PHOTOCHEMICAL E-Z ISOMERISATION AND CYCLISATION IN AN ARYLIDENECYCLOALKANONE OXIME ETHER SYSTEM

A Thesis presented for the Degree of Doctor of Philosophy

by

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under the supervision of Prof. Albert C. Pratt

at

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School of Chemical Sciences

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Declaration

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of Ph.D. is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

Signed: Mark Austin Date: 13/10/94

To

My Parents

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Abstract

The synthesis and photochemistry of a number of arylidenecycloalkanone oxime ethers has been investigated. Irradiation of E,E-2-benzylidenecyclopentanone oxime O-allyl ether results in rapid E-Z isomerisation around the carbon-nitrogen double bond accompanied by slower E-Z isomerisation around the carbon-carbon double bond, yielding four geometrical isomers which have been isolated and characterised . This indicates that isomerisation around the carbon-nitrogen double bond is the more facile process. Prolonged irradiation in methanol leads to the formation of 2,3-dihydro-1*H*-cyclopenta[b]quinoline, involving a 6π-electron photocyclisation process via an unisolated dihydropyridine intermediate followed by elimination of allyl alcohol.

The scope of the cyclisation has been investigated with a series of arylidenecycloalkanone oxime O-methyl ethers. Substitution at the aromatic ring with a methyl or methoxy group also yields the expected photocyclised product on irradiation, whilst substitution with chloro or nitro groups does not. Irradiation of furylidene and 1-naphthylidene derivatives yields new heterocyclic compounds and irradiation of the cyclohexanone derivative yields 1,2,3,4-tetrahydroacridine.

Heating of 2-diphenylmethylenecyclopentanone oxime O-methyl ether under reflux in ethylene glycol yields no products whilst irradiation yields the expected quinoline derivative indicating that the cyclisation is solely a photochemical and not a thermal process.

Acknowledgements

I would firstly like to thank my supervisor, Prof. Albert C. Pratt, for his supervision, advice, encouragement and patience over the last four years.

I am very grateful to the academic and technical staff of the School of Chemical Sciences, particularly Dr. Paraic James and Mick Burke for their assistance in the recording of NMR spectra. I am also grateful to the final year undergraduate project students who have worked with me, particularly Rory O'Donovan.

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1. Introduction: The Photochemistry of the Carbon-Nitrogen Double Bond

1.1 Introduction

Compounds containing a carbon-nitrogen double bond undergo a wide variety of photochemical reactions. In 1972 Wettermark first attempted to group these diverse reactions[1] and in 1977 two reviews were published dealing with the photochemistry of imines[2] and of compounds containing a carbon-nitrogen double bond in general[3]. The following survey concentrates on the literature from 1977 onwards in which time much investigation has been carried out in the area. Many of the photochemical transformations reported are more detailed investigations of photochemical reactions previously reported. Others such as the aza-di-π-methane rearrangement and the cyclodimerization of imines had not previously been reported. The photochemistry of N-oxides and nitrones and that of iminium salts have been excluded for the most part since their transformations have been well reviewed[4,5].

1.2 Excitation

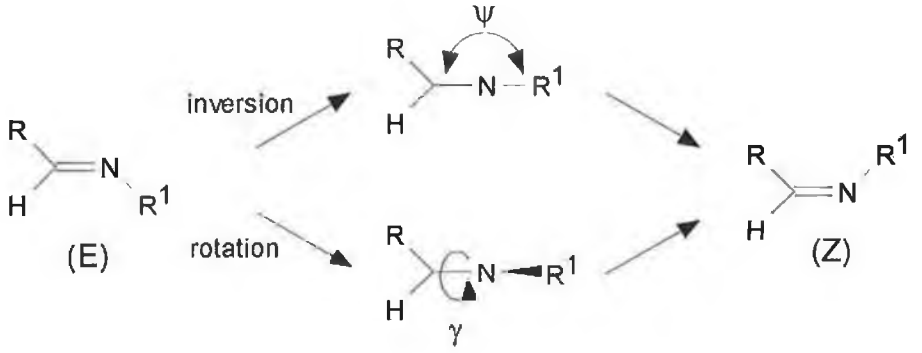
Unconjugated alkyl imines show two absorption bands in the ultraviolet region of the spectrum; a band at 240nm assigned as an n–π^* transition and a band at 180nm, of a greater intensity, assigned as a π–π^* transition[1,2]. Conjugation of the carbon-nitrogen double bond greatly alters the spectrum since the π–π^* transition will be shifted to longer wavelengths and submerge bands due to n–π^* transitions. Bands appearing in the 240nm region of the spectrum of conjugated imines may be unambiguously assigned as π–π^* since their extinction coefficients are much greater than those expected for n–π^* transitions.

1.3 E,Z photoisomerisation

Compounds containing a carbon-nitrogen double bond, where the double bond is not fixed in a ring system, readily undergo photochemical E-Z isomerisation[1-3]. In simple imines this isomerisation is short lived and the carbon-nitrogen double bond will thermally reisomerise, at ambient temperatures, back to the thermally more favoured isomer. The carbon-nitrogen double bond of oximes and, particularly, oxime ethers show much greater configurational stability, making them more attractive candidates for mechanistic photostudies.

The mechanism for E-Z photoisomerisation of the carbon-nitrogen double bond, whether by planar inversion, rotation or a combination of the two (Scheme I), provided some controversy[3]. In the ground (S_0) state the favoured mechanism is inversion since the rotational mechanism involves scission of the double bond. However, in the excited state the double bond character is reduced thus allowing the rotational mechanism to become a possibility. Several workers have investigated theoretically the mechanism of the photochemical E-Z isomerisation around the carbon-nitrogen double bond of simple imines and it is now clear from their results that the rotational mechanism is the favoured process[6-9]. Both Nishimoto and co-workers[6] and Ertl and Leska[7] have calculated the optimized geometries of methanimine, the parent compound of the imine group, in the ground and the S_1 states (Fig.1). Both workers show similar symmetries for the S_1 state. It can be seen that in the S_1 state, the optimized geometry has a 90° twist around the carbon-nitrogen double bond. Furthermore, calculation of the energy variation on rotation or inversion yields the potential curves (Fig. 2) which show that the γ variation is made more easily than the ψ variation in both the S_1 and T_1 states in contrast with the results obtained for the ground state S_0[8]. Substitution of a methylene proton with a phenyl[8] or vinyl[9] group, or with fluorine[7] does not

affect the mechanism.



SCHEME I

(ψ=angle of inversion, γ=angle of rotation)

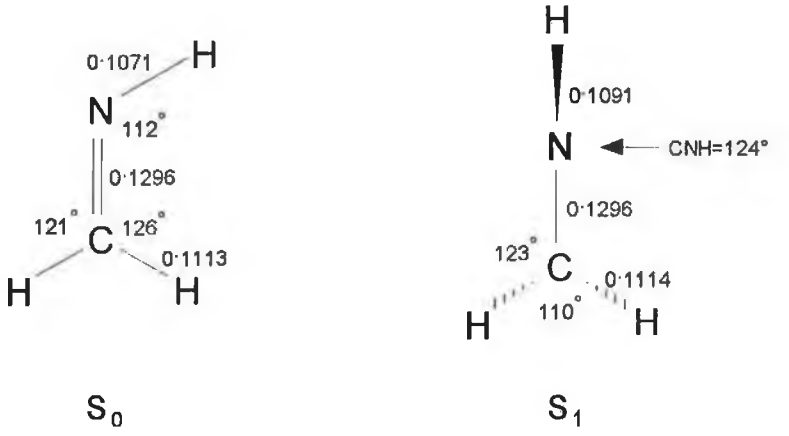


Fig.1. *The optimized geometry of methanimine in the S_0 and S_1 states (bond lengths in nm)*[7].

Although in most cases E-Z isomerisation around the carbon-nitrogen double bond is a two way process involving establishment of a photostationary state[2,3], a number of examples have appeared in the literature reporting one way photoisomerisation around the carbon-nitrogen double bond[10-13]. Under direct or sensitised irradiation the E- isomer of 2-benzoylpyridine-4-nitrophenylhydrazone (1) undergoes irreversible isomerisation to the Z-isomer, whereas the E- isomer of 3-benzoylpyridine-4-nitrophenylhydrazone (2)

undergoes reversible photoisomerisation[10]. The lack of photochemical activity of the Z- isomer of (1) can be attributed to hydrogen bonding present in the ground and excited states since, when a hydrogen bond connects two π systems, there is an increase in the rate of internal conversion, resulting in a shortening of the excited singlet (S_1) lifetime and therefore a quenching of photoreactivity.

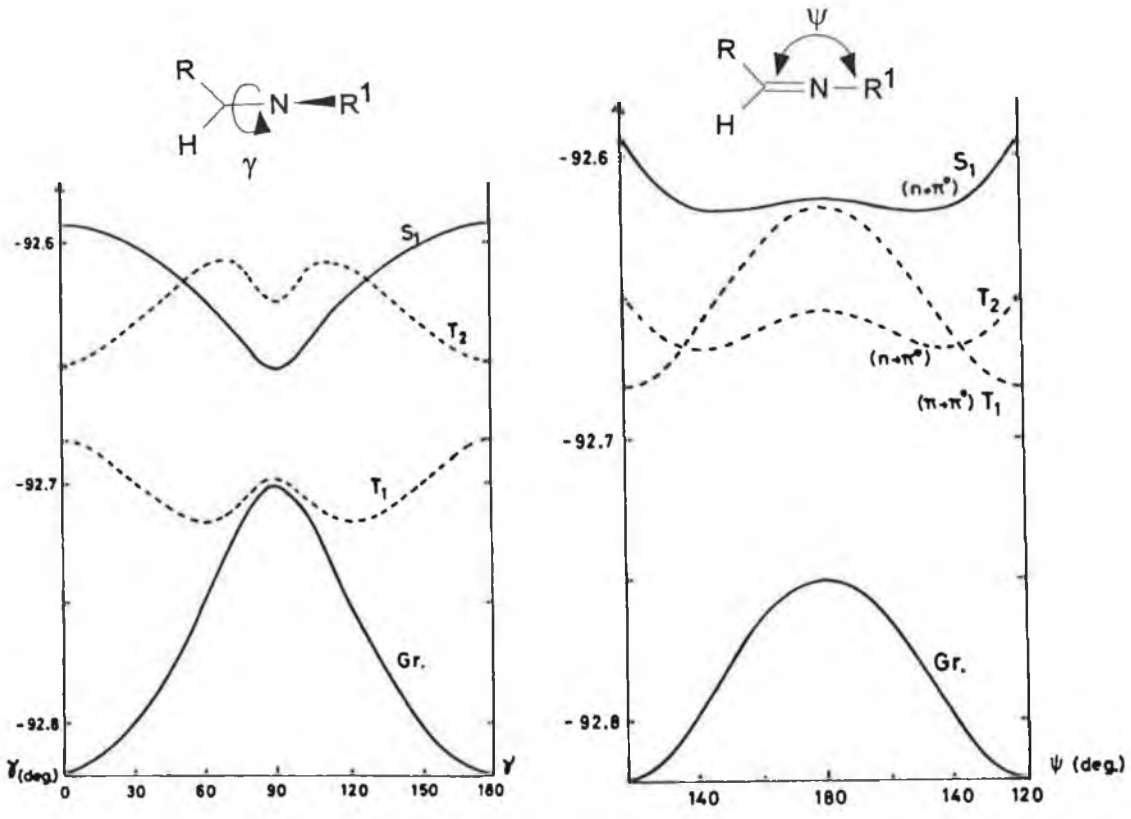
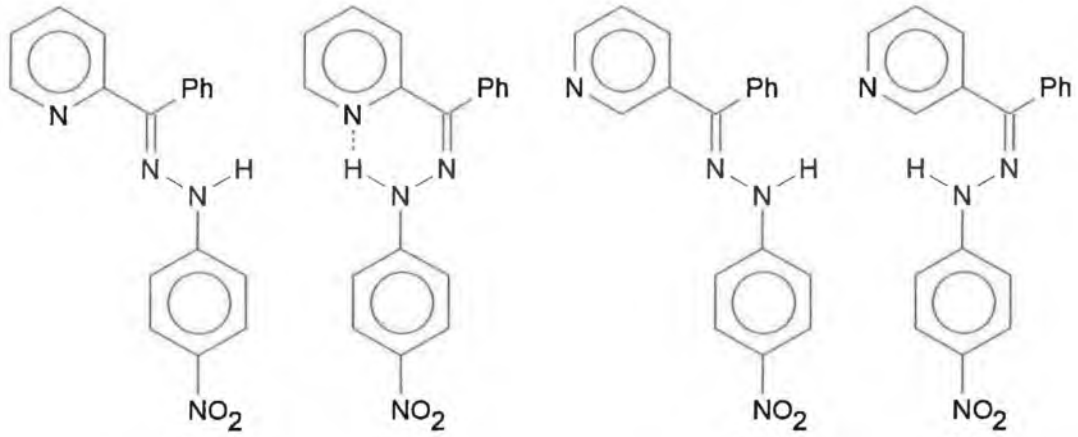


Fig.2. *Potential curves for energy variation on rotation (γ) or inversion (ψ) of the low lying states of methanimine[8].*

On triplet sensitised irradiation, the Z- isomer of N-methoxy-1-(2-anthryl)-ethanimine (3) undergoes one way photoisomerisation to the E-isomer[11]. This has been attributed to the localization of excitation mostly on

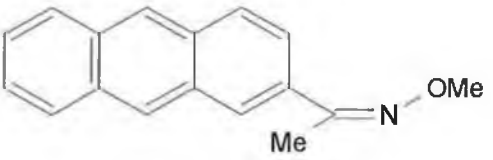
the anthracene nucleus of E-(3) resulting in rotational isomerisation of the anthracene nucleus around the single bond (s-*trans* to s-*cis*) in the excited state in preference to the isomerisation from E- to Z- around the double bond.

One way E-Z photoisomerisation has also, surprisingly, been reported on irradiation of the E- isomer of the acetyl derivative of acetonitrolic acid (4, R=NO_2, R^1=Me) which gives 100% isomerisation to the Z- isomer[12]. This is in contrast to the similar acetyl derivatives of the α-chloro-oxime (4, R=Cl, R^1=Ph) which undergoes competing E-Z isomerisation to give a photostationary state of E- and Z- isomers of 1.5:1[13].

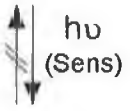


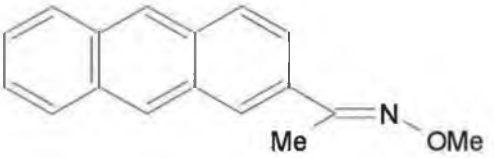
A number of reports have appeared in the literature concerning the photochemistry of α,β–unsaturated oxime ethers[14-17]. It had previously been reported that the E,E- isomer of benzylideneacetone oxime O-methyl ether (E,E-(5)) undergoes isomerisation only around the carbon-carbon double bond, with no isomerisation occurring around the carbon-nitrogen double bond[18]. It has now been shown that E,E-(5) undergoes isomerisation around both the carbon-carbon and carbon-nitrogen double bonds, and that carbon-nitrogen double bond isomerisation is the more facile process, both under direct and triplet sensitised irradiation[14]. The photostationary state of the four isomers at

equilibrium on direct irradiation was 46:17:3:34 for isomers E,E-(5), Z,E-(5), E,Z-(5) and Z,Z-(5) respectively.

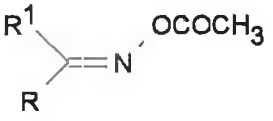


Z-(3)

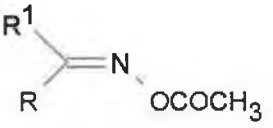




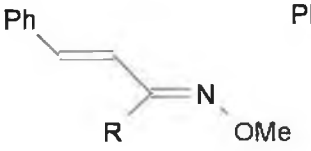
E-(3)



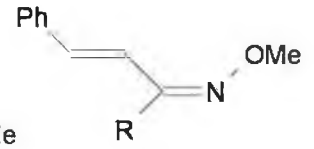
E-(4)



Z-(4)

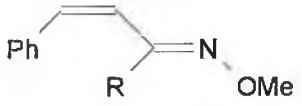


E,E-

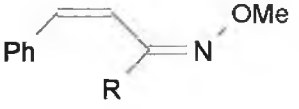


Z,E-

(5) R=Me
(6) R=H



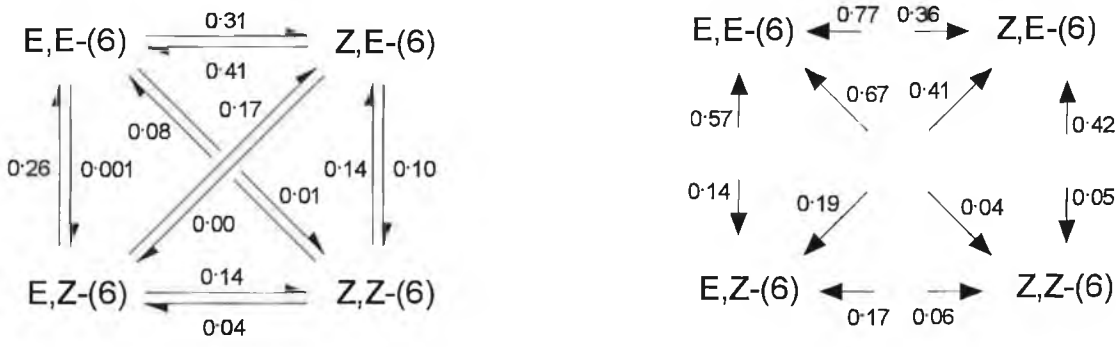
E,Z-



Z,Z-

Direct irradiation of the E,E-isomer of 1-methoxyimino-3-phenyl-2-propene (E,E-(6)) also leads to isomerisation around both double bonds to give a

photostationary state product ratio of 37:31:6:26 for E,E-(6), Z,E-(6), E,Z-(6) and Z,Z-(6) respectively[15]. Tokumaru has calculated the quantum yields for this direct process (Fig.3a) and has concluded that, as well as isomerisation around individual double bonds, isomerisation may occur around both double bonds simultaneously (except in the case of Z,E-(6) to E,Z-(6)). On triplet sensitised irradiation of E,E-(6) it was seen that the quantum yield for the formation of a given isomer was similar, irrespective of the starting isomer, and concluded that isomerisation occurs via a common triplet intermediate[16] (Fig 3b).

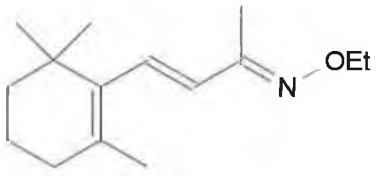


(a) (b)

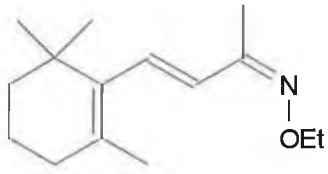
Fig.3. *Quantum yields for the isomerisation of (6) on (a) direct[15] and (b) triplet[16] sensitised irradiation.*

The photochemistry of (E)-β-ionone oxime O-Ethyl ether (7) has also been studied[17]. Direct irradiation of E,E-(7) yields the geometrical isomers E,Z-(7) and Z,Z-(7) along with Z,E-(8) and Z,Z-(8), formed by a 1,5-hydrogen shift, E,Z-(7) and Z,E-(8) being the primary photoproducts. Triplet sensitised irradiation of E,E-(7) however, yields a mixture of the four geometrical isomers of (7) as photoproducts, with differing ratios at the photostationary state according to the sensitiser used. It was concluded that E-Z isomerisation on direct irradiation occurs exclusively from the singlet excited state since the

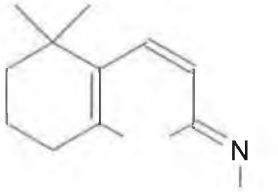
triplet excited state product Z,E-(7) is not formed on direct irradiation. The addition of ethyl iodide, which enhances singlet to triplet intersystem crossing, does not alter the composition of photoproducts on direct irradiation.



