction. In no case could ground state dienols be trapped by dienophiles but, since deuterium exchange was noted[58] when the ketones were irradiated in deuteriomethanol for long periods, they deduced that dienols *were* first formed and that these then underwent ring closure to give the cyclobutenols. This argument is inconsistent with the above evidence and with steric commonsense, the dienol being far more hindered than the corresponding cyclobutenol. Furthermore, a simple alternative could explain the low degree of deuterium incorporation noted. Exchange of hydrogen with deuterium could occur at the cyclobutenol stage, followed by a photosensitised ring opening reaction to give the triplet diradical; collapse back to the starting ketone by hydrogen reversion would effect the observed incorporation of label into the *ortho*-alkyl groups (Scheme 9). In this way incorporation of deuterium need not involve a ground state dienol. Some of the results of Matsuura and Kitaura are tabulated (Table 2). For the trimethyl series **74**, cyclobutenols were obtained when $R = CH_3$, C_2H_5 or $i\text{-}C_3H_7$. In the case of the t-butyl derivative (**74**, R = t-butyl) the predominant process was one of α-cleavage leading to the aldehyde **75**, mesitoic acid and isobutylene. For the isopropyl ketone deuterium incorporation was also noted in the isopropyl methine position. Although an enolisation mechanism was suspected, no explanation was afforded. It is likely, however, that a hydrogen reversion process is again occurring, involving the methine hydrogen atom rather than the hydroxyl hydrogen, as in the process **76** to **77**. "Anomalous" photochemical behaviour has also been noted for 2,6-disubstituted benzophenones,[8,59,60] including benzocyclobutenol formation[61,62] and the failure to observe chemical trapping of any ground state dienols by dienophiles. Interestingly, on heating these benzocyclobutenols (e.g. **78**) the starting ketones (e.g. **79**) were



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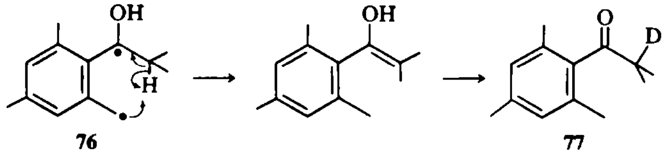
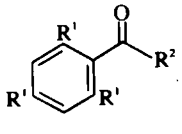
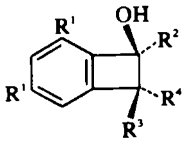
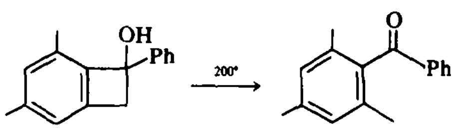


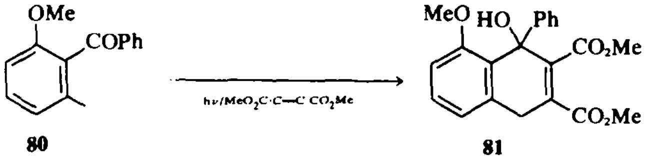
76 **77**

Table 2. Photolysis of 2,4,6-trialkylphenyl ketones[58,61]

 A	 B	Yield, %	Comments
$R^1 = R^2 = Me$	$R^1 = R^2 = Me, R^3 = R^4 = H$	70	hν/isopropanol
$R^1 = Et, R^2 = Me$	$R^3 = Et, R^2 = R^3 = Me, R^4 = H$ or R^3 and R^4 reversed	78	One isomer only, various solvents
$R^1 = iPr, R^2 = Me$	$R^1 = iPr, R^2 = R^3 = R^4 = Me$	100	hν/isopropanol
$R^1 = Me, R^2 = Ph$	$R^1 = Me, R^2 = Ph,$	40	hν/benzene
	$R^3 = R^4 = H$	0	hν/isopropanol-photo-reduction preferred
$R = Et, R^2 = Ph$	$R^1 = Et, R^2 = Ph, R^3, R^4 = H, Me$	40	isomer ratio varied with solvent
$R^1 = iPr, R^2 = Ph$	$R^1 = iPr, R^2 = Ph, R^3 = P^4 = Me$	100	hν/isopropanol
$R^1 = Me, R = t\text{-}Bu$	—	0	α-cleavage only



78 **79**



80 **81**

formed but again a diradical process seems to be involved since no trapping of any intermediate dienols by dienophiles was observed.

To summarise, photoenolisation with 2,6-disubstituted aromatic ketones does *not* appear to occur unless some influence to stabilise the resulting ground state dienol is present, as in photoenolisation of the chromones **2** to **3**, where H-bonding appears to be important. A pertinent case is the result obtained with 2-methoxy-6-methylbenzophenone **80**, which is comparable, in steric size, with 2,6-dimethylbenzophenone. Whereas the latter does not form a trappable dienol, the former does, producing the alcohol **81** in high yield with dimethyl butynedioate.[63]

6. ON THERMOLYSIS OF BENZOCYCLOBUTENOLS

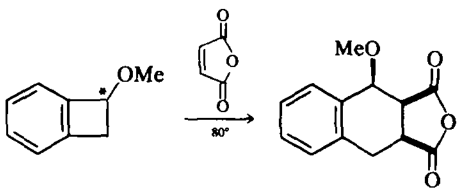
The detection of benzocyclobutenol in the photolysis of 2-methylbenzaldehyde immediately generated the possibility of forming the ground state dienol species by a non-photochemical process. The conrotatory opening of benzocyclobutenes under thermal conditions was well established,[64] as was the knowledge that benzocyclobutenol gives 2-methylbenzaldehyde on heating[65] or on treatment with base.[66].

When benzocyclobutenol was heated with maleic anhydride at 80° it was not surprising to find that the acid lactone **81** formed in high yield;[35] this acid is the thermal product of the hydroxy-anhydride adduct **56**. Based on previous stereochemical arguments the selective conrotatory opening of the cyclobutenol ring to the (E)-dienol must occur. Furthermore, the dienol is formed in a dark reaction and must therefore generate only ground state species.† As in the photochemical process, no trapping of any (Z)-dienol could be detected, implying its absence. The thermal method thus complements the photochemical process and enables further information to be gleaned on the photoenolisation process as well as closer control in the formation of the dienols, which is important for synthetic applications.

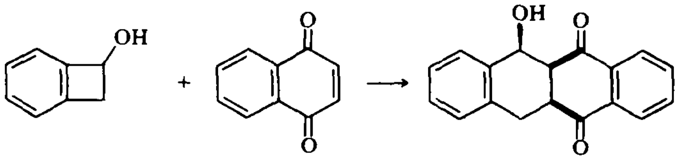
On heating optically active benzocyclobutenol no racemisation was detected but only reversion to the aldehyde took place, indicating that proton transfer processes are faster than cycloreversion to the starting alcohol. It was also noted that the rate of disappearance of the optically active alcohol was identical to the rate of appearance of 2-methylbenzaldehyde, thus ruling out the possibility of dimer formation occurring in the dark. Only photolytic processes must therefore be responsible for the formation of dimers during irradiation of 2-methylbenzaldehyde.[38]

The reversibility of the benzocyclobutene—*ortho*-quinonedimethide reaction can be demonstrated by alkylating the benzocyclobutenol. The optically active methyl ether **82** racemises on heating, with an activation energy of 128 kJ mol^{-1}. The incipient reactivity of the derived dienol ether thus generated is illustrated by the fact that racemisation is not observed in the presence of maleic anhydride. That the adduct so formed, viz. **83**, was racemic points to the formation of a planar *ortho*-quinonedimethide species before trapping.

An immediate consequence of the thermal generation of the dienols rather than by a photochemical reaction is the extension of synthetic potential (Section 8). An example is illustrated by reaction of the alcohol **84** with 1,4-naphthoquinone in refluxing benzene, which produces good yields (75%) of the tetracyclic naphthacene **85** directly and stereoselectively. The photochemical equivalent of this reaction is not possible because of the



82 **83**



84 **85**

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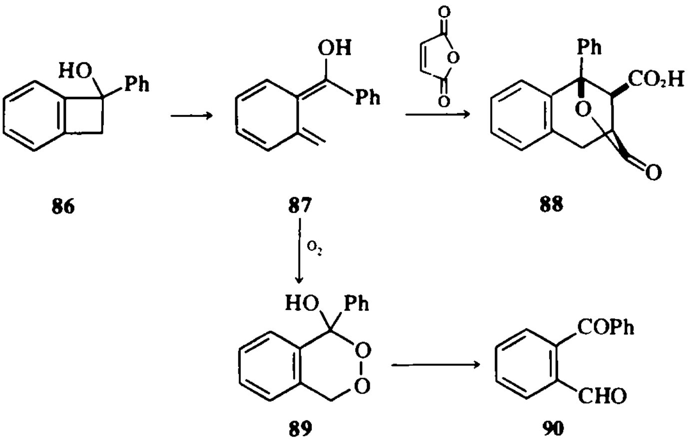
†Assuming, in this instance, that there is not enough strain energy present in the opening of the benzocyclobutene system to attain an excited state![67]

numerous alternative photochemical fates of the quinone.[68] A second consequence of this thermal process is the provision of a direct method for studying the stereochemistry of the ring-opened dienols.