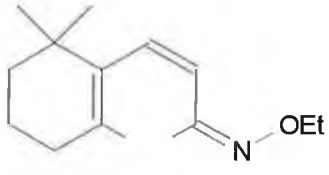
E,E-(7)



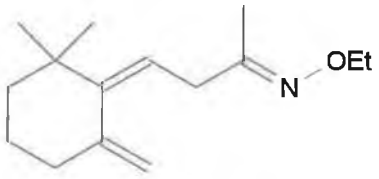
E,Z-(7)



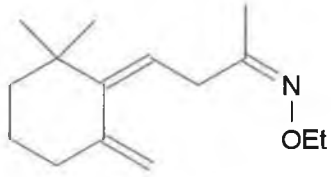
Z,E-(7)



Z,Z-(7)



Z,E-(8)

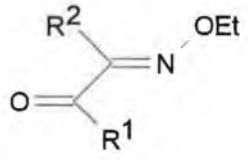


Z,Z-(8)

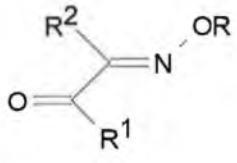
Baas and Cerfontain and co-workers have studied the photochemistry of a series of α-oxo oximes, ethers and acetates[19-22]. Oxime ethyl ether (9a), which exists in the s-*trans* conformation, undergoes triplet sensitised E,Z isomerisation (from the T_1 (π–π^*) state) to yield the Z isomer which has been found to exist preferentially in a slightly non planar s-*cis* conformation[19,20], while compounds that possess more bulky groups at R^1 and R^2 (9b,c) also undergo E,Z isomerisation but yield Z isomers in the s-*trans* conformation[20]. On direct irradiation (λ>300nm) E,Z isomerisation also occurs, but is accompanied by competing photodecomposition (probably from the S_1 (n–π^*) excited state) and in the case of (9c), a competing γ-hydrogen abstraction

(Type II) process, by the carbonyl function, followed by ring closure yielding cyclobutanol derivatives, also occurred[21].

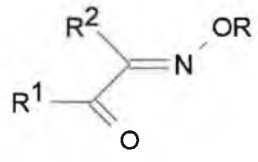
Irradiation of α-oxo oximes (10b-e and j) and (11a) and the α-Oxo oxime acetates (12b-e and j) and (11b) led to E-Z isomerisation with eventual formation of a photostationary state, the ratio of which depended on the structure of the α-oxo oxime function[22]. The E isomers of the α-oxo oximes (10a, f-i), and the α-oxo oxime esters (12a,f and h) and (13a-c) did not photoisomerise. All of the α-oxo oxime esters studied photodecomposed readily while the α-oxo oximes did not photodecompose to any significant extent. On irradiation at shorter wavelengths (λ=254nm) the photodecomposition of α-oxo oxime ethers[23,24] and esters[25] was found to be far more rapid and involved radical formation via initial nitrogen-oxygen bond cleavage.



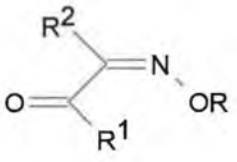
(9) a; $R^1=R^2=Me$
b; $R^1=Ph$, $R^2=Me$
c; $R^1=Pr^i$, $R^2=Bu^i$



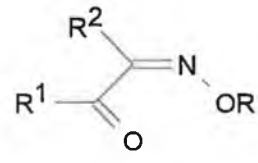
s-*trans*-(E)



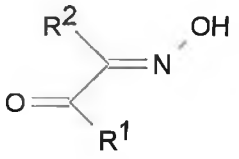
s-*cis*-(E)



s-*trans*-(Z)

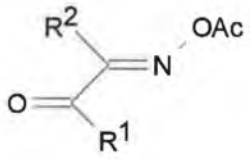


s-*cis*-(Z)



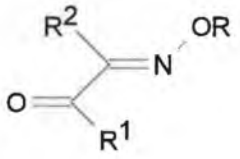
(10)

a, R^1=R^2=Me
b; R^1=Ph, R^2=Me
c; R^1=Me, R^2=Ph
d; R^1=Me, R^2= 
e; R^1=  , R^2=Ph



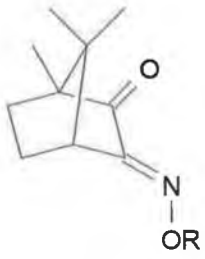
(12)

f, R^1=Et, R^2=Me
g, R^1=Me, R^2=H
h, R^1=Me, R^2=Et
i, R^1=Me, R^2=CH_2Ph
j, R^1=R^2=Ph

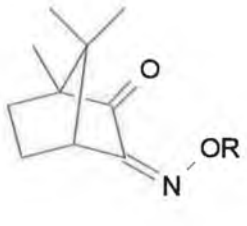


(13)

a; R=COEt, R^1=R^2=Me
b; R=COPh, R^1=R^2=Me
c; R=COEt, R^1=Me, R^2=CH_2Ph



E- (11)

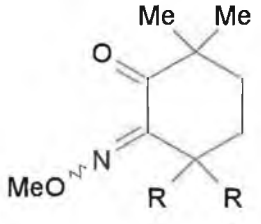


Z- (11)

a; R=H
b; R=Ac

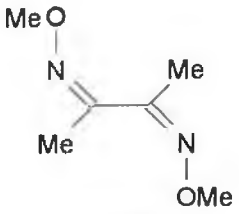
Cerfontain has also studied the effects of steric control on the photochemical E-Z isomerisation of the carbon-nitrogen double bond in some overcrowded α-oxo oxime ethers[26]. These compounds may be divided into two classes: (a) where the E- isomer is thermally favoured *e.g.* (14) and (b) those where the Z- isomer is thermally favoured *e.g.* (15). The photoisomerisation proceeds, as with other α-oxo oximino compounds, from triplet states having π–π* excited character via a rotation mechanism. For the oxime ethers in the first group *e.g.* (14), the potential free energy surfaces of the excited triplet and the ground state are almost mirror images, in the sense that the maximum of the ground (S_0) state between the two geometrical isomers roughly coincides with the minimum of the triplet (T_1) state (Fig 4). The photochemical E-Z

isomerisation of (14) therefore proceeds from the excited triplet state of E-(14) and Z-(14), followed by rapid relaxation by twisting to the triplet potential minimum. At this stage intersystem crossing from the twisted triplet to the twisted ground state occurs and this then undergoes partition to the two geometrical isomers yielding a photostationary state of E-(14)/Z-(14) of approximately 0.6. With the second group, such as (15), there is, in addition, a steric effect in the E- isomer in the region of 120-180° twist of the carbon nitrogen double bond due to the interaction between the σ-type lone pair electrons of the methoxyimino oxygen and the adjacent methyl substituents (Fig.5). The curves thus obtained for (15), as a typical α-oxo oxime ether of the second group (Fig.4) show that the relaxation of the excited triplet state of the E- isomer has a free energy of activation and will thus be retarded and its rate of intersystem crossing to the ground state will be increased. More importantly, the partitioning of the twisted ground state (formed by intersystem crossing from the triplet excited state), will now strongly favour the Z-isomer. Consequently the photostationary state of the E-(15)/Z-(15) is 0.06.

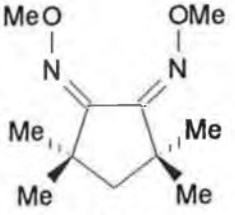


(14) R=H
(15) R=Me

For a series of α-bis(oxime O-methyl ether) alkanes such as (16) or (17) triplet sensitised irradiation leads only to E,Z-isomerisation. Direct irradiation leads to E,Z-isomerisation and also to some photodecomposition resulting from nitrogen-oxygen bond homolysis[27].



(16)



(17)

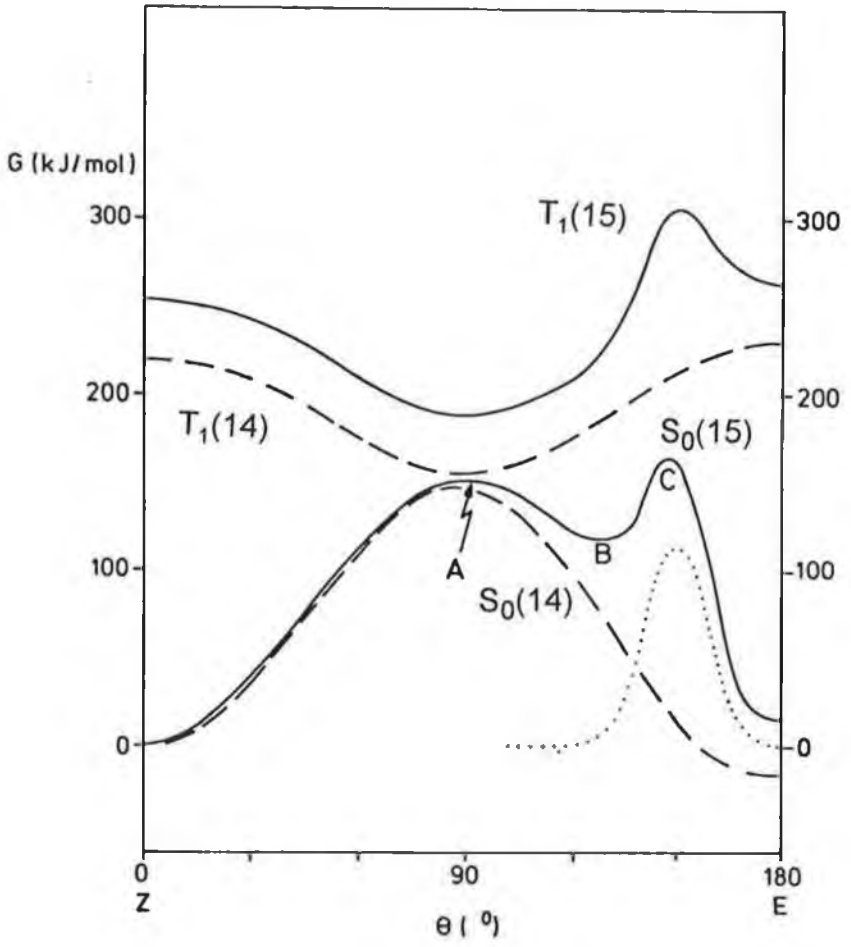


Fig.4. *Proposed ground and triplet state free energy surfaces for (15), solid lines, and (14), broken lines, plotted as a function of twist about the C-N bond. The dotted line represents the free energy due to steric repulsion in the ground state of (15). The free energies of both Z-(15) and Z-(14) were arbitrarily chosen to be zero*[26].

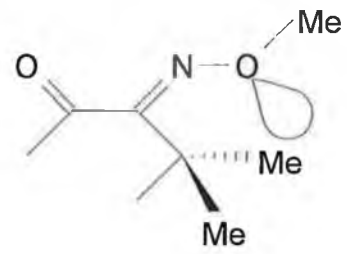


Fig.5. *Orientation of the σ-type lone-pair of the methoxyimino oxygen in an overcrowded E-α-oxo oxime ether*[26].

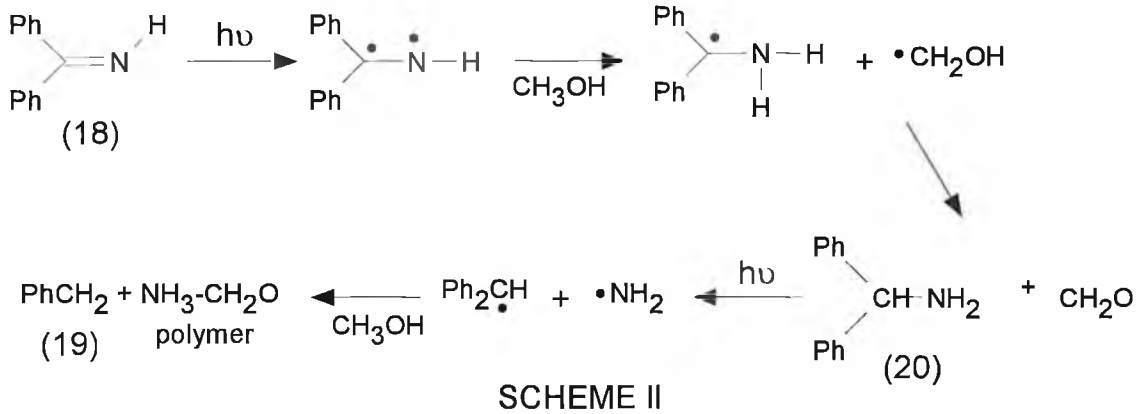
1.4 Hydrogen Abstraction

Imines have a reduced tendency to inter- and intra-molecular hydrogen abstraction when compared to those compounds containing the carbonyl chromophore[2,3]. It has been suggested that deactivation by rapid radiationless decay to the ground state may account for this low activity[28] and that the presence of a lowest π–π^* T_1 state may also be a factor for certain imines[29]. However some examples of hydrogen abstraction by the nitrogen atom of the imino-chromophore were known[2,3], and further reports have appeared in the literature[30-35].

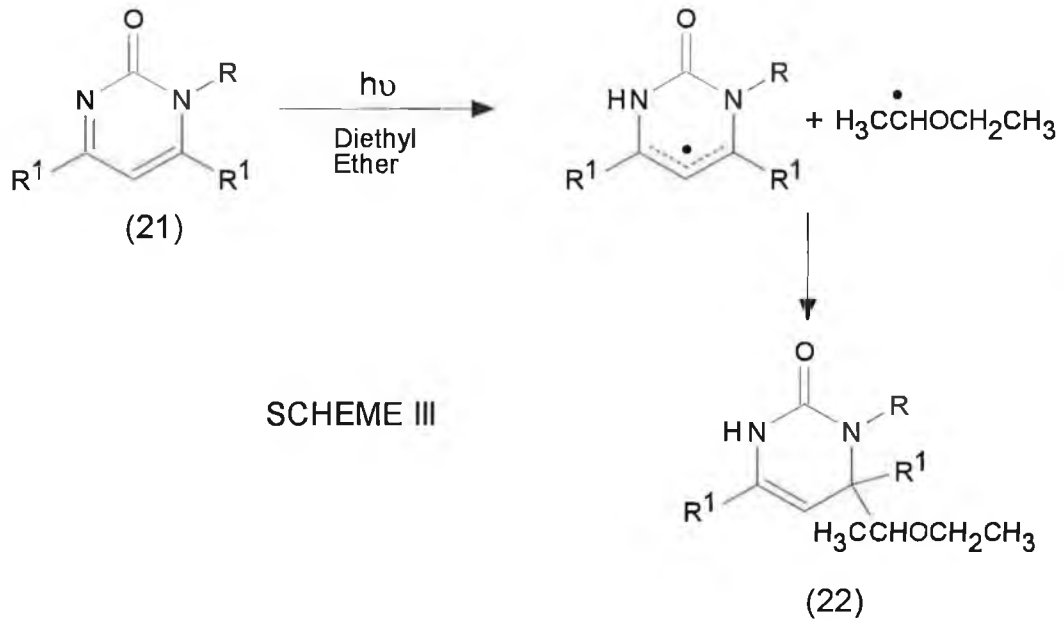
Benzophenoneimine (18)[30] is reduced to diphenyl methane (19) on irradiation. It has been proposed that (19) is formed via initial addition of hydrogen, abstracted from solvent, across the double bond, to yield the corresponding amine (20) followed by carbon-nitrogen bond cleavage (Scheme II). Indeed irradiation of amine (20) also yields (19). A similar result was seen for fluorenoneimine which photofragments more rapidly[31].

Compounds containing an imino chromophore may also undergo photoalkylation via an initial hydrogen abstraction process[32-35]. Thus for example pyrimidin-2-one (21) yields addition product (22) on irradiation in

benzene containing diethyl ether (Scheme III)[32]. Other examples include the addition of cyclic olefins to N-acetyldiphenylmethyleneamine (23) to form (24)[33], and the addition of anilines to *p*-benzoquinonediimine derivatives (25) to form (26)[34], via similar mechanisms.

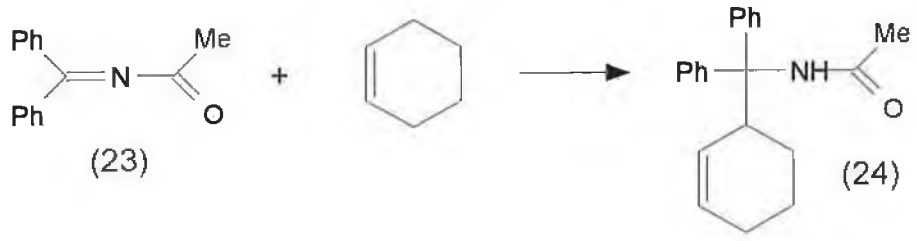


SCHEME II

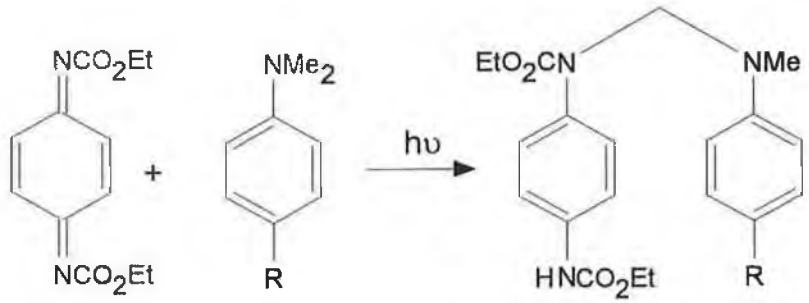


SCHEME III

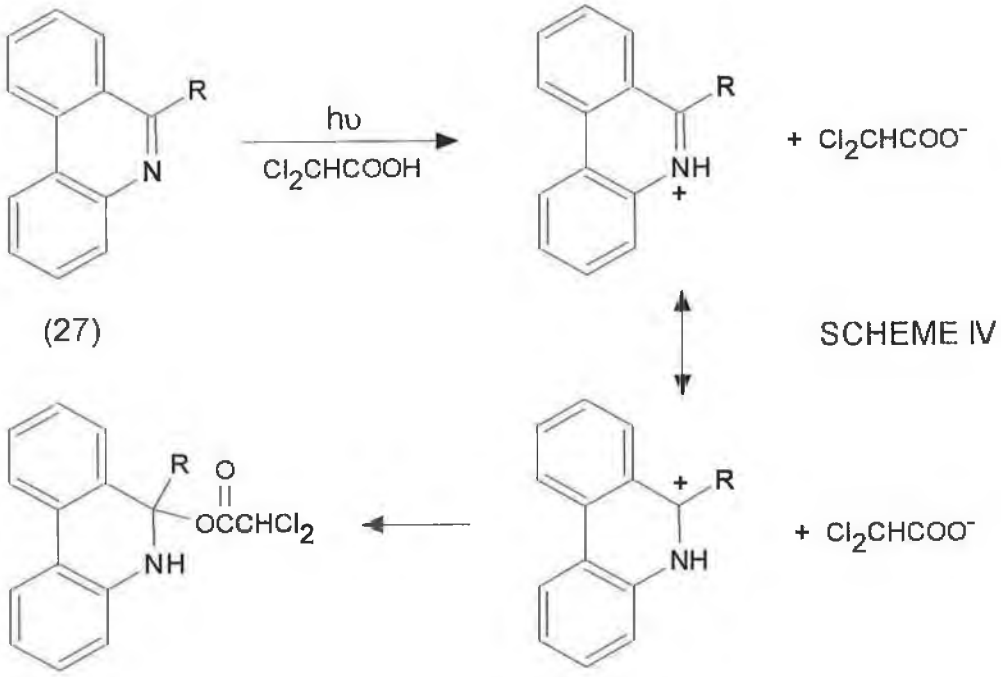
Interestingly, the phenanthridine (27) undergoes photoaddition of dichloroacetic acid across the carbon-nitrogen double bond but the authors have proposed that addition occurs via protonation of the nitrogen followed by nucleophilic attack (Scheme IV), rather than via a radical mechanism (addition of radical scavengers does not affect the conversion)[36].



(23) (24)



(25) (26)



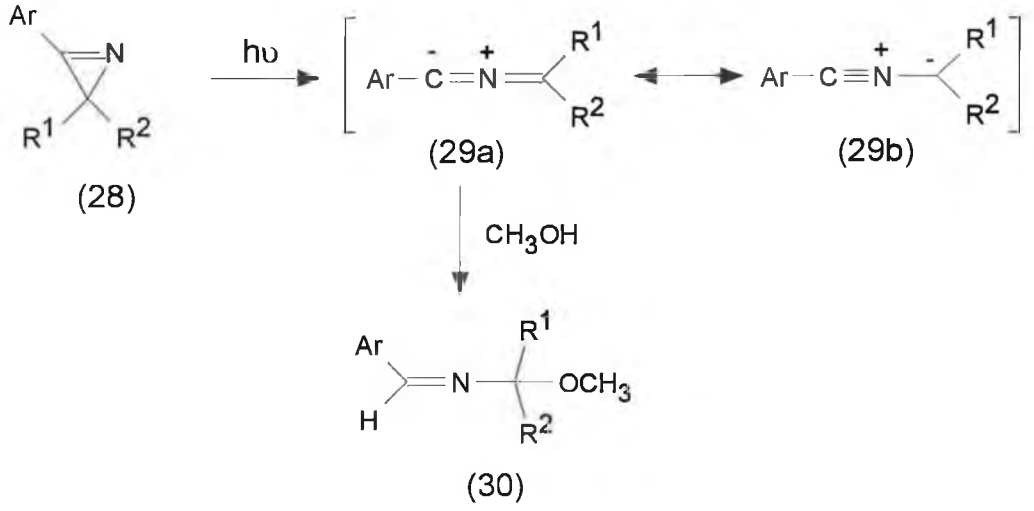
(27)

SCHEME IV

1.5 Azirine Photochemistry

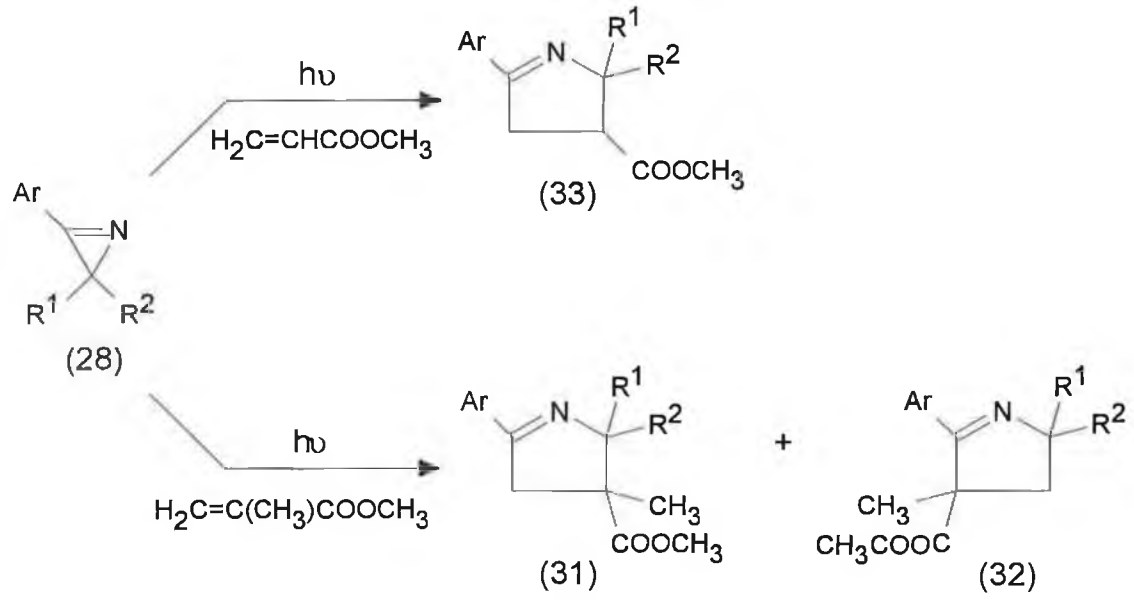
Azirines (28) readily undergo carbon-carbon bond cleavage from the n-π^* singlet state to form nitrile ylides (29), highly reactive intermediates, which in turn react with dipolarophilic groups, generally via a 1,3-dipolar cycloaddition, to form heterocycles[3]. This allows a useful synthetic approach to quite complex heterocyclic compounds. Addition is believed to be concerted and to occur from interaction of the highest occupied molecular orbital (HOMO) of the nitrile ylide with the lowest unoccupied molecular orbital (LUMO) of the dipolarophile. The degree of reactivity of the nitrile ylide is therefore governed by the extent of stabilisation of the transition state by this interaction.

Addition of methanol to the nitrile ylide (29) proceeds with regiospecificity to give alkoxyimines (30) indicating that in the HOMO of the nitrile ylide, electron density is greater at the disubstituted than the trisubstituted carbon.

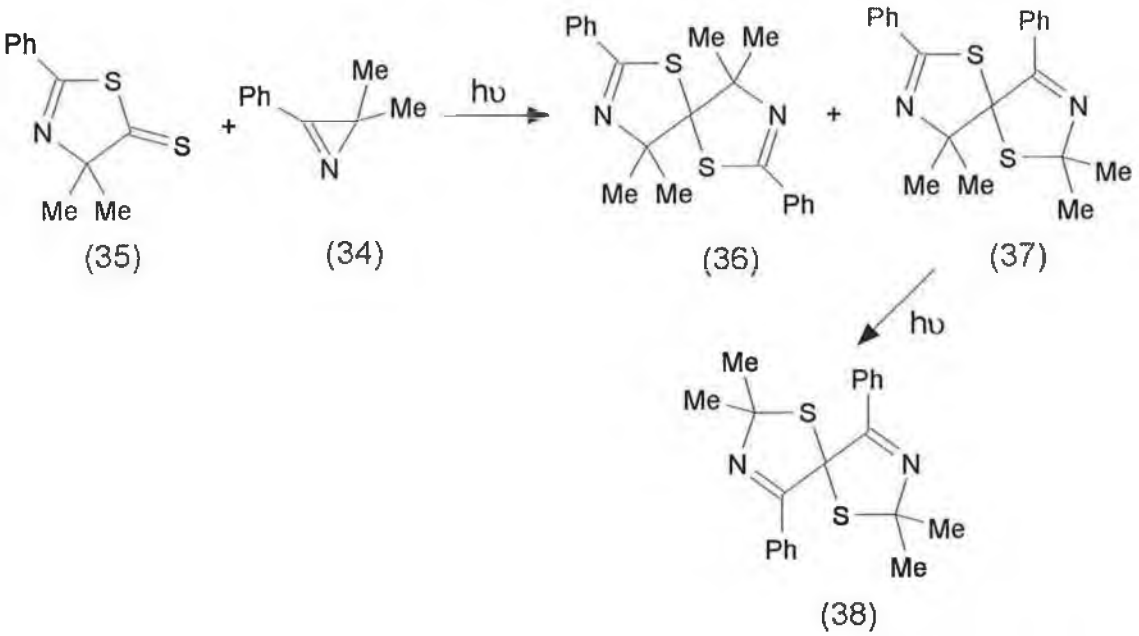


A variety of dipolarophiles undergo cycloaddition to the nitrile ylides and the regioselectivity is dependent on the polarization of the LUMO of the dipolarophile[3]. Thus methyl methacrylate, where the terminal coefficients are nearly the same, yields two regioisomers (31) and (32) on irradiation with

azirine (28), whilst methyl acrylate, where the terminal coefficient of the unsubstituted carbon is greater, yields only one (33).



Numerous further examples of this type of addition have appeared in the literature[37-45]. Thus, for example, irradiation of azirine (34) in the presence of thiazolinothione (35) yields cycloadducts (36) and (37) along with (38), formed by photochemical isomerisation of (37)[37]. Azirine (34) undergoes preferential cycloaddition to the carbon-carbon double bond of 1,4-napthoquinone (39, R=H) to form cycloadduct (40), whilst with the 2,3-dimethyl substituted napthoquinone (39, R=CH_3), cycloaddition preferentially occurs at the carbon-oxygen double bond, forming cycloadduct (41). This effect is again explained by differences in the polarization of the LUMO of the dipolarophile[38]. Pfoertner has utilised the 1,3-dipolar additions of azirines to synthesise compounds which have potential biological activity[39,40]. Padwa has also reported the novel [3+3] photocycloaddition of azirine (34) with fulvene (42) to give cycloadduct (43) as the major product along with small amounts of cycloadduct (44)[46].


Ph
S
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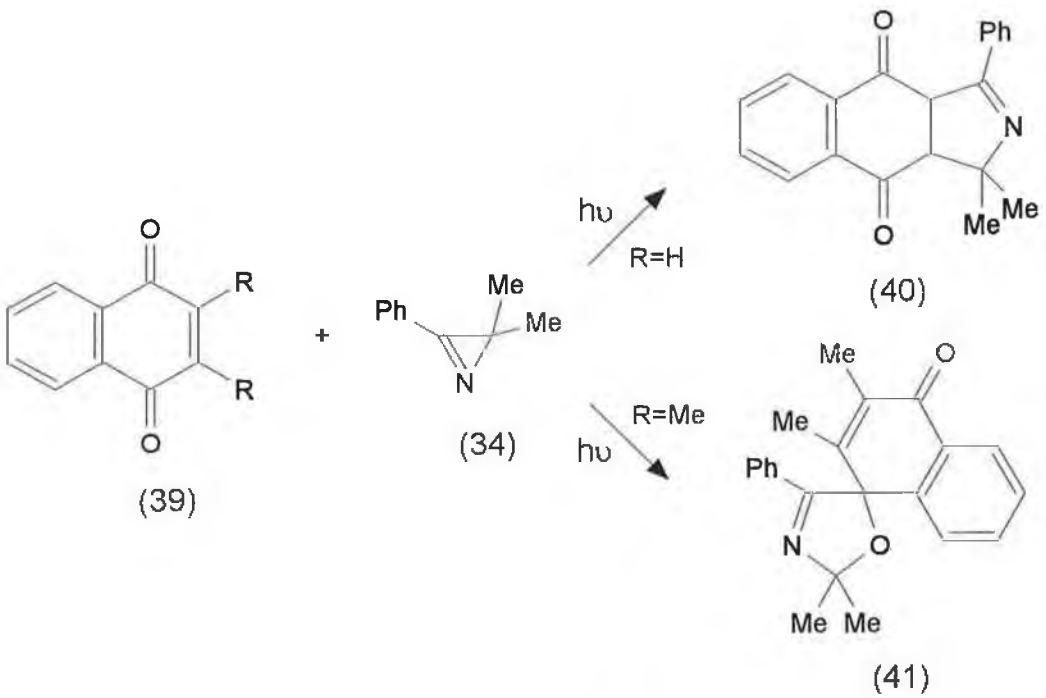
(38)


O
R
R
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(39)
+
Ph
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Me
N
(34)
hυ
R=H
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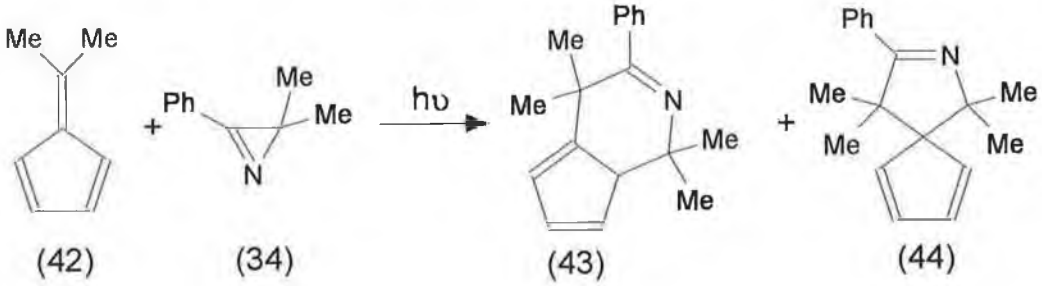
Me Me
(41)


Me Me
(42)
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(34)
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Me
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(43)
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N
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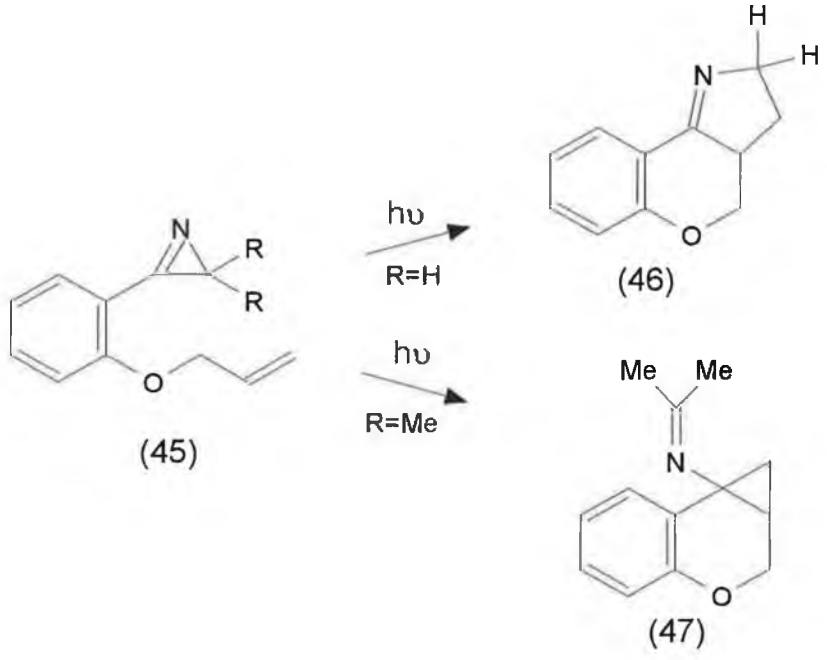
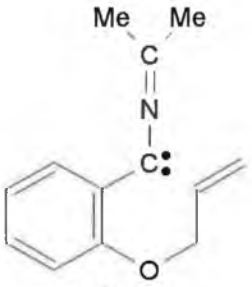
Me
Me
Me
(44)

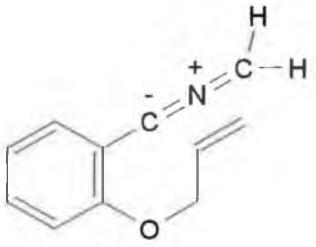
Padwa has investigated intramolecular cycloaddition reactions of nitrile ylides bearing appropriate substituents and has found that the photoproducts formed depend greatly on the nature of the substituent[47-50]. For a series of azirines bearing unsaturated ortho substituents on the aromatic ring, the intramolecular reaction may proceed to give either 1,1- or 1,3-cycloadducts[47,48]. Thus irradiation of the 2*H*-azirine (45, R=H) yields the 1,3-cycloadduct (46) as the sole photoproduct, whilst irradiation of the dimethyl derivative (45, R=Me) exclusively yields the 1,2-cycloadduct (47)[47].



Padwa has proposed that the mode of addition may be due to the geometry of the nitrile ylide. Those compounds bearing electron releasing substituents, such as the methyl groups, in the C-3 position of the nitrile ylide have preference for a bent geometry making the nitrile ylide more carbene-like, e.g. (48), and facilitating formation of the 1,1-cycloadduct whilst those compounds dihydro substituted at the C-3 position give nitrile ylides (49) with a more linear geometry, yielding the 1,3-cycloadducts[47].

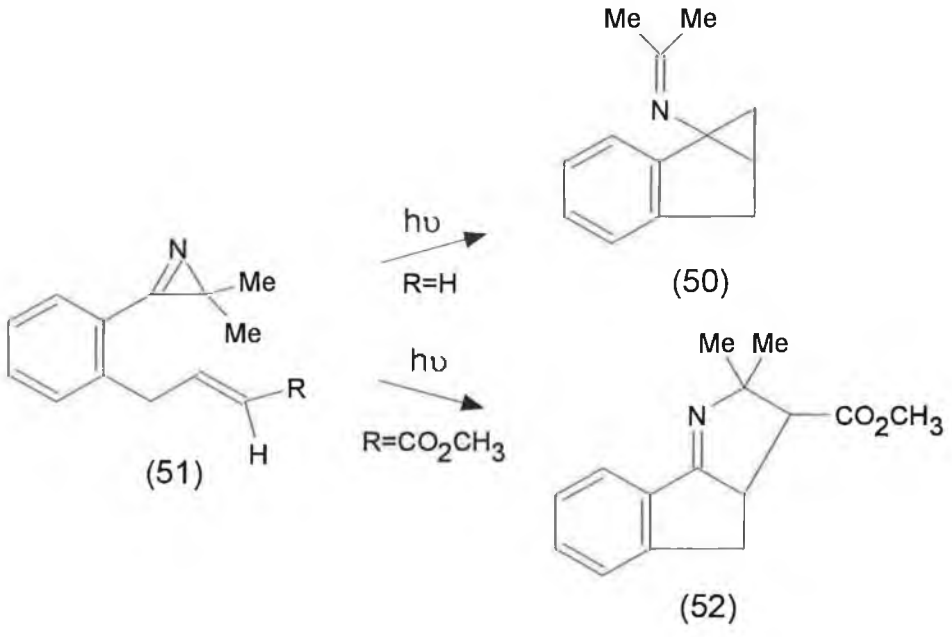


(48)



(49)

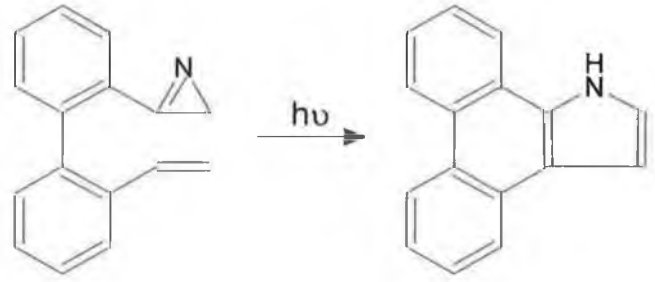
Similarly a 1,1-cycloadduct (50) was formed on irradiation of the dimethyl 2*H*-azirine (51, R=H). However irradiation of the corresponding caboxylate (51, R=$COOCH_3$) yields the 1,3-cycloadduct (52) indicating that the presence of an electron withdrawing group on the double bond also affects the outcome of the intramolecular cycloaddition reaction[48].



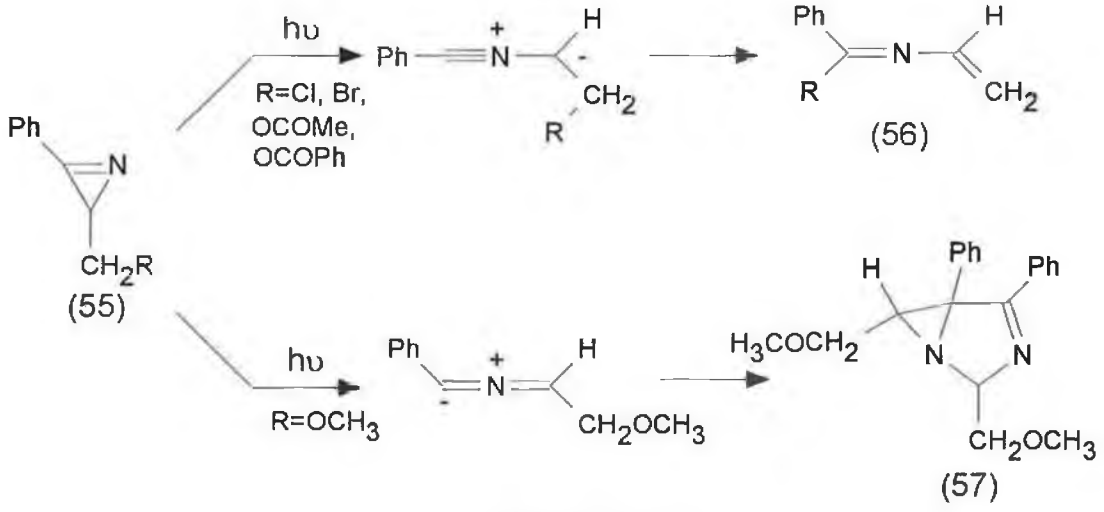
Irradiation of the azirine (53) yields pyrrole (54) as the only identifiable photoproduct, formed by 1,3-photocycloaddition, followed by air oxidation[49].