It was expected that introduction of a group sterically larger than, and adjacent to, the alcohol function would force the latter group into the (Z)-configuration during the thermal ring-opening of a substituted benzocyclobutenol. In all the cases studied, however, this process was not observed.[32] Thus, when the 1-phenyl derivative **86** was heated at 110° with maleic anhydride only the known acid lactone **88** formed. Despite the steric bulk of the phenyl group, this product must occur via the (E)-dienol **87**, the same as is obtained from the photolysis of 2-methylbenzophenone.[7] If any (Z)-dienol formed it would either trap, but no corresponding adducts were detected, or revert to 2-methylbenzophenone by a 1,5-hydrogen shift. In the presence of one equivalent of dienophile only traces of the ketone could be detected and these arose mainly towards the end of the reaction, when the concentration of dienophile itself was low, and probably arise by intermolecular proton transfers from the (E)-dienol. Of further interest was the observation that heating the alcohol **86** alone gave only 2-methylbenzophenone, with no trace of any anthracene derivatives, thus confirming the flash photolysis results that for this system, a thermal Elbs-type cyclisation does not occur.

Dienols of the type **87** are known to react with oxygen in the dark[3,6,8,31] and when the alcohol **86** was heated in the presence of oxygen the peroxide **89** formed; this readily decomposed into the aldehyde **90**.

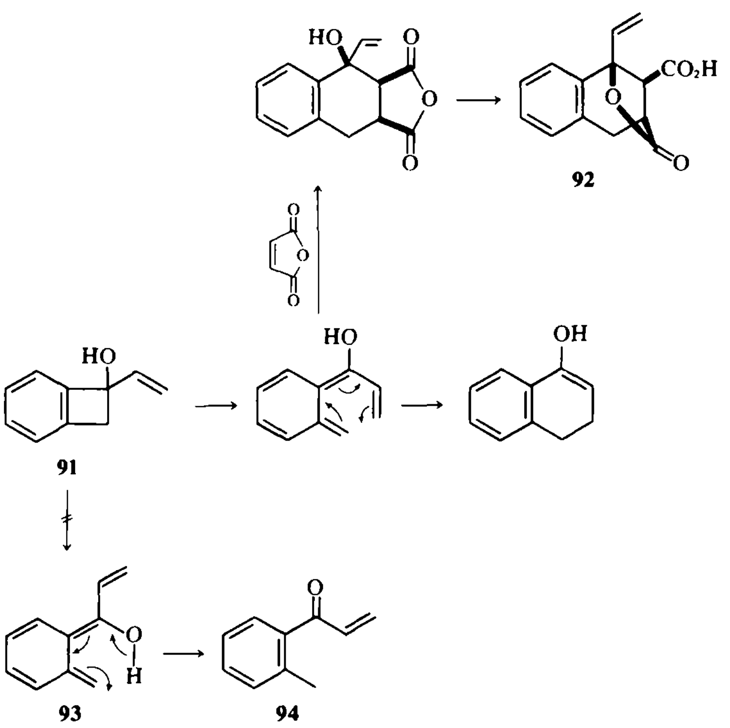


86 **87** **88** **89** **90**

Although no dihydroanthracene formation was observed by cyclisation of the phenyl substituted dienol **87**, such cyclisations are, in principle, possible and should occur in the ground state by a disrotatory ring closure. This reaction is precluded in the phenyl substituted system by the energy barrier required to offset the aromatic character of the phenyl ring. This objection was removed by preparation of the vinyl substituted alcohol **91**.[32] This alcohol proved to be thermally unstable and on heating to 100° it rapidly formed α-tetralone (Scheme 10). That this reaction was proceeding via a hexatriene intermediate was demonstrated by a trapping experiment with maleic anhydride. Cycloaddition competed with internal cyclisation to give a mixture of α-tetralone and the lactone acid **92**. Again no (Z)-dienol **93** was detected. If so this should have produced the acrylophenone **94**, by a 1,5 hydrogen shift, but none was detected.