Padwa has also reported that azirines (55, R=Cl, Br, $OCOCH_3$, OCOPh) undergo a 1,4-substituent shift on irradiation to form azabutadienes (56) whilst (55, R=OMe) only affords (57) by 1,3-addition of the nitrile ylide across the

carbon-nitrogen double bond of the starting azirine and has concluded that the ability of (55) to undergo the 1,4-substituent shift is a function of leaving group ability[50] (Scheme V).



(53) (54)

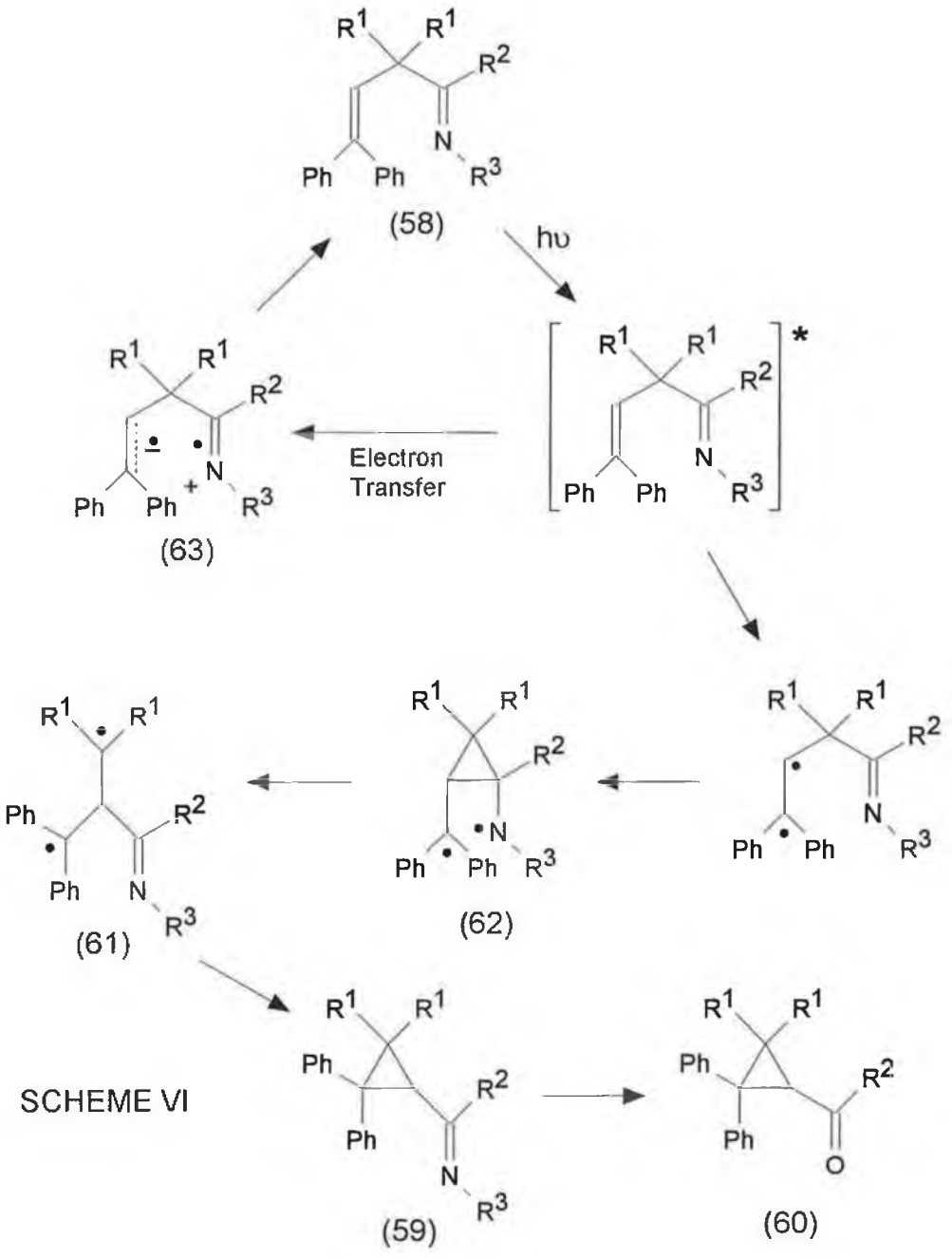


SCHEME V

1.6 Rearrangements involving Substituent Migration

Although the di-π-methane rearrangement of 1,4-dienes was a well established reaction[51], and β,γ-unsaturated carbonyl compounds had been shown to undergo an analogous oxa-di-π-methane rearrangement[52], it is only recently that the corresponding β,γ-unsaturated aza-analogues have been the subject of photochemical investigation[53-70]. Armesto, Horspool and co-workers have since shown that an aza-di-π-methane rearrangement does occur and have thoroughly investigated the scope of the process[53-67]. Initially it was shown that imine (58, R^1=Me, R^2=H, R^3=CH_2Ph) undergoes rearrangement on direct irradiation to cyclopropane (59), whilst triplet sensitised irradiation leads to higher yields and it has been proposed that rearrangement occurs via excitation of the 1,1-diphenyl alkene moiety following a path analogous to the di-π-methane and oxa-di-π-methane processes (Scheme VI)[53,54]. The resultant imines undergo facile hydrolysis to aldehydes (60). The corresponding β,γ-unsaturated aldehydes do not undergo an equivalent oxa-di-π-methane rearrangement but rearrange via a 1,3 acyl migration[71]. Thus the imino substituted derivatives give a convenient route to the cyclopropanes.

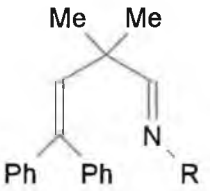
Changing the nature of the substituents greatly affects the efficiency of the cyclisation. Imines bearing phenyl substituents at the central carbon atom (58, R^1=Ph) cyclise far more readily than the corresponding dimethyl substituted imines[55]. This may be the result of the greater stabilising effect of the phenyl substituents on the diradical intermediate (61), allowing for more efficient 'unzipping' of the intermediate (62). Phenyl substitution at the imino-carbon atom (58, R^2=Ph) shifts the absorbance of the imino chromophore to longer wavelengths, allowing it to compete with that of the diphenyl alkene moiety. Irradiation of the phenyl substituted derivative yields a large number of photoproducts which may be due to Norrish type 1 cleavage of the imino group[55]



SCHEME VI

The nature of the substituent at nitrogen plays an important role in the cyclisation. It has been proposed that electron transfer from the nitrogen lone pair to the diphenyl alkene moiety may result in formation of radical cation/radical anion (63) which may then decay to the ground state, thus diminishing the efficiency of the rearrangement[56]. Compounds containing groups which can prevent this electron transfer therefore undergo cyclisation

more readily. Imines (64a-c) were seen to be comparatively more efficient compared to imines (64d,e). Imines (64a-c) are either capable of direct or homoconjugative orbital overlap with the nitrogen lone pair, whilst imines (64d,e) do not have or have a diminished tendency to this possibility[54]. In the aryl substituted imines (64f-i) which are capable of direct overlap with the nitrogen lone pair electrons, changing the nature of the substituent increases or decreases the availability of the nitrogen lone pair to undergo electron transfer to the diphenylalkene moiety[56]. *p*-Cyano derivative (64i), in which the availability is least, gives a thirty two fold enhancement in yield over the *p*-methoxy derivative (64f), in which availiability of the lone pair is greatest. For the benzyl imines (64j-m), capable of homoconjugative interaction with the nitrogen lone pair, constructing a Hammett plot of quantum yield Φ , against σ^+, a measure of the electron withdrawing potential of the aromatic ring, gave excellent linearity, with increasing quantum yield occurring with increasing electron withdrawing ability of the substituent (i.e. decreasing availability of nitrogen lone pair to undergo electron transfer to the diphenylalkene group)[57].

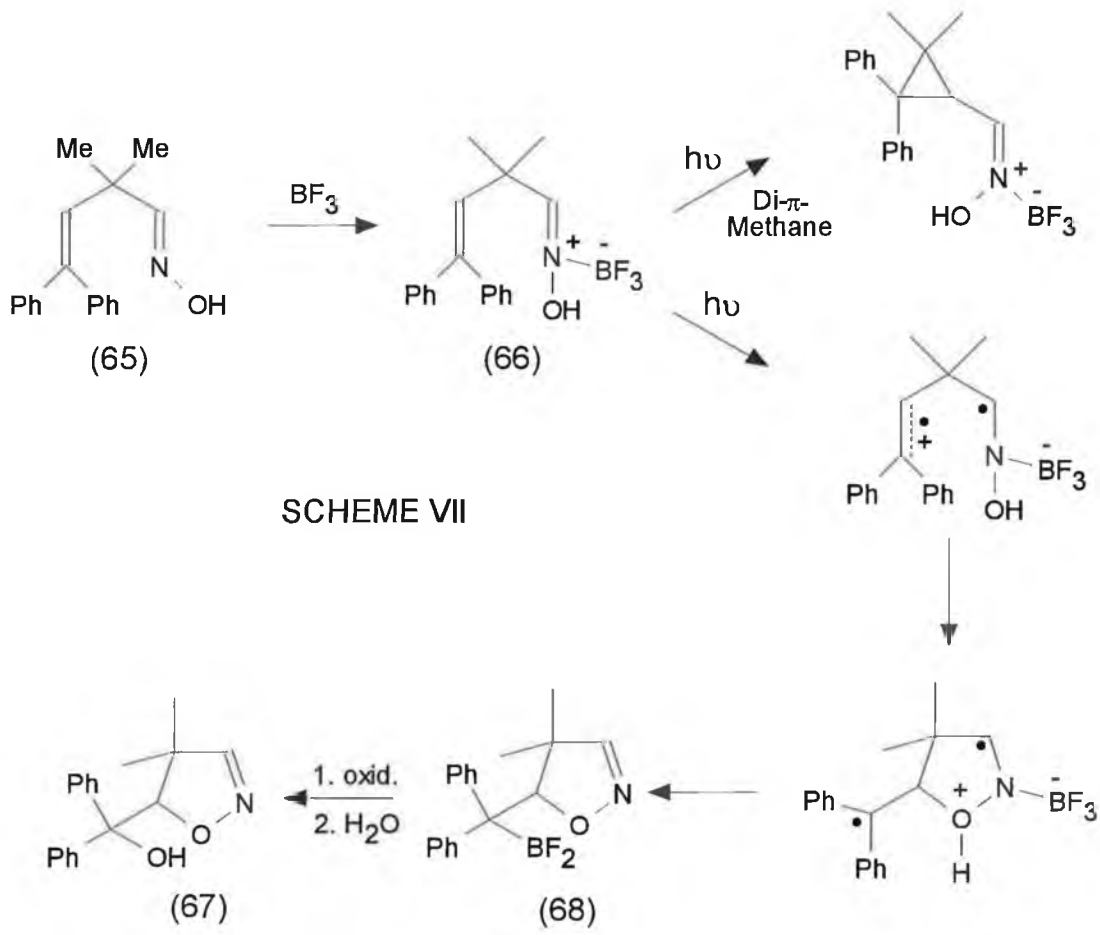


(64)

a; R=$PhCH_2$
b; R=Ph
c; R=PhCHMe
d; R=$PhCH_2CH_2$
e; R=i-Pr
f; R=*p*-$MeOC_6H_4$
g; R=*p*-ClC_6H_4
h; R=*m*-$MeOC_6H_4$
i; R=*p*-CNC_6H_4
j; R=*p*-$MeC_6H_4CH_2$
k; R=*p*-$ClC_6H_4CH_2$
l; R=*m*-$FC_6H_4CH_2$
m; R=*p*-$CF_3C_6H_4CH_2$

Oximes[55] and oxime ethers[68], which have low ionisation potentials, generally do not undergo the aza-di-π-methane rearrangement (with the exception of a cyclic oxime, see (75) page 30). Addition of boron trifluoride to

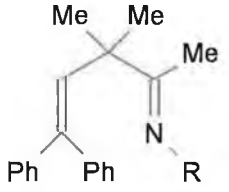
oxime (65), to form the oxime/BF_3 complex (66) which has a greater ionisation potential than (65), does facilitate the aza-di-π-methane rearrangement[58]. However in this case the major product on irradiation was found to be the dihydroisoxazole (67). It is believed that this may be formed by electron transfer from the diphenylalkene moiety to the imminium salt followed by cyclisation and formation of borane (68) which then undergoes facile oxidation and hydrolysis (Scheme VII).



SCHEME VII

Oxime acetates (64, R=OAc) which have a greater ionization potential than oximes do undergo an aza-di-π-methane[59,60] and they do so with a greater efficiency than the corresponding imines. Semicarbazones (64, R=$NHCONH_2$) and benzoates (64, R=OBz), also undergo rearrangement with the benzoates being more efficient again than the corresponding acetates[61].

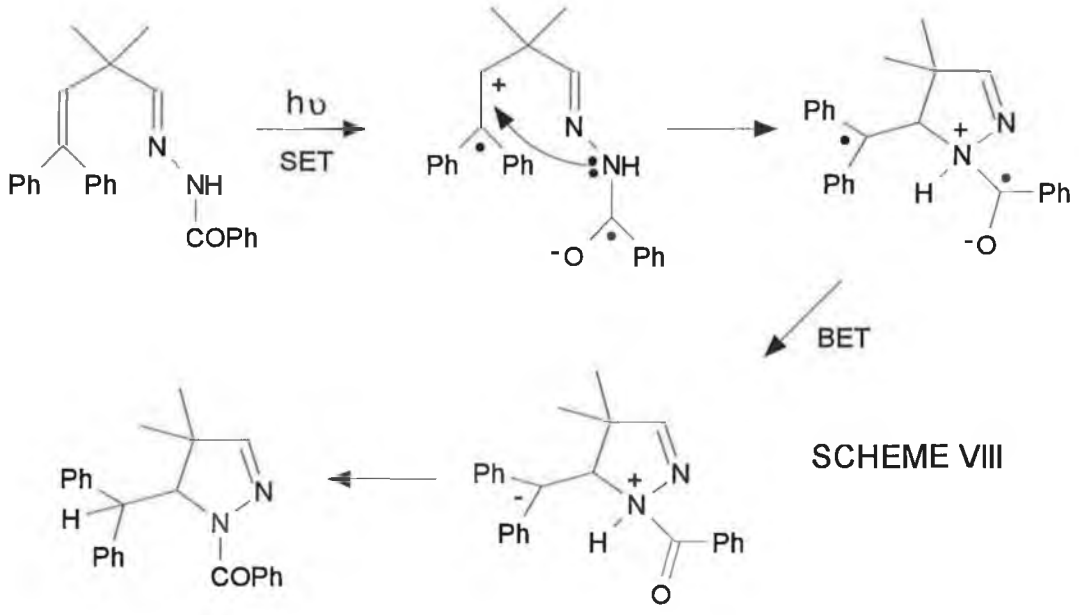
The most successful rearrangement occurred with the trifluoroacetate derivative (64, R=$OCOCF_3$) which gave the corresponding cyclopropane derivative in 90% yield after only ten minutes[62]. However irradiation of the ketoxime trifluoroacetate derivative (69. R=$OCOCF_3$) leads to a photofragmentation reaction believed to involve single electron transfer followed by hydrogen abstraction from the C-2 methyl group[62]. Further investigation showed that the acetyl, benzoyl and tosyl hydrazones (64, R=NHCOMe, NHCOPh, and NH-Tosyl respectively), undergo a competing novel cyclisation to form dihydropyrazoles, whilst the 2-methyl tosylhydrazone (69, R=NH-Tosyl) yields exclusively the corresponding dihydropyrazole[63]. The pyrazole product is believed to be formed via the pathway outlined in Scheme VIII, involving single electron transfer, ring closure and back electron transfer (BET)[63].



(69)

Replacement of the phenyl groups on the alkene moiety with other substituents, with a view to the synthesis of the cyclic components of pyrethroid insecticides has been investigated[64,65]. Oxime acetate (70, $R^1=CO_2Me$, R^2=Me) undergoes the aza-di-π-methane rearrangement. However on replacing the methyl group with a proton at the C-5 position (70, $R^1=CO_2Me$, R^2=H), no rearrangement occurs and irradiation only gives E,Z-isomerisation products[64] as does the cyano derivative (70, R^1=CN, R^2=H)[65]. Although the presence of the electron withdrawing group at C-5, allowing for an electron transfer process to become available again, could account for this deactivation, replacement by acetoxymethyl (70, $R^1=CH_2OCOMe$, R^2=H) or methoxymethyl

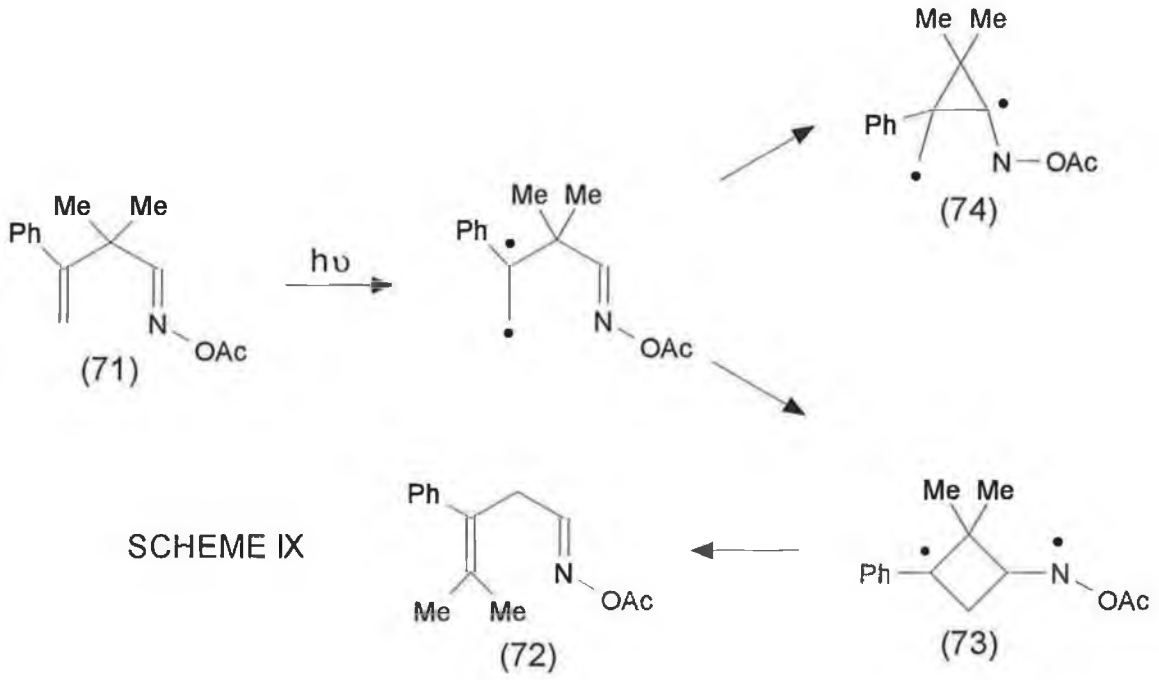
groups (70, R^1=CH_2OMe, R^2=H) should decrease the affinity of the group towards electrons. However in these cases too, only E,Z-isomerisation occurs and no cyclisation was noted[65]. Deactivation is also unlikely to be caused by a free rotor effect as had been originally proposed[64,65], since the C-5 mono-phenyl derivative (70, R^1=Ph, R^2=H) undergoes successful aza-di-π-methane rearrangement, whilst the cyclohexyl analogue (70, R^1=C_6H_{11}, R^2=H) which would have equivalent steric hindrance to rotation does not[66]. It is therefore likely that the ability of the substituent at C-5 to stabilise the intermediate biradical after cyclisation plays an important role in the success or failure of the aza-di-π-methane process.