The latter test for (Z)-dienol formation might be prejudiced in that there is some evidence that aryl and unsaturated groups can readily adopt the more hindered (Z)-site in electrocyclic processes,[69–71] perhaps because of some secondary orbital overlap effects. The failure to observe the (Z)-dienol from either of the alcohols **86** or **91** might then reflect such a preference rather than any inherent disinclination on the part of the hydroxyl group to adopt the (Z)-orientation. Further 1,1-disubstituted benzocyclobutenols have therefore been examined. Since the methyl group is sterically larger than the hydroxyl group, 1-methylbenzocyclobutenol was prepared. On heating this alone it cleanly produced 2-methylacetophenone. With maleic anhydride the acid lactone **95** was produced, although considerable quantities of the ketone were also formed. For this system the ketone can arise as a result of intramolecular hydrogen transfer in either of two ways involving 1,5-hydrogen shifts, viz. hydrogen transfer from the hydroxy group in a (Z)-dienol or by hydrogen transfer from the methyl group of the (E)-dienol. That the latter process is possible was realised by heating the methyl ether **96** when it was quantitatively converted into the substituted styrene **97**. The results with the 1-methylbenzocyclobutenol are therefore entirely consistent with formation of only the (E)-dienol but do not completely exclude the possible formation of the alternative isomer. Two further systems, however, substantiate the forbiddeness of formation of (Z)-dienols.

Electrocyclic thermal opening of the acetal **98** must result in one of the ethereal oxygens adopting a (Z)-configuration. In the event, attempted trapping of the resulting diene with maleic anhydride completely failed, even when the reaction temperature was raised to the decomposition temperature of the acetal (>140°, elimination of alcohol and formation of complex reaction mixtures, but no adducts). A more striking example was provided by a comparison of the two 1,2-disubstituted benzocyclobutenes **99** and **100**. Whereas the *trans*-dimethoxy derivative **99** reacted readily with dienophiles, the *cis*-isomer **100** was inert, even at much higher temperatures. For the *trans*-isomer conrotatory opening can proceed to give either the all-*trans*-diene **101**, or the all-*cis*-isomer **102**, the former being expected by steric arguments alone. The *cis*-cyclobutene **100** can only open



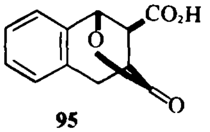
Scheme 10.

up to place one methoxy substituent into a *cis*-disposition **103**, which appears to be forbidden.

Some recent results on the thermal behaviour of simple cyclobutenes[72] complement the above results. When 2-methylcyclobut-2-enol **104** was heated at 100° for 5 min, tiglic aldehyde **106** formed, the reaction proceeding according to Scheme 11, involving the (E)-dienol **105**. No traces of angelic aldehyde **107** were detected. The result illustrates the general refusal for oxygen to adopt the (Z)-configuration and that this effect is not compromised by the constraints of the fused aromatic ring with the benzocyclobutenes.

7. ATTEMPTED PHOTOCHEMICAL FORMATION OF (Z)-DIENOLS

The evidence for the formation of (Z)-dienols is extremely limited. It arises mainly from the flash photolysis results of Porter and Tchir.[8] As described above, the fact that only one of the two postulated dienol transients from 2,4-dimethylbenzophenone can be trapped with



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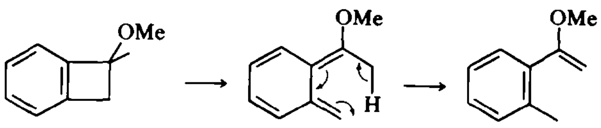
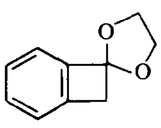


96 **97**



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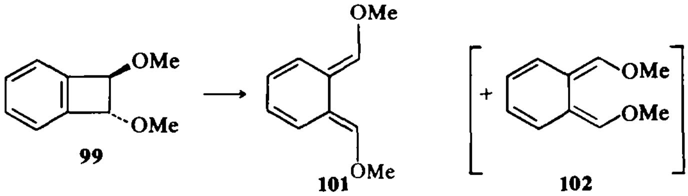
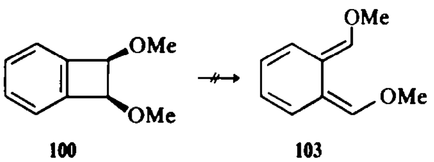
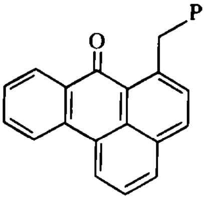