SCHEME VIII

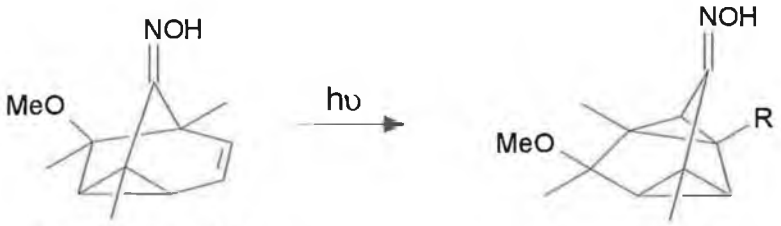
(70)

Finally, irradiation of the C-4 phenyl substituted β,γ-unsaturated system (71) does not lead to an aza-di-π-methane rearrangement, but instead gives (72) via a 1,3-acyl migration[67]. This may be explained by the preferential formation of the more stable biradical (73) over the less stable (74), resulting in rearrangement to (72) (Scheme IX).

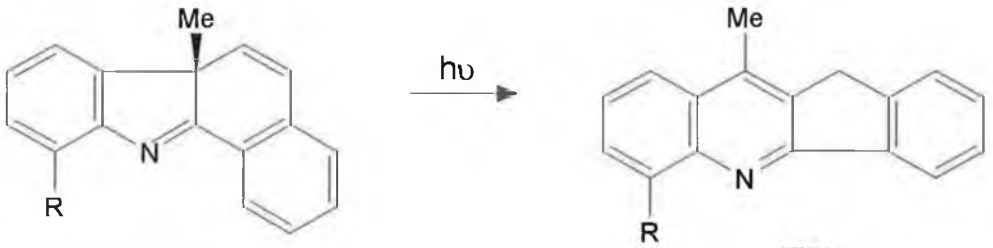


SCHEME IX

The aza-di-π-methane rearrangement has also been reported to occur in cyclic systems. Thus oxime (75) rearranges to (76) through a proposed singlet excited state[69], which is in contrast to Armesto and Horspool's results where rearrangement was seen to occur via an excited triplet. Heterocycle (77) also undergoes aza-di-π-methane rearrangement to yield the rearranged product (78)[70].



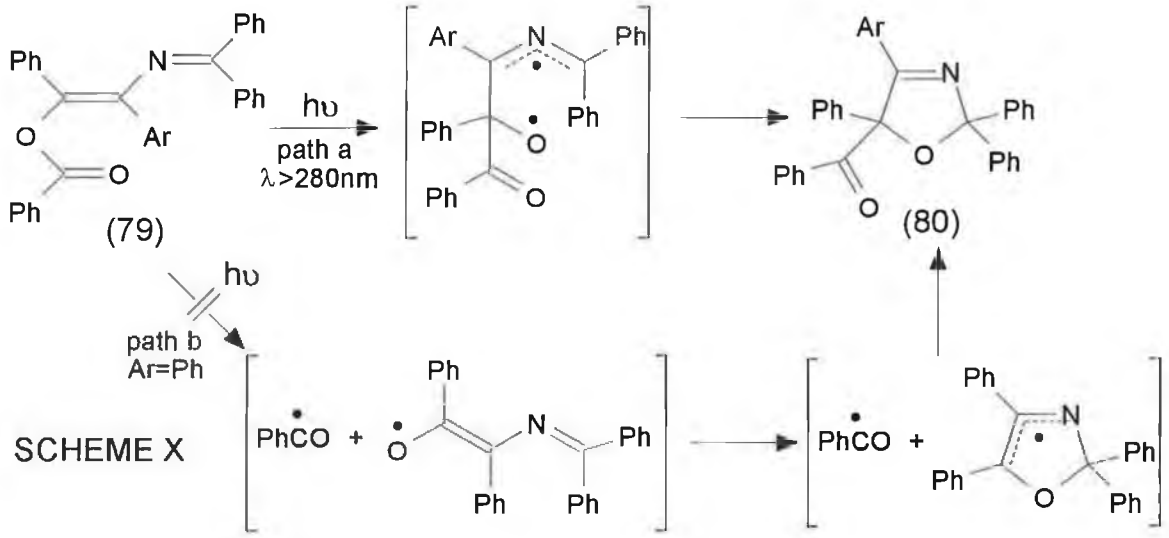
(75, R=H or Me) (76)

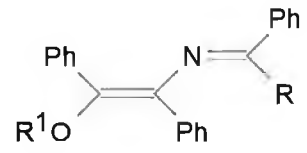


(77, R=H or Me) (78)

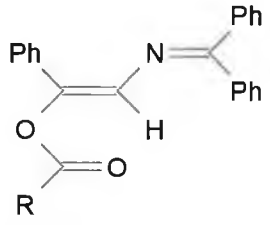
It has been found that irradiation of the 2-azabuta-1,3-dienes (79) results in the formation of 3-oxazolines (80), via a 1,2-benzoyl migration process defined as a 1,3-dioxa-di-π-methane (Scheme X, path a)[72]. This is believed to be the first example of a process resulting in 1,2-migration across an oxygen atom. The 4-alkoxyazadienes (81) which cannot undergo such a migration yield only E,Z-isomerisation products thus ruling out the alternative pathway involving carbon-oxygen bond scission, cyclisation and recombination. (Scheme X, path b)[73]. The rearrangement has been found to be conformationally dependent, *i.e.* dependent on the ability of the nitrogen lone pair to overlap with the enol ester moiety and undergo single electron transfer[74]. Azadienes (79) have an extreme twist arround the C(3)-N bond allowing overlap. Azadienes (82, R=Ph or Me), which are flat and have full conjugation between the imino and enol ether moieties undergo only E,Z-isomerisation. The intermediately twisted azadienes (83a-d) bearing a methyl substituent at C-3 either do not yield photoproducts (as in the case of (83a,b)) or (as in the case of (83c,d)) yield a benzoyl migrated photoproduct (84) on direct irradiation (the benzoyl group here being the principal absorbing moiety).

Sensitised irradiation of these compounds leads to E,Z-isomerisation. When the electron transfer step is supressed by protonation of nitrogen, the azabutadienes (79) undergo a photochemical Mannich type reaction resulting in cyclisation to isoquinolinone derivatives (85)[75]. Irradiation of (79) in the presence of high concentrations of cycloocta-1,3-diene yields cycloadducts[76].

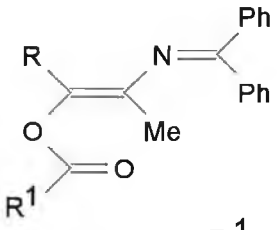




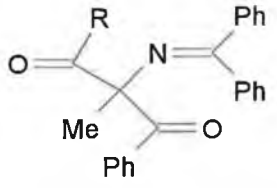
(81, R^1=Me or $PhCH_2$)



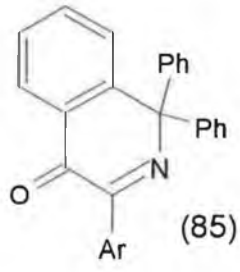
(82, R=Ph or Me)



(83)	R	R^1
a	Me	Me
b	Ph	Me
c	Me	Ph
d	Ph	Ph

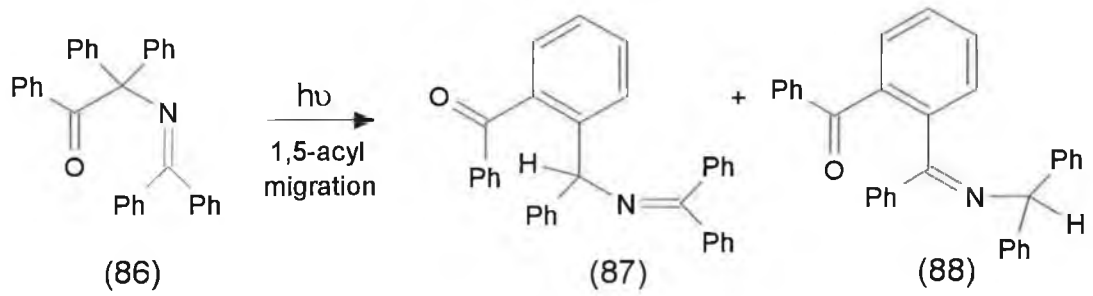


(84, R=Ph or Me)



(85)

The azapentaphenylbutenone (86) has been found to undergo a 1,5-acyl migration on irradiation to yield products (87) and (88)[77].

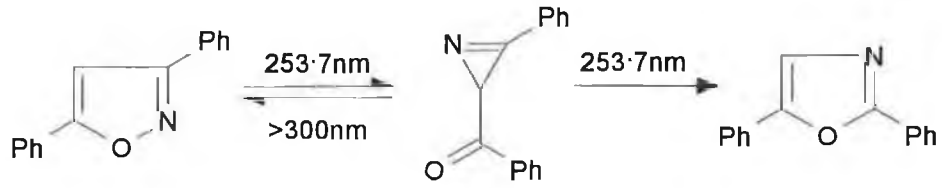


(86) (87) (88)

1.7 Photorearrangements of Five Membered Heterocycles containing a Carbon-Nitrogen Double Bond

The photochemistry of five membered heterocyclic compounds containing a carbon-nitrogen double bond has been the subject of much investigation, and the products formed are dependent on a number of factors including wavelength of irradiation, ring substitution and solvent.

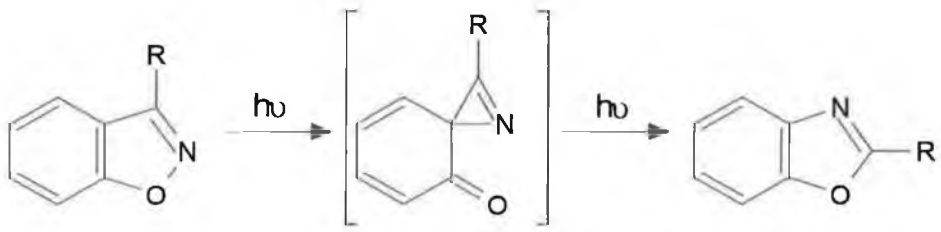
For isoxazoles two primary photoprocesses have been noted; ring contraction to azirines or rearrangement to unstable ketenimine intermediates. Ullman and Singh first demonstrated that the rearrangement of the isoxazole (89) proceeds via an isolable azirine intermediate (90) which may undergo photochemical ring expansion to revert to the starting isoxazole (89) or to the oxazole (91) depending on the wavelength of irradiation[78]. The formation of the isoxazole has been suggested to occur from the cabonyl n-π* state whilst oxazole formation has been proposed to occur from the azirine n-π* state.



(89) (90) (91)

Various further examples of this type of photorearrangemnt have been reported in the literature[79-84]. Benzisoxazoles (92) undergo rearrangement to

benzoxazoles (93), but in these cases it proves impossible to isolate the proposed spiroazirine intermediates (94) due to their thermal instability. However on irradiation of benisoxazole (92, R=Ph), at low temperature, Grellmann and Tauer have found IR and UV spectroscopic evidence for its intermediacy[79].



(92)
R=Ph, Me, H

(94)

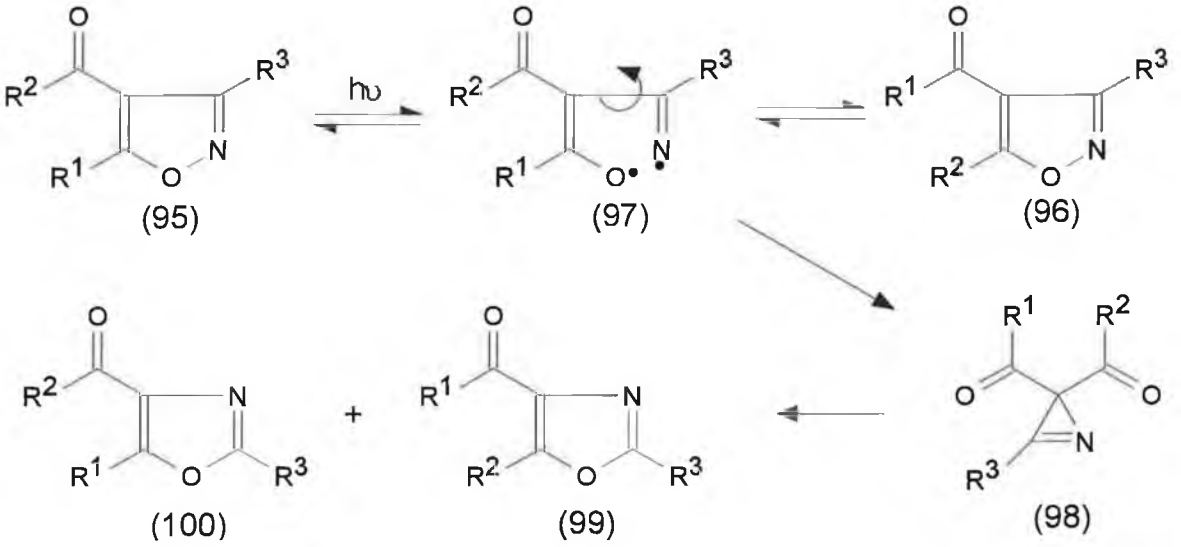
(93)

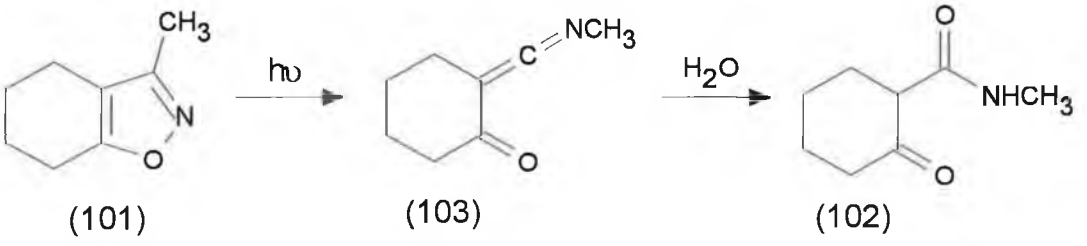
Sauers and co workers have found that on irradiation of a series of 4-acylisoxazoles (95) a variety of photoproducts may be formed[80]. Isomeric isoxazoles (96) may be formed from rotation and ring closure of the diradical (97) formed on nitrogen-oxygen bond homolysis. Alternatively the diradical may form the 2*H*-azirine intermediate (98) which may in turn form oxazoles (99) and (100) by ring expansion. An unisolated ketenimine was also formed and this has been rationalised by initial formation of an electronically distinct version of the diradical (97).

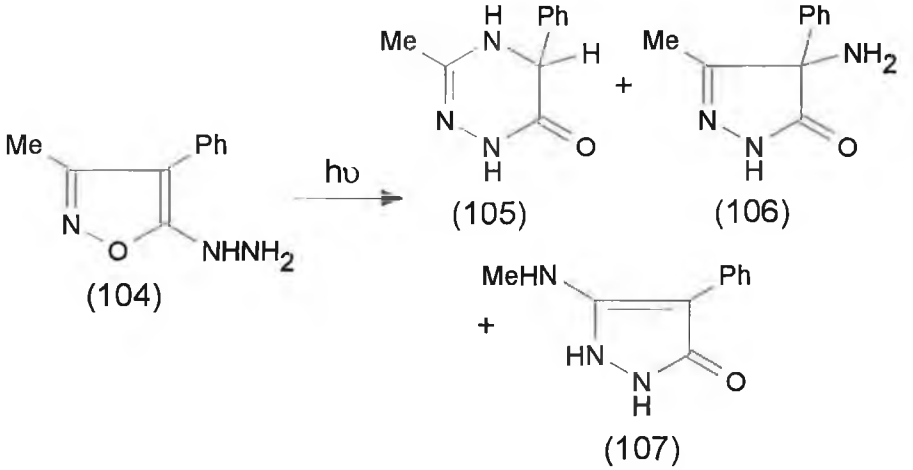
Ketenimine formation on irradiation has also been reported in a number of other isoxazole systems. Irradiation of isoxazole (101) in methyl cyclohexane followed by hydrolysis yields amide (102) via ketenimine (103) formation[85]. It has been proposed that this mechanism is favoured in non hydroxylic solvents since irradiation in methanol leads to rearrangement to the expected oxazole.

It has been found that on irradiation of isoxazoles bearing hydrazinic

substituents at the 4 or 5 positions, product formation results from ring closure of the intermediates with the hydazinic rather than the ketone group[86-90]. For example irradiation of (104) yields (105) and (106) expected from an azirine intermediate, along with (107) whose presence may only be explained by formation of a nitrene intermediate with a 1,2-shift of the methyl group[86].

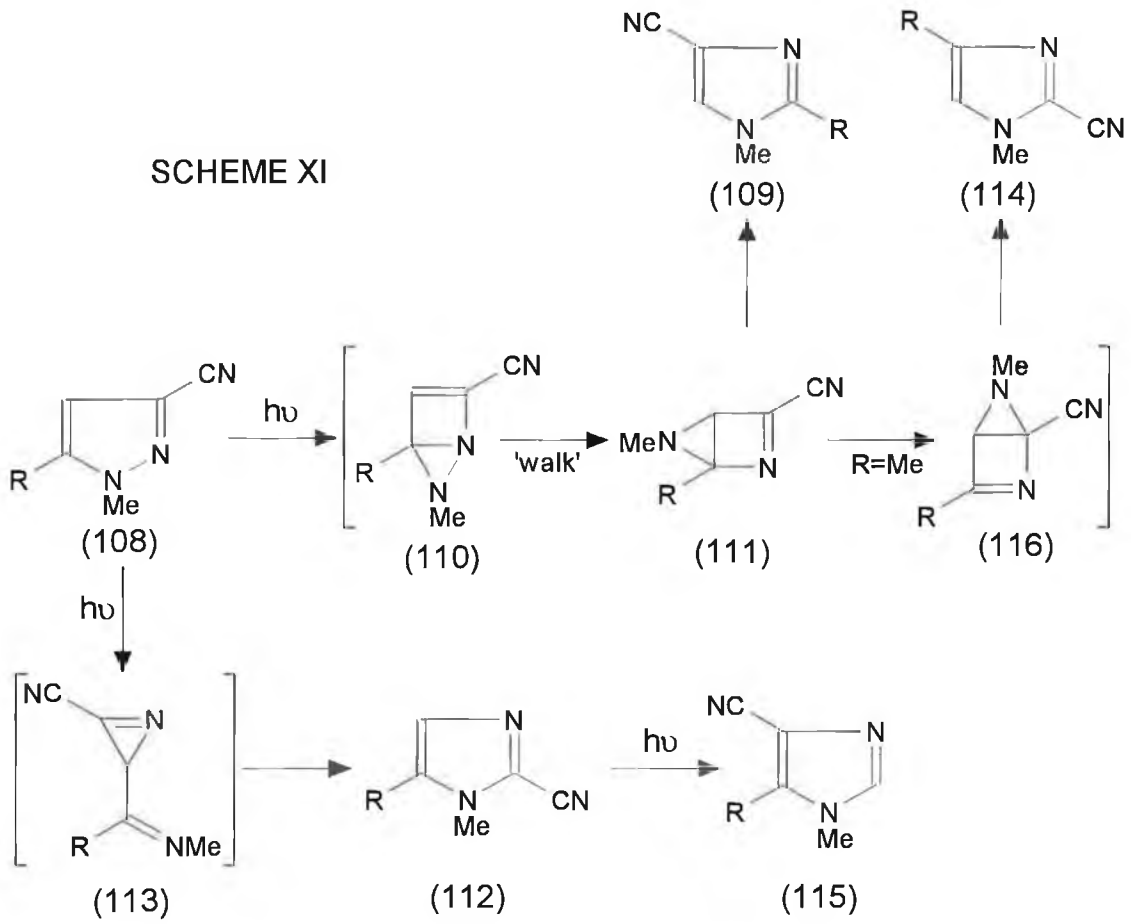






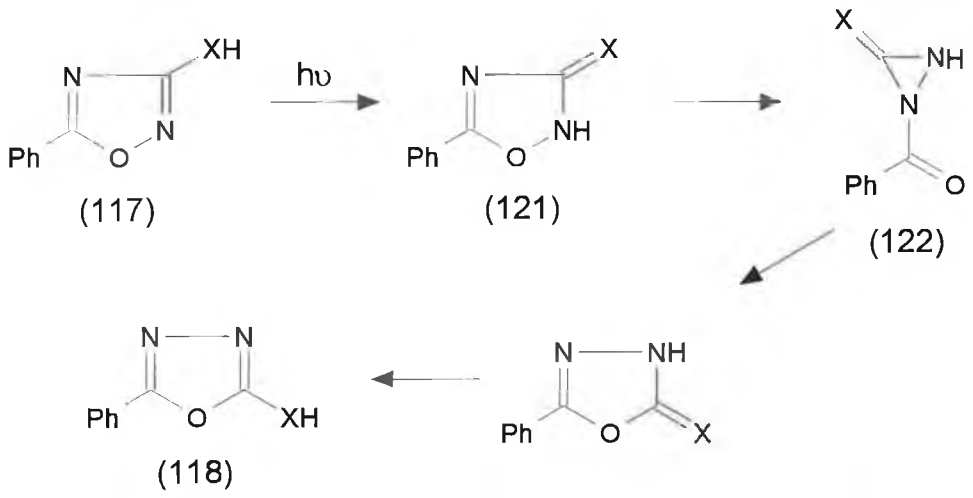
In pyrazole photochemistry the formation of photoproducts via 2*H*-intermediates is accompanied by product formation via 2,5-bonding followed by a 'walk' of the heteroatom[91-93]. Irradiation of pyrazole (108, R=H or D) yields imidazoles (109) from 2,5-bonding to (110) followed by heteroatom 'walk' to (111) and ring opening, whilst product (112) is formed by the ring contraction ring expansion reaction via (113) similar to that of the isoxazoles[91] (Scheme XI). Irradiation of (108, R=Me) also leads to the formation of (114) and (115) which may be explained by a further 'walk' step which gives a more stable intermediate (116) with methyl substitution at the polar carbon-nitrogen double bond rather than at the bridgehead position.