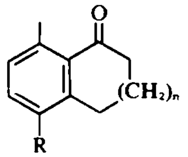
100 **103**



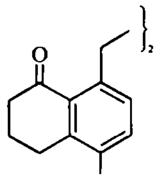
108

dienophiles throws some doubt on the spectroscopic assignments. The observation that 2-benzylbenzophenone only gives two detectable dienols is to be expected if only the (E)-dienol forms; there are a total of four possible isomers from this ketone. Another result which, at first sight, appears to demand the existence of (Z)-dienol formation comes from the photolysis of 2-benzylbenzanthrone **108**, which gives both a yellow transient when irradiated at low temperatures and shows incorporation of deuterium when photolysed with deuteriomethanol.[2] In this case, however, cycloaddition trapping reactions failed. This system might thus fall into the same class of compound as the 2,6-disubstituted benzophenones.[58,61] Deuterium incorporation may arise by hydrogen reversion of a diradical species formed from either a transient cyclobutenol species or from diradical intermediates, as described previously. The coloured species obtained at low temperature could possibly be a diradical or photo-Elbs type intermediate.

It was decided to investigate two systems for which formation of (E)-dienols is restricted.[28] These involved the α-tetralone **109** and its homologue the benzocycloheptenone **110**. Ring strain dictates, in these cases, that only the (Z)-dienols should be capable of existence. As expected, irradiation of the α-tetralone did *not* give a dienol, no addition to dienophiles being observed. A photochemical reaction involving the methyl group adjacent to the carbonyl function was observed. However, since the dimer **111** could be isolated. Furthermore, irradiation in the presence of oxygen gave the peroxide **112**. Thus it can be concluded that the photochemical reaction proceeds, by hydrogen abstraction, as far as the diradical species, which can be trapped by oxygen; it either does not collapse back to the (Z)-dienol or, if it does, hydrogen reversion is extremely fast. No cyclobutenol formation was noted in this case although it would be expected that such a product would be extremely strained. In contrast, photolysis of the benzocycloheptenone **110** proceeded smoothly to give the isomeric cyclobutenol **113** but, again for this ketone no dienol trapping products with dienophiles could be obtained. Heating this alcohol in the presence of maleic anhydride at 110° for 40 hr did not give an adduct, the alcohol being recovered. Under more vigorous conditions elimination to give the olefin **114** was observed.



109: n = 1, R = Me
110: n = 2, R = Me
115: n = 2, R = H
116: n = 3, R = H
117: n = 4, R = H
121: n = 5, R = H



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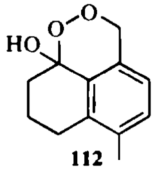

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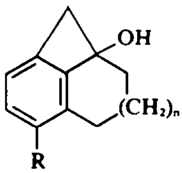
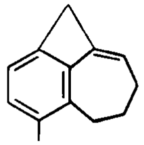


113: n = 2, R = Me
118: n = 2, R = H
119: n = 3, R = H
120: n = 4, R = H
122: n = 5, R = H



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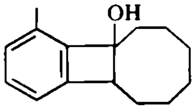
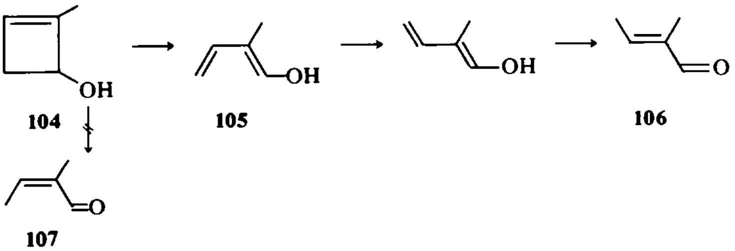


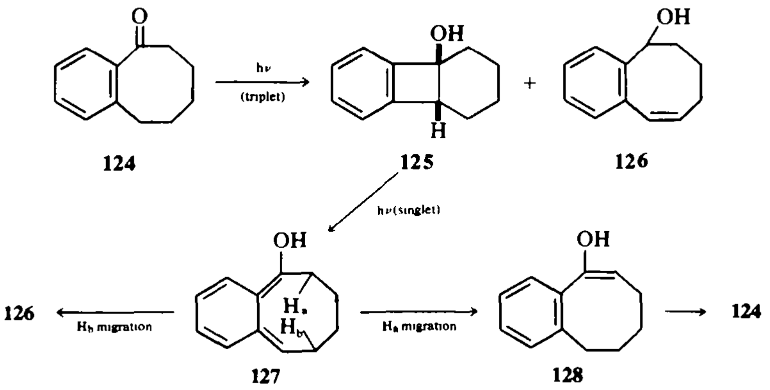
123

Related results have been obtained with the ketones **115–117**.[73] With n = 1, 2 or 3 the related alcohols **118–120** formed, but with the benzocyclodecanone **121** the alternative hydrogen abstraction process, leading to the alcohol **123** competed with formation of the alcohol **122**, reflecting torsional constraints on the disposition of the carbonyl group. The unsubstituted alkanone **124** gave both the cyclobutenol **125** and the alcohol **126** by a triplet state process, the reaction being essentially quenched by piperylene. The alcohol **126** must arise by a transannular hydrogen migration which competes with cyclobutenol formation. An interesting observation made in this work was the discovery of a photocatalysed reversion of the alcohol **125** to the ketone **124** and the alcohol **126** by a singlet process. The existence of a ground state dienol could not be confirmed since trapping with maleic



104 **105** **106** **107**

Scheme 11.



Scheme 12.

anhydride failed. Presumably, for this reaction, a disrotatory (excited state) ring opening of the *cis*-fused alcohol takes place and this can give the dienol **127**. Because of the ring size competing thermal 1,5-hydrogen shifts can occur, to give either the enol **128** of the ketone **124** or the alcohol **126** (Scheme 12).

8. SYNTHETIC APPLICATIONS

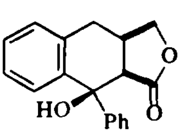
The synthetic potential of dienols has been illustrated in the preceding discussions. Despite the reactivity of these species, however, relatively few non-trivial applications have been reported.

The photochemical preparation of dienols has the advantage of ease of accessibility of the necessary precursors but is limited by the possibility of photochemical side-reactions. The complementary thermal method of generation from benzocyclobutenes has a wider synthetic scope but suffers from a scarcity of efficient methods for making the starting materials.[64]

Capitalising on the original work of Yang and Rivas,[3] two groups have envisaged a simple entry into some arylnaphthalene lignan systems.[74,75] A variety of dienophiles will add to the photoenol from 2-methylbenzophenone, including unsymmetrical dienophiles (Table 3). Regioselectivity, as well as stereoselectivity, is observed in these cycloadditions. For example, 4-hydroxybut-2-enoic acid lactone reacts to give the adduct **129** as the principal product.[74]

In order to develop a synthesis of arylnaphthalene ligands bearing a phenolic function at position 4, appropriately substituted aldehydes were selected as starting materials.[75] Photolysis of the derivative **130** in the presence of dimethyl butynedioate gave an adduct, which could either be dehydrated, to give the naphthalene **131** or oxidised, with manganese dioxide, to give the naphthol **132** (cf. Scheme 5). Subsequent chemical manipulations afforded the corresponding lactones. In this manner tetradehydropodophyllotoxin **133**, taiwanins E **134**, and C **135**, and justicidin E **136** have been prepared.

In a series of papers dealing with the trapping reactions of *o*-quinonedimethides Oppolzer and Keller[76] have photolysed the aldehyde **137**. An intramolecular addition reaction between the dienol so created and the olefinic bond took place to give a mixture of two adducts. The major isomer was the expected *endo*-adduct **138**. The minor product was the *exo*-addition adduct **139**. Because of the intramolecular nature of this reaction ring constraints impose a restriction on the mode of cycloaddition allowing competion between the *endo*- and *exo*-addition processes.



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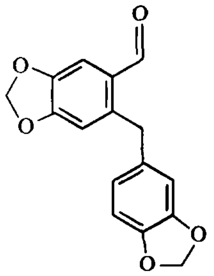

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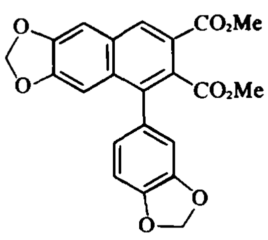

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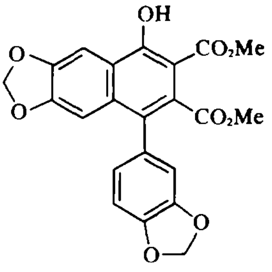

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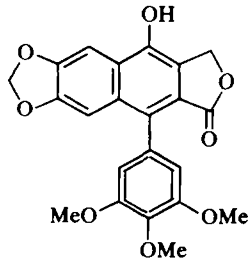

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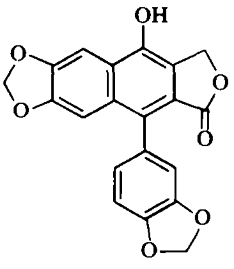

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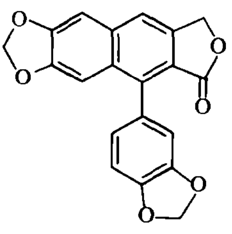

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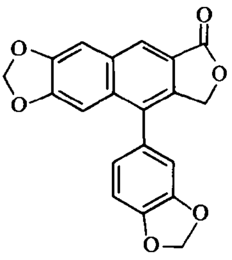