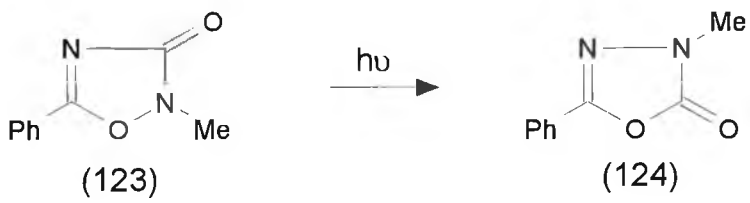
SCHEME XI



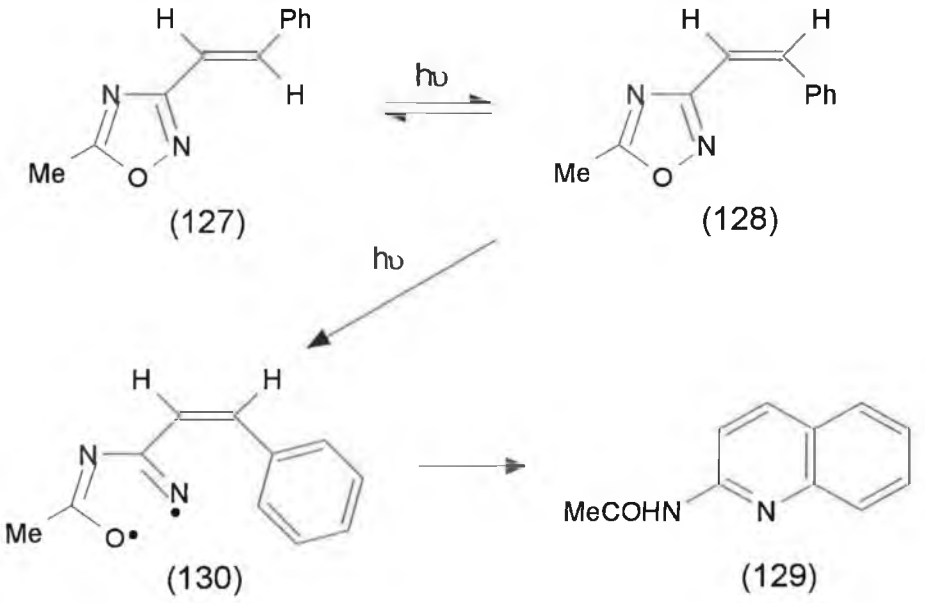
In 1,2,4-oxadiazole derivatives photorearrangement to the 1,3,4-oxadiazoles is dependent on the substitution at the 3-position[94,95]. Irradiation

of derivatives bearing a primary or secondary amino or a hydroxyl group (117, X=NH, NR or O) at C-3 yields the corresponding 1,3,4-oxadiazole (118). However irradiation of other derivatives such as (119, R=NMe_2 or OMe) give the open chain compounds (120). This difference may be explained by tautomerisation of the oxadiazole to (121) followed by ring contraction to diazirines (122) and ring expansion. Indeed oxadiazolin-3-one (123) yields the isomeric oxadiazolin-2-one (124) on irradiation. Those compounds unable to undergo such tautomerisation yield only solvent adducts believed to be formed by initial heterolytic nitrogen-oxygen bond cleavage followed by addition to the zwitterionic (125) or nitrene (126) intermediate.



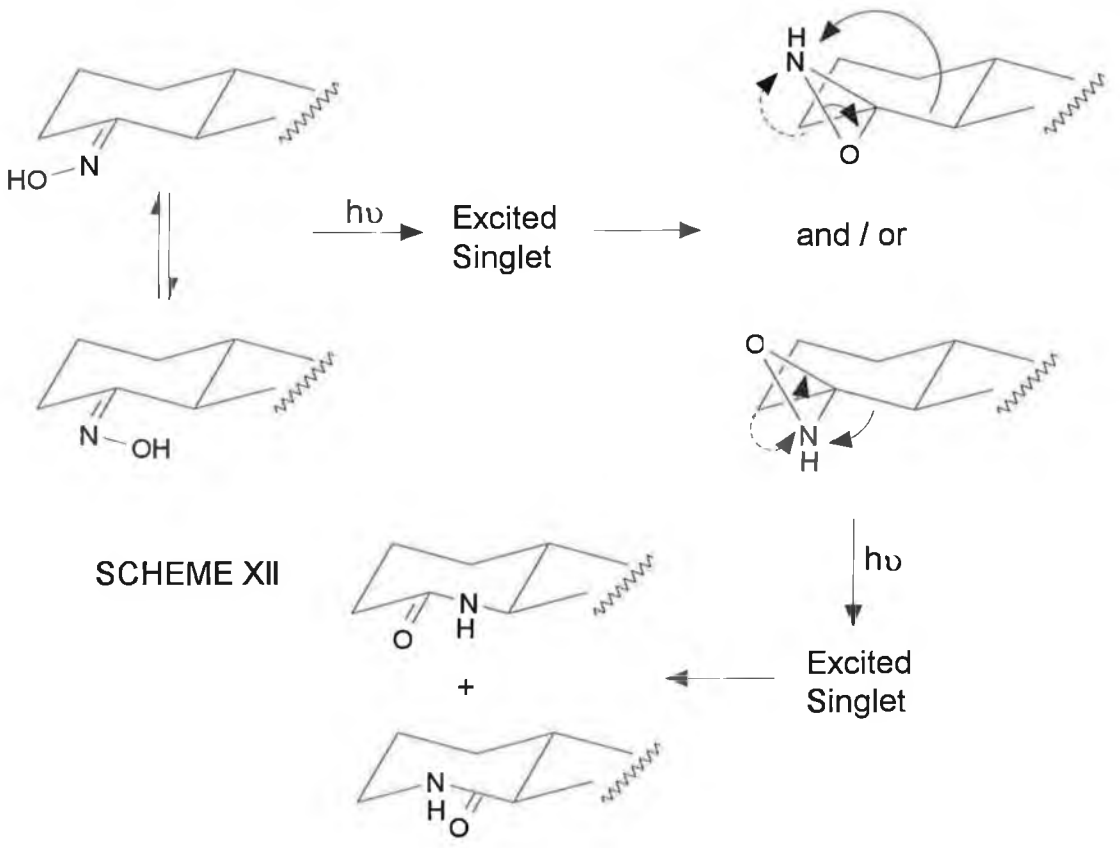


On irradiation the 3-styryl-1,2,4-oxadiazole (127) has been found to undergo E,Z-isomerisation around the carbon-carbon double bond to (128) followed by cyclisation to yield the quinoline derivative (129)[96]. It has been proposed that this intermediate is formed via initial nitrogen-oxygen bond cleavage to (130) rather than via a 6π-electron electrocyclic ring closure.



1.8 Photo-Beckmann Rearrangement

The photo-Beckmann rearrangement of cyclic, and particularly, steroidal oximes has been extensively studied and a number of general points may be made about the rearrangement. The steroidal oximes generally yield two lactam isomers on irradiation, with the lactam obtained by migration of the more substituted carbon being slightly more favoured. Small amounts of the parent ketone are also normally formed on irradiation and secondary products arrising from the lactams or ketones may also occur. The rearrangement proceeds from the oxime singlet excited state, almost certainly via an oxaziridine intermediate which is again excited to the singlet state and then rearranges to give lactams[97] (Scheme XII).

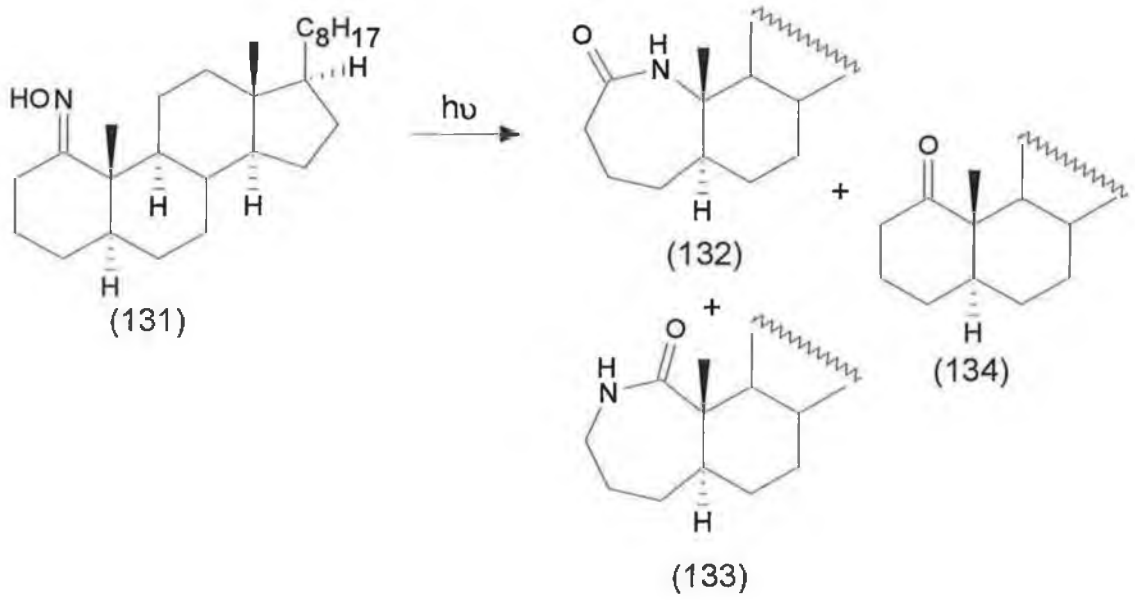


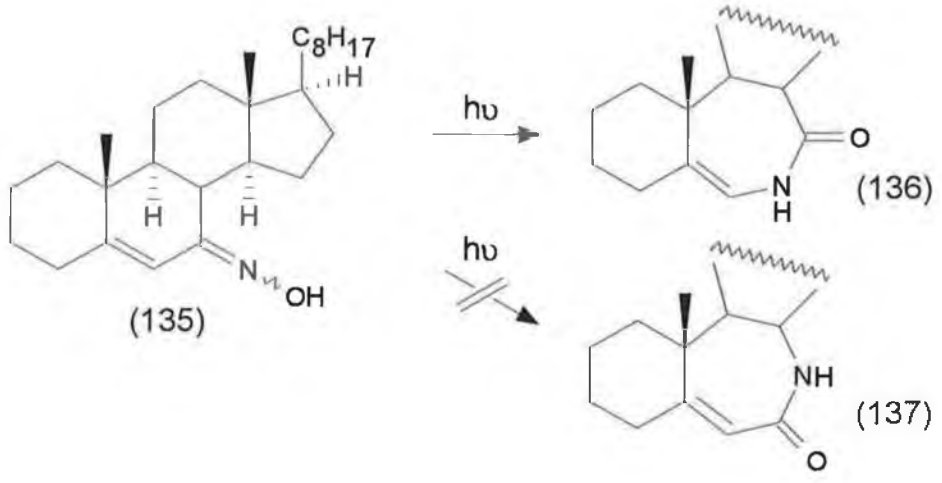
SCHEME XII

The lactams formed, with few exceptions (see below), show retention of chirality indicating that no cleavage of ring bond to give diradical or zwitterionic intermediates occurs. Thus for example 5α-cholestan-1-one oxime (131) yields lactam (132), novel lactam (133) and parent ketone (134) on irradiation[97]. Other examples include those of cholestan-4-one oximes[97], cholestan-6-one oximes[98], cholestan-3-one oximes[99], norcholestan-3-one oxime[100,101] and the oximes of camphor and fenchone[102].

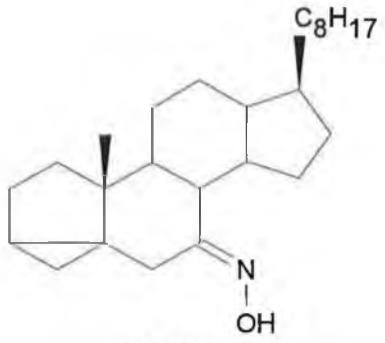
The advantage of photochemical over non-photochemical Beckmann rearrangement is that photolysis leads to the formation of two lactams whilst thermal methods yield only one isomer (for example in the case of (131), lactam (132) is the sole thermal lactam product). This allows access to lactams that may not be prepared by thermal Beckmann rearrangement. An exception to this is for the steroidal α,β–unsaturated oximes[103]. Irradiation of the cholest-5-en-7-one oxime (135) yields lactam (136) but none of the isomeric lactam

(137). Although the reasons for the regioselectivity of the reaction is not clear, a stereoelectronic factor is likely to play an important role.

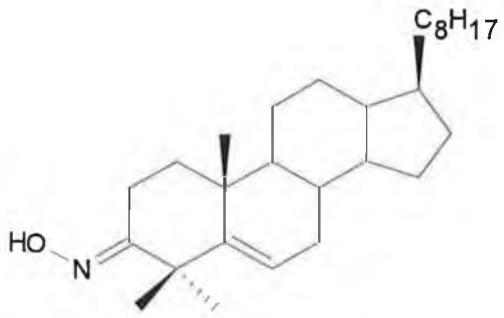




That no diradical or zwitterionic intermediates are formed by α-scission of the oxaziridine intermediate may be demonstrated in the cases of the β,γ–cyclopropyl oxime (138)[104] and the β,γ–unsaturated oxime (139)[105].

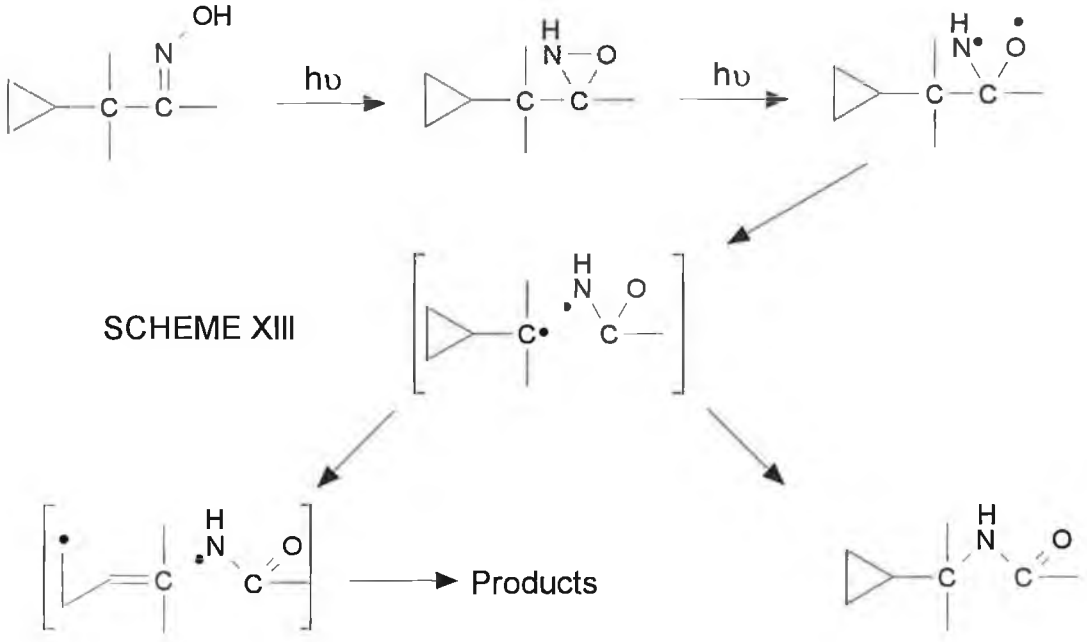


(138)



(139)

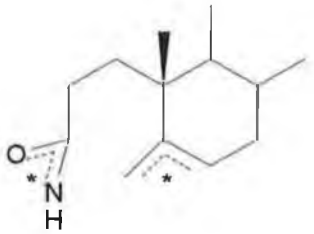
Irradiation of (138) gives expected lactam products, with no products arising from α–scission. Cyclopropylcarbinyl radicals readily isomerise to allylcarbinyl radicals, thus if α–scission had occurred, products arising from opening of the cyclopropane ring would be expected (Scheme XIII)[104]. Irradiation of (139), which is considered to be particularly susceptible to α–scission into biradical or ionic species which would generate stabilised allyl radicals or ions (140), again gave lactam products but no products arising from α–scission[105].



SCHEME XIII

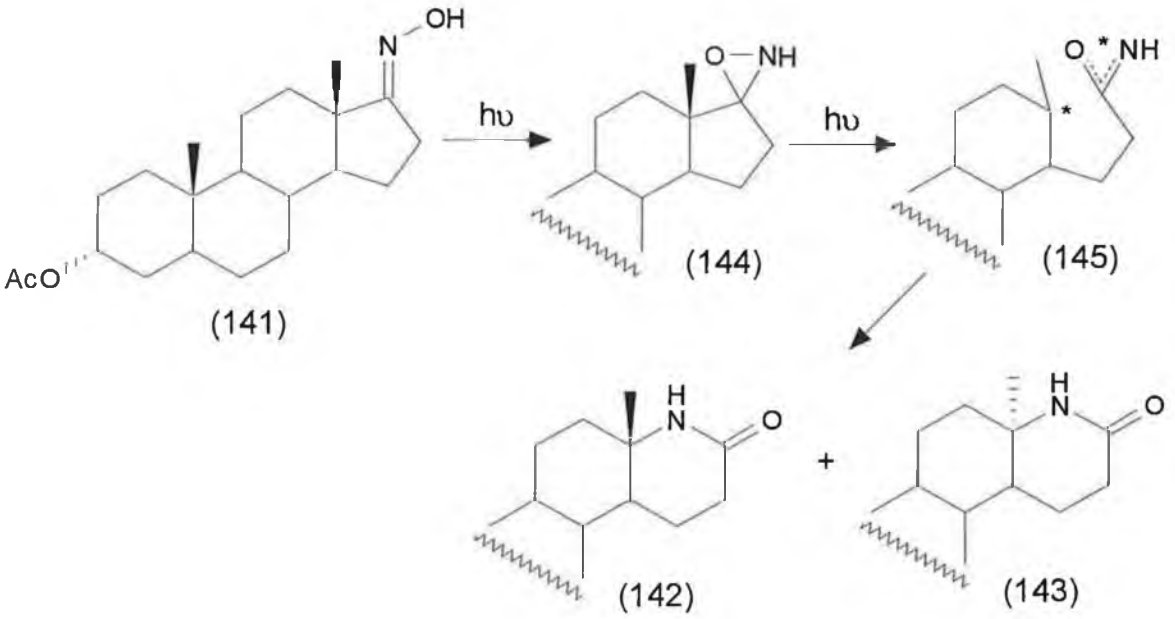
However there are a number of exceptions to the above, found in oximes in which a non-bonding interaction or strain in the molecule would be expected

by the formation of the oxaziridine intermediate. O-Acetyl androsterone oxime (141) undergoes photo-Beckmann rearrangement with loss of chirality to yield lactam isomers (142) and (143), presumably formed by α–scission of the oxaziridine intermediate (144) to (145)[106]. A similar loss of chirality has been seen in a steroidal cyclobutanone oxime (146)[107]. Cyclohexadienone oxime (147) has been seen to undergo heterolytic α–scission on irradiation to yield a variety of photoproducts[108].