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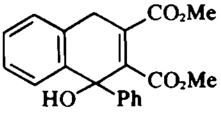
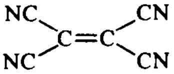
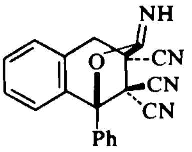
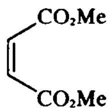
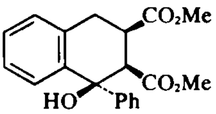
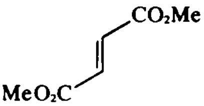
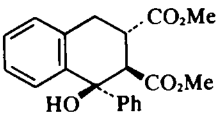
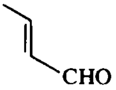
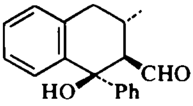
Table 3. Cycloadducts from 2-methylbenzophenone[74]

Dienophile	Adduct	Yield (%)
$MeO_2C{\cdot}C{\equiv}C{\cdot}CO_2Me$		53
		22
	**129**	50 (refluxing benzene) 7 (cold benzene)
		35
		58
		27

Use of cyclobutenol precursors complement the above photochemical reactions.[32,35] Kametani has repeatedly used the opening of benzocyclobutene derivatives, as the reactive *o*-quinonedimethides, in some elegant alkaloid syntheses.[77] In particular he found that the benzocyclobutenol **140** reacted with the imine **141** to give the cycloadduct **142**, which was then converted into the alkaloid xylopinine **143**.[78] The photochemical equivalent of this reaction has not so far been attempted.

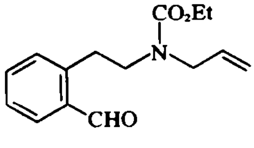
9. CONCLUSIONS

Whilst the scope of this review has been limited to the behaviour of aromatic carbonyl compounds it is apparent from the chemical literature that a much wider range of substrates will also undergo analogous transformations. For example, sulphur and nitrogen analogues of the photoenolisation process have been reported. 2-Benzylthiobenzophenone is reported to form the photoenethiol **144** on irradiation at 589 nm.[79] This report is somewhat suspect, however, as the enethiol would not be expected to be colourless as was reported in this note; formation of the benzocyclobutene **145** is a distinct possibility in this case. Similarly, N-acetyl-2-methyldiphenylmethane-imine **146**, and the benzyl analogue **147**, exhibit photochromic properties at 77°K, attributed to the formation of enamine isomers **148** via intramolecular hydrogen transfer.[80] Irradiation at room temperature produced no colour change, although incorporation of deuterium into the methyl group was observed from deuteriomethanol.

Photoenolisation in alkyl systems is well known. $\alpha\beta$-Unsaturated ketones isomerise to their $\beta\gamma$-isomers on irradiation and such isomerisations appear to occur via dienol intermediates, which are then reprotonated at the alternative site, viz. the α-position.[81] The more general utility of $\alpha\beta$-unsaturated ketones is restricted, however, by the host of competing photochemical reactions which can also occur.[82]

Studies on photoenolisation have so far afforded:

(a) An understanding of the photochemical processes



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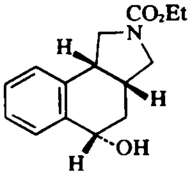

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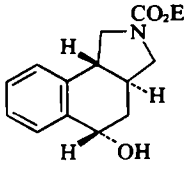

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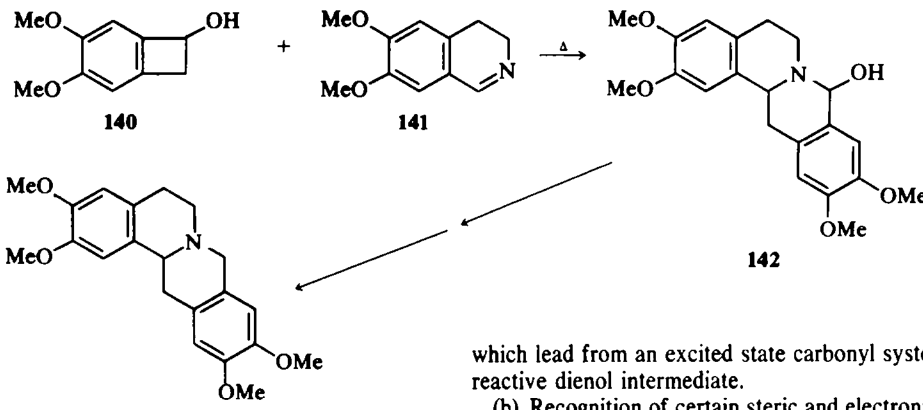
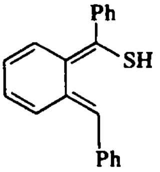