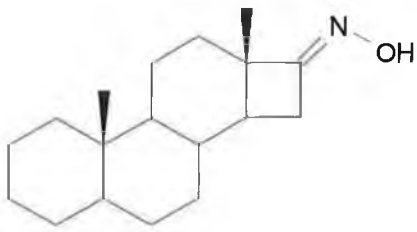
*=radical or ion

(140)



The α,β-unsaturated oxime (148) does not undergo a photo-Beckmann rearrangement on irradiation in methanol, but yields isoxazoline (149) along with parent ketone and methanol adducts[109]. Formation of (149) has been

explained by hydroxyimino-proton transfer to the twisted carbon-carbon double bond to generate a carbocation, followed by bond cleavage and an intramolecular 1,3-dipolar addition.



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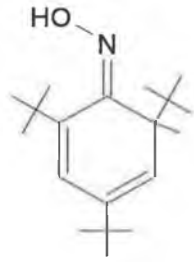

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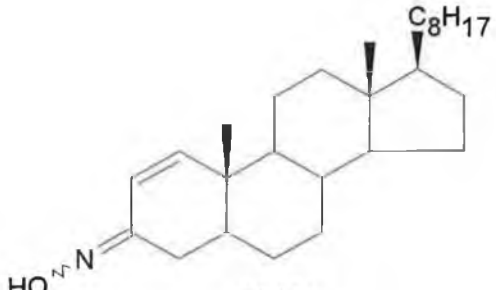

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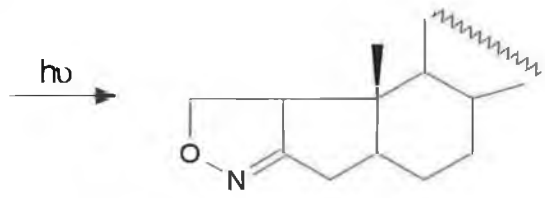


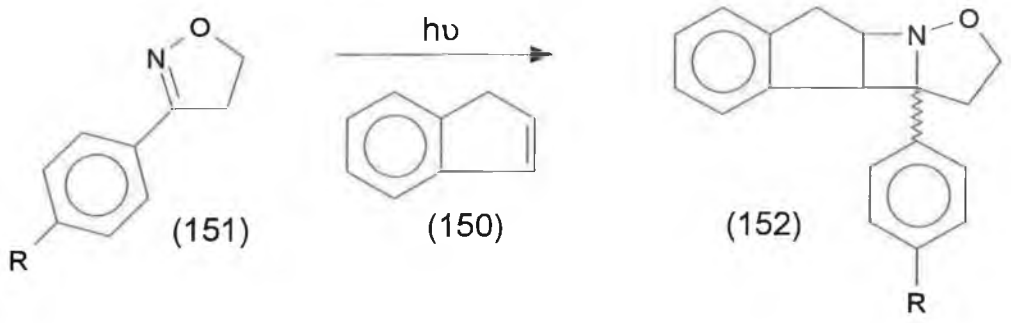
(149)

1.9 Photocycloaddition

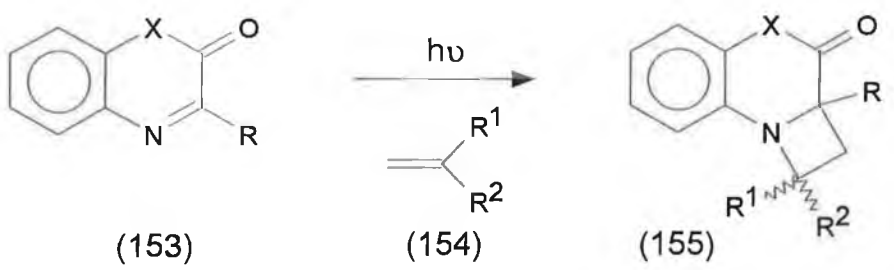
Unlike carbon-carbon and carbon-oxygen double bonds, photocycloaddition to the carbon-nitrogen double bond is not often encoutered[2,3]. Koch postulated that [2+2] cycloaddition occurs only when the carbon-nitrogen double bond has a low energy π–π^* state, whilst those with a low energy n–π^* excited state do not undergo this reaction but yield reductive photodimerisation products[110].

[2+2] Photocycloadditions of olefins to the carbon-nitrogen double bond most commonly occur in two classes of compounds. The first is those compounds where the carbon-nitrogen double bond is constrained in a ring system with one end of the imino linkage attached to a heteroatom[111,112], as in the addition of indene (150) to the carbon-nitrogen double bond of the 3-

phenylisoxazolines (151, R=CN or $COOCH_3$), to yield the azetidine (152) from the π–π^* singlet state[111].



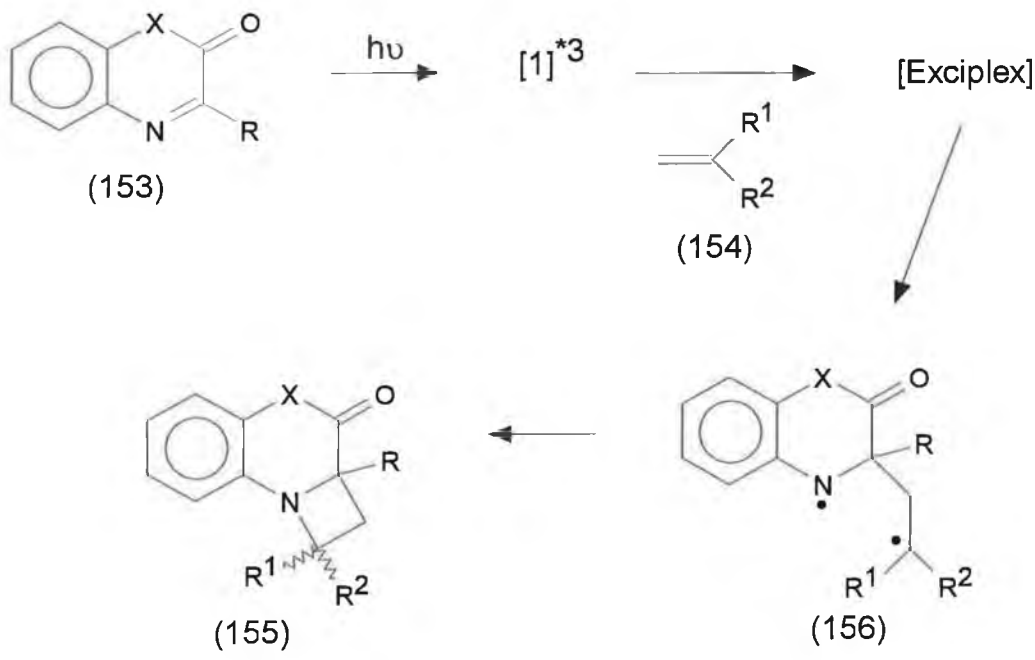
The second class of compounds is those where the carbon-nitrogen double bond is conjugated with a carbonyl group. Nishio has extensively studied [2+2] photocycloaddition to the carbon-nitrogen double bond of quinoxalin-2-ones (153, X=O), and benzoxazin-2-ones (153, X=NH, NMe or NEt), with a variety of olefins[113-117]. Photocycloaddition of the quinoxalin-2-ones[113] and benzoxazin-2-ones[114] with electron deficient olefins such as acrylonitrile (154, R^1=H, R^2=CN) or methyl methacrylate (154, R^1=Me, R^2=CO_2Me), leads to the regiospecific (in no cases could the head to head regioisomer be detected), but non-stereospecific formation of the corresponding [2+2] adduct (155) in varying yields. This situation contrasts with that of the Paterno-Büchi reaction where ketones are found not to undergo photocycloadditions with electron deficient olefins[118]. The quinoxalin-2-ones and benzoxazin-2-ones were also seen to undergo [2+2] photocycloaddition to a number of aryl alkenes (154, R^1=H, Me, Ph; R^2=Ar).



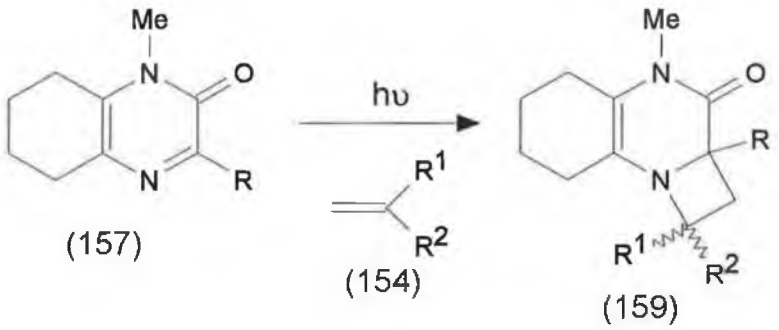
That most of these photocycloadditions proceed with lack of stereospecificity, yielding two stereoisomers, has lead Nishio to suggest that the formation of the azetidines may arise by the initial interaction of the quinoxalin-2-ones or benzoxazin-2-ones in the triplet state, with the olefin, forming an exciplex which proceeds via a diradical intermediate (156) to yield the final products. (Scheme XIV).

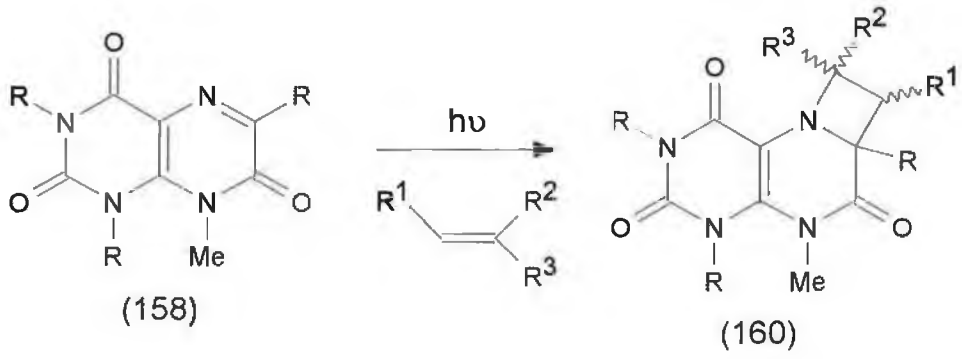
Nishio has also reported [2+2] photocycloaddition to occur on irradiation of 5,6,7,8-tetrahydro-3-phenylquinoxalin-2(1*H*)-one[116] (157) and pteridine-2,4,7-triones[117] (158) in the presence of olefins, to yield the corresponding azetidines. (159) and (160) respectively, but has found that monocyclic pyrazin-2-ones do not undergo photocycloaddition reactions[116].

Other researchers have also reported similar [2+2] photocycloaddition reactions to occur. Ketene (161) has been found to undergo addition across carbon-nitrogen double bonds to form lactam derivatives[119]. Thus 3-trifluoromethylquinoxalin-2(1*H*)-one (162) yields the corresponding azetidine-2-one (163)[119a].

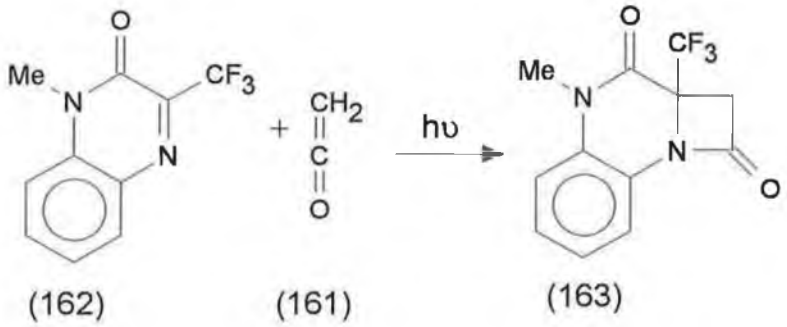


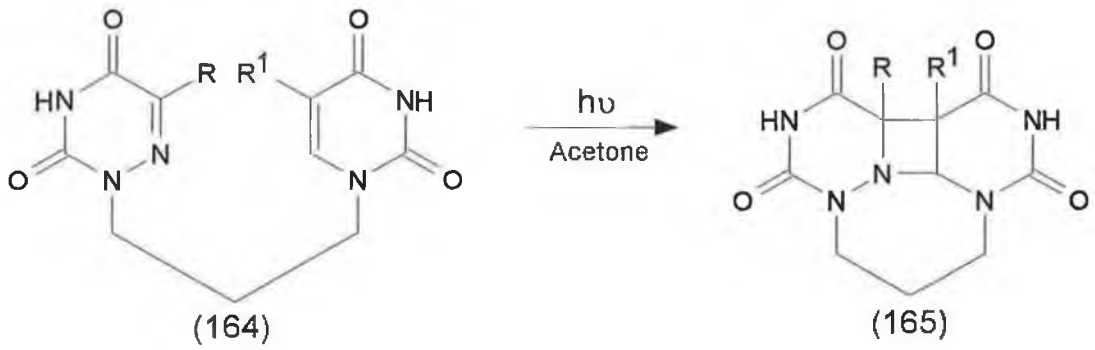
SCHEME XIV





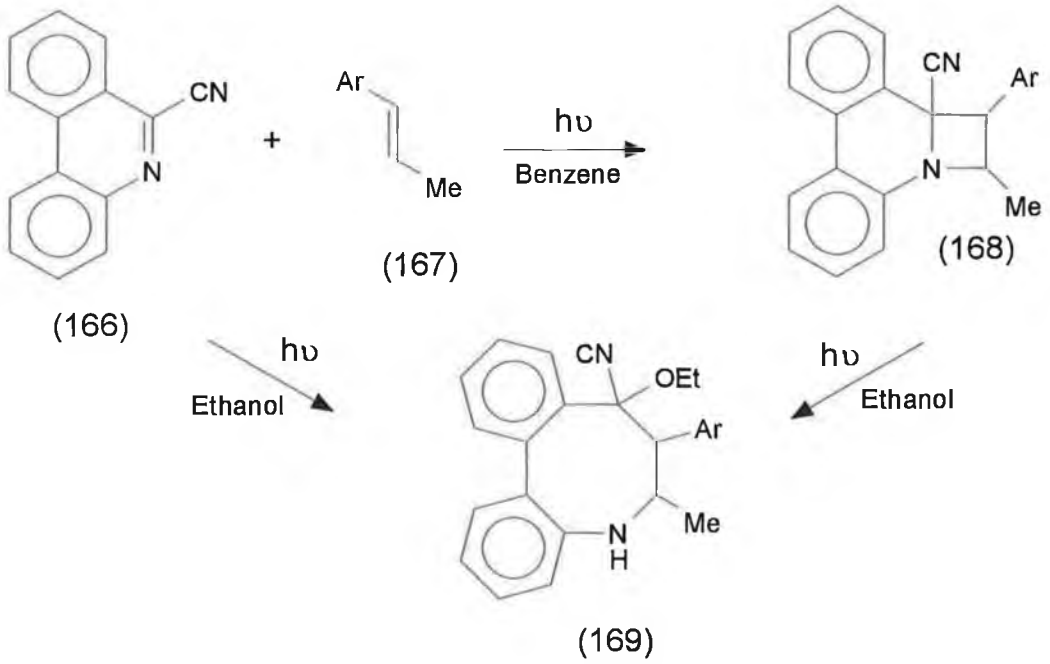
Golankiewicz has shown that dinucleotide analogues, in which uracil and azauracil are connected by a trimethylene chain (164), undergo an intramolecular [2+2] photocycloaddition to form azetidines (165)[120].

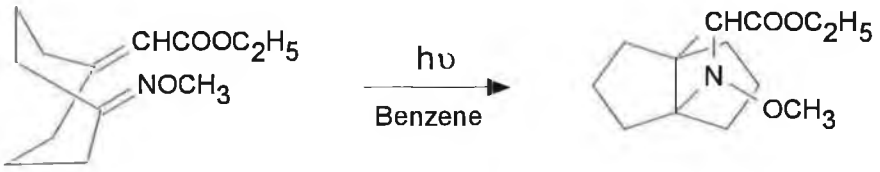




[2+2] Photocycloadditions of olefins to the carbon-nitrogen double bond seldom occur outside of the first two classes of compounds. However, Ohta has shown that the carbon-nitrogen double bond of phenanthridines, such as (166), undergoes addition to electron rich olefins, such as (167), in benzene, to yield the adduct (168)[121]. On irradiation in ethanol the azocine derivative (169) was formed. Irradiation of azetidine (168) in ethanol also yielded (169) indicating that the photocycloaddition reaction is the first step in the formation of azocine (169) in ethanol.

Intermolecular photocycloadditions of olefins to an imino group , where the carbon-nitrogen double is not constrained in a ring system have not been reported. This is not suprising since there would be stong deactivation by processes such as bond rotation. Nicolaides has however reported an intramolecular [2+2] photocycloaddition of the carbon-carbon and carbon-nitrogen bonds of the oxime (170), forming azetidine (171) in good yield, where only one end of the double bond is fixed in a ring[122].





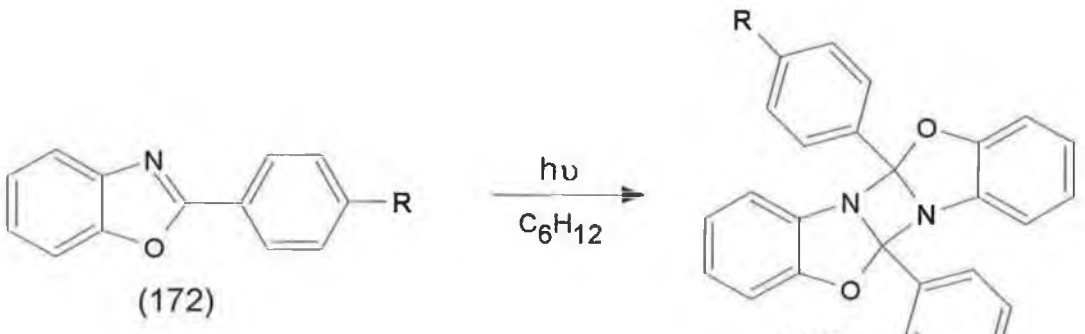
(170) (171)

Photodimerisation of compounds containing a carbon-nitrogen double bond rarely occurs. Original claims that a 1,3 diazetidine was formed by a [2+2] photodimerization of benzaldehyde cyclohexylimine had been dissproved[2,3].