140 **141** **142**

143



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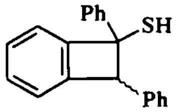

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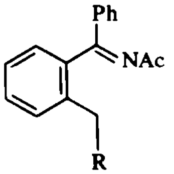
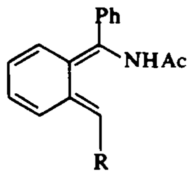


146: R = H
147: R = Ph



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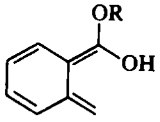

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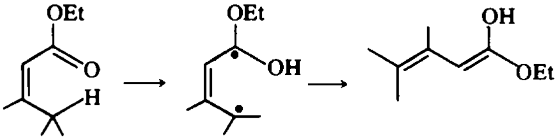
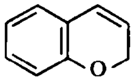


150 **151**



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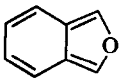

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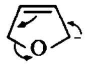

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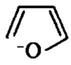

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which lead from an excited state carbonyl system to the reactive dienol intermediate.

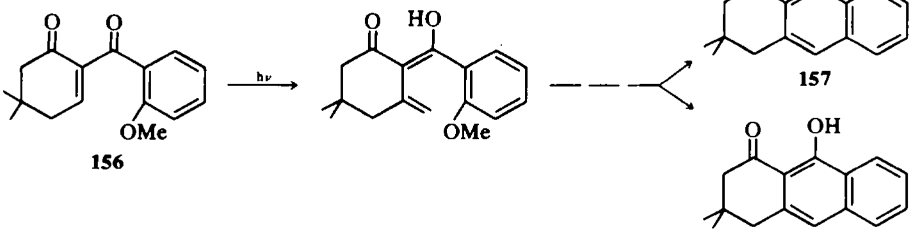
(b) Recognition of certain steric and electronic restrictions on the process. Thus, 2,6-disubstituted systems (e.g. **74**, Scheme 9) do not undergo photoenolisation unless the dienol can be stabilised (e.g. for **80**, where H-bonding can occur in the dienol). Only strong evidence for the formation of (E)-dienols has been obtained; the corresponding (Z)-isomers appear to be forbidden.

The consequences of the latter effect are of importance in attempting to extend the scope of the photoenolisation process (and in its thermal counterparts). Thus, the photo-reduction of aromatic esters by intermolecular hydrogen abstraction has been demonstrated,[83] although intramolecular examples have so far not been investigated. On the basis of the above results with aromatic ketones one would predict that a true photoenolisation reaction of a suitably substituted aromatic ester would not occur. It can be seen that any derived photoenol must adopt a structure, e.g. **149**, in which one of the two oxygen functions is in a cisoid relationship to the diene; results with the acetal **98** suggest that such a disposition is also disfavoured.

Isomerisation of aliphatic esters upon irradiation have been reported.[84] Although such processes need not involve ground state dienols, the problem associated with formation of cisoidal structures of the type **149** might not be pertinent since, for aliphatic systems, free rotation about the $\alpha\beta$-bond could possibly lead directly to the *trans*-oriented dienol (e.g. **150** to **151**).

The molecular reasons why dienols of the type **4** appear to be disfavoured are not yet completely clear. Totally bonded analogues, such as the chroman **152** and benzoisofuran **153** systems are well established. A more esoteric example is the formation of dienolate anion analogues. Opening of 2,5-dihydrofuran **154** with strong base gives the 1,2-*cis*-dienolate anion species **155**.[85]

(c) Photoenolisation studies have also given a lead for the investigation of new synthetic methods for annelations, which have been complemented by the corresponding work on the benzocyclobutenes.



156 **157** **158**

Much work remains to be carried out in order to extend the scope of the reaction. For example, applications of the photo-Elbs reaction have been very limited and could easily be improved. An interesting example, which should have further scope, is the observed cyclisation of the ketone **156**, which undergoes photoenolisation followed by a cyclisation and eventual elimination of either hydrogen, to give the naphthol **157**, or methanol, to give the product **158**.[86] Further work varying both the substitution pattern on the aromatic groups and on replacing them by heteroaromatic groups, etc. is also required.

Acknowledgements—The author wishes to place on record his sincere thanks to Drs. Susan Mellows, Barry Arnold and Timothy Wallace who have borne the brunt of our modest contribution to this area of chemistry.

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