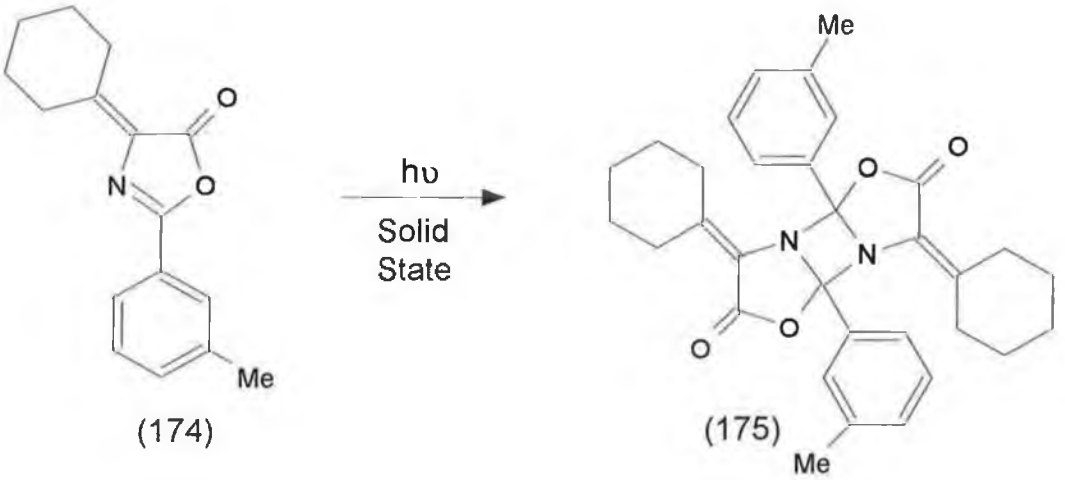
Paillous has since shown that 2-phenylbenzoxazoles (172) undergo successful intermolecular [2+2] photodimerisations to yield 1,3-diazetidines (173)[123,124] in high yields. That the products formed are the 1,3 derivatives and not the corresponding 1,2 derivatives, has been proved by X-ray analysis[125]. The efficiency of the dimerisation decreases on going from the 2-phenylbenzoxazole (172, R=H) to the 4-fluorophenyl derivative (172, R=F), and again on going from the 4-fluorophenyl to the 4-chlorophenyl derivative (172, R=Cl), which also undergoes a competing photodehalogenation reaction to yield 2-phenylbenzoxazole. No photodimers were formed on irradiation of the 4-bromophenyl (172, R=Br) or 4-iodophenyl (172, R=I) derivatives, these compounds only undergoing the photodehalogenation reaction. This result may be due in part to decreasing solubility in the series of compounds, since the yield of the dimerisation is concentration dependent. The similar 4-cycloalkylidene-oxazol-5(4*H*)-ones such as (174) have been seen to undergo successful photodimerisation in the solid state to yield the corresponding diazetidine ((175) in the case of irradiation of (174))[126].

Paillous has suggested that the photodimerisation of 2-phenylbenzoxazole (172, R=H) may be of possible use in the conversion of radiant energy to heat since the dimerisation is almost instantaneously

reversed on addition of traces of trifluoroacetic acid or *p*-toluenesulphonic acid with liberation of energy[124]. This photochemical / thermal reaction shows long term recyclability, with up to eighty repeated photochemical / thermal cycles achieved before the concentration of phenylbenzoxazole (172) was too low for dimerisation to occur (i.e. when residual concentration of (172) was approximately 10^{-2}M).

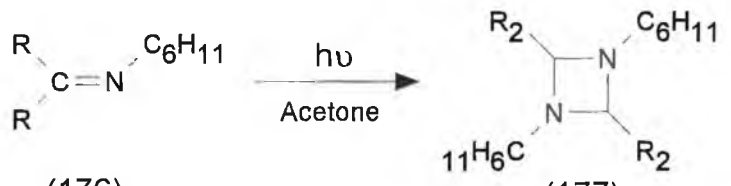


(172) (173)



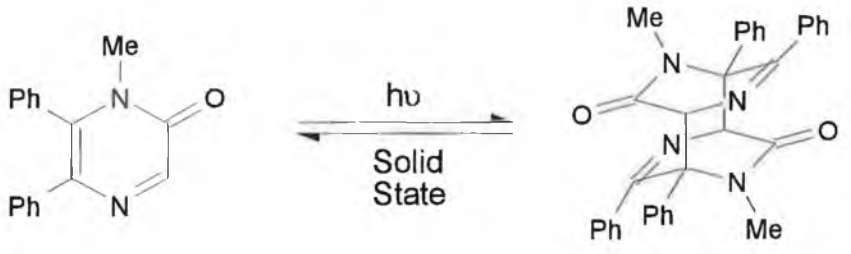
(174) (175)

The fluorinated *N*-isopropylidene cyclohexylimine (176, R=CH_2F) also undergoes photodimerisation, to yield diazetidine (177)[127]. However the parent compound (176, R=Me) does not dimerise on irradiation.



(176) (177)

Compounds containing a carbon-nitrogen double bond have also been seen to undergo [4+4] photocyclodimerisations in the solid state[128]. Thus 2-pyrazinone (178) yields dimer (179) on irradiation in the solid state, however in benzene or methanol solution no such dimerisation takes place.

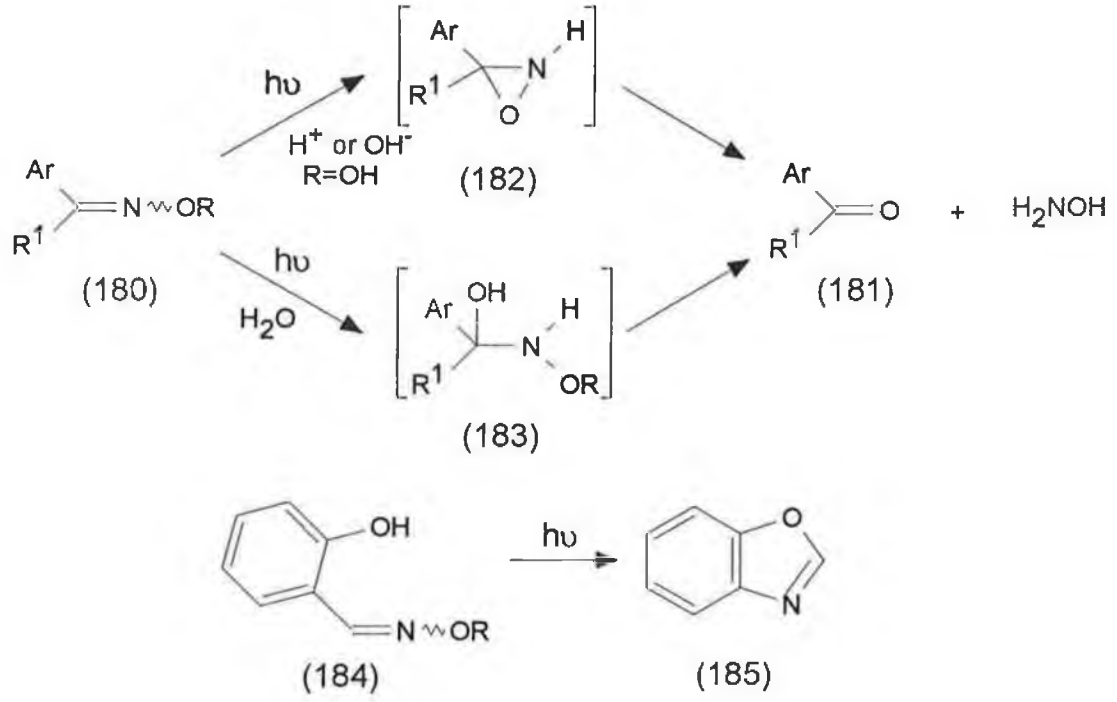


(178) (179)

1.10 Photohydrolysis

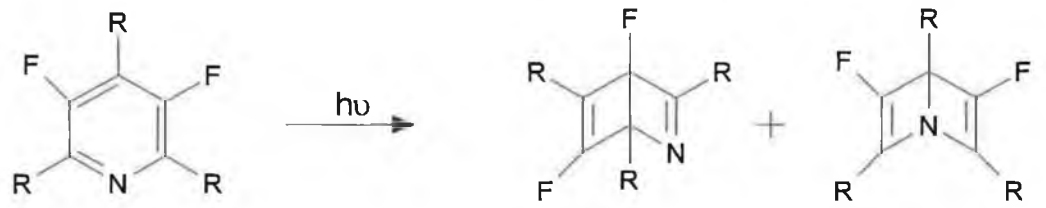
Oximes (180, R=H) and oxime O-methyl ethers (180, R=Me) have been found to undergo photohydrolysis to their parent carbonyl compounds (181) on irradiation in aqueous solution[129]. Irradiations were carried out at 4°C to reduce the possibility of thermal hydrolysis and irradiation times were kept short to avoid the possibility of a competing photo-Beckmann rearrangement. Photohydrolysis of oximes in acidic or basic solution is believed to occur via an oxazirine intermediate (182) similar to that formed in the photo-Beckmann rearrangement, whilst photohydrolysis of oximes in neutral solution, and of oxime ethers is believed to occur via intermediate (183) formed by addition of a water molecule accross the carbon-nitrogen double bond. The *o*-hydroxy

substituted aromatic oxime and oxime ether (184, R=H or Me) form oxazoles (185) on irradiation in aqueus solution, believed to be via initial formation of an isoxazole followed by rearrangement (see rearrangements of five membered heterocycles)[130].

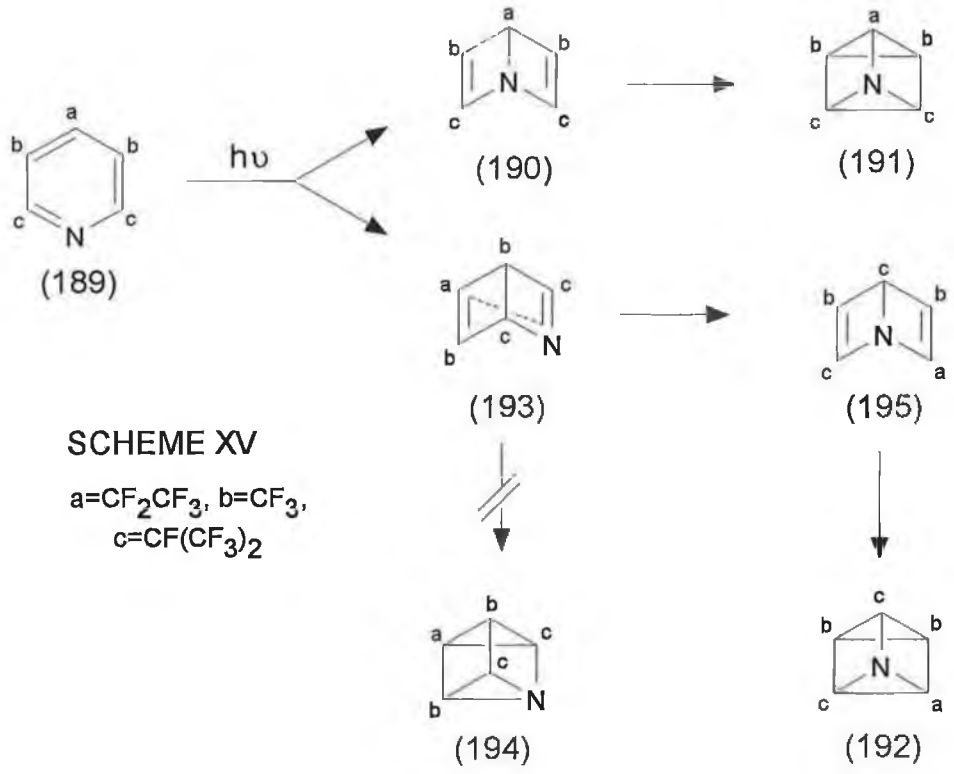


1.11 Electrocyclic Photorearrangements

The photorearrangement of nitrogen heterocycles to their Dewar forms, via intramolecular 4π-electron electrocyclic ring closure, appears to be a general phenomenon[3]. Chambers and Ogata have investigated the photorearrangements of substituted pyridines and have found that the products formed depend on the nature of the ring substituents[131-135]. It appears that, in general, the 2-aza-skeleton is preferred over the 1-aza-skeleton. For example pyridine derivative (186) rearranges to both the 1-aza- (187) and 2-aza- (188) Dewar forms with a ratio of 99:1 in favour of the 2-aza-isomer[131]. However irradiation of the pyridine (189) yields the 2-aza-Dewar pyridine (190) along with the two azaprismanes (191) and (192)[132]. Azaprismane (191) is formed from cyclisation of (190), but azaprismane (192) cannot be accounted for by cyclisation of the expected 1-aza-Dewar pyridine (193) since this would yield the azaprismane isomer (194). It has therefore been proposed that (193), which contains four bulky perfluoroalkyl substituents on the cyclobutene ring, is initially formed, but rearranges to (195), which only contains three of the perfluoroalkyl groups on the cyclobutene ring, to relieve steric strain. Azaprismanes are subsequently formed by cyclisation of (195) (Scheme XV). A similar rearrangement has been reported for tetrachloropyridazine (196) which rearranges to tetrachloropyrazine (197) on irradiation, via rearrangement of its Dewar form[136].

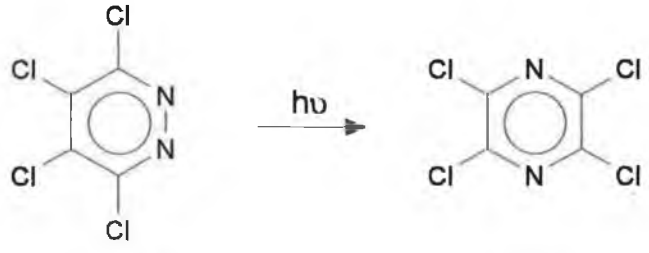


(186) R=$CF(CF_3)_2$ (187) 99% (188) 1%



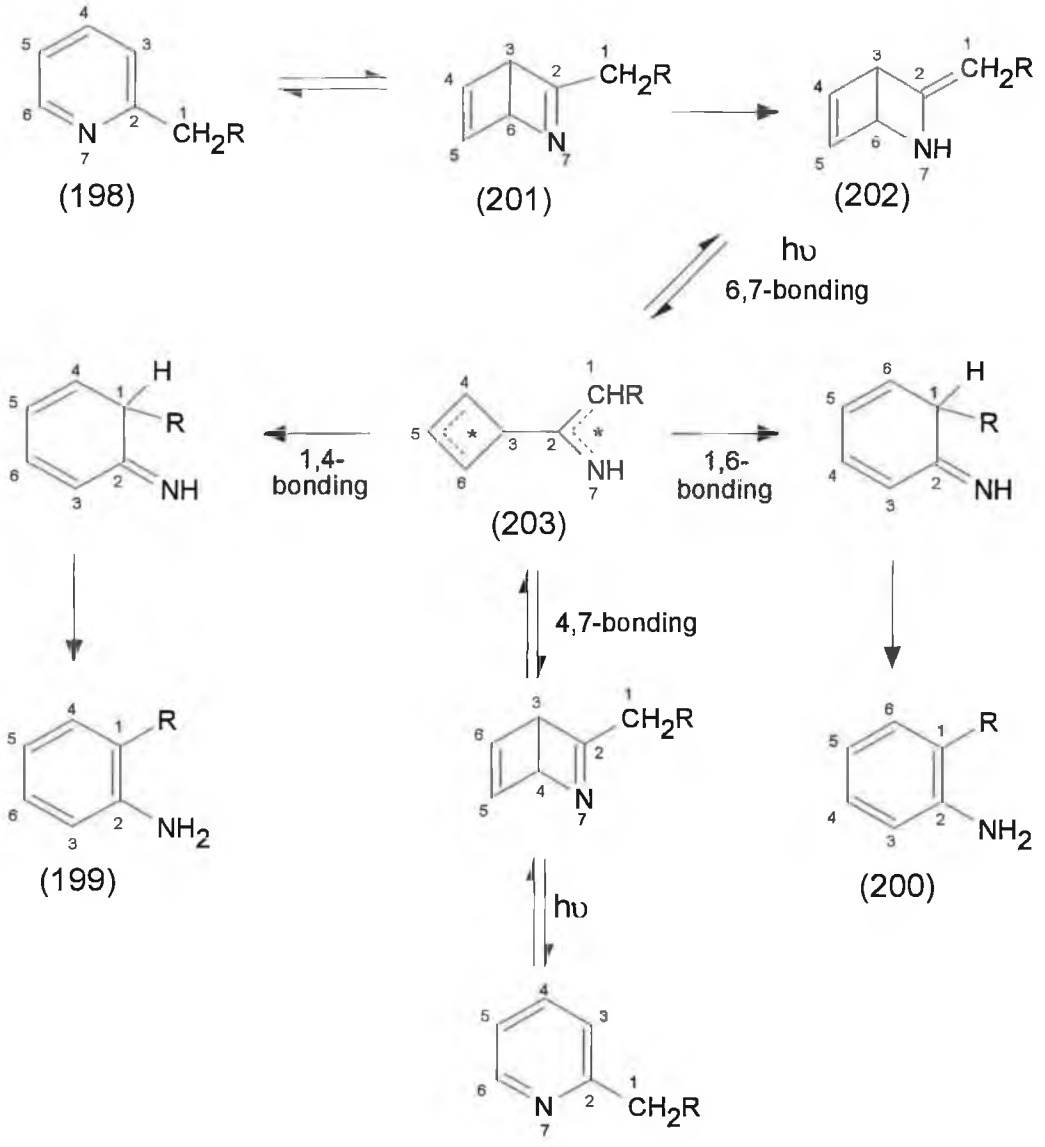
SCHEME XV

a=CF_2CF_3, b=CF_3, c=$CF(CF_3)_2$



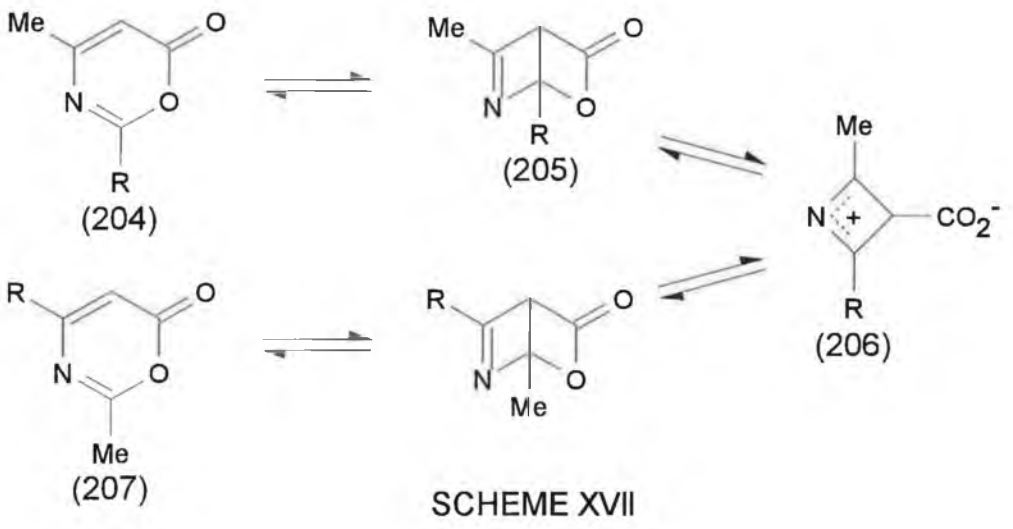
On irradiation, 2-methylpyridines (198), substituted in the side chain, undergo rearrangement to the corresponding anilines (199) and (200)[133-135]. The rearrangement again involves initial formation of the 2-aza-Dewar-pyridine (201) intermediate which isomerises to (202) in polar solvent. This intermediate then undergoes ring opening to give a zwitterionic or diradical intermediate (203) which subsequently undergoes ring closure to yield the corresponding anilines (Scheme XVI)[133]. Intermediate (202) has been isolated, and on irradiation also forms anilines (199) and (200)[134]. Although no

evidence is available for the formation of the species (203) the observed rearrangement and the formation of two photoproducts (199) and (200) on irradiation of methyl substituted[133] and deuterium labelled[135] derivatives suggests its intermediacy.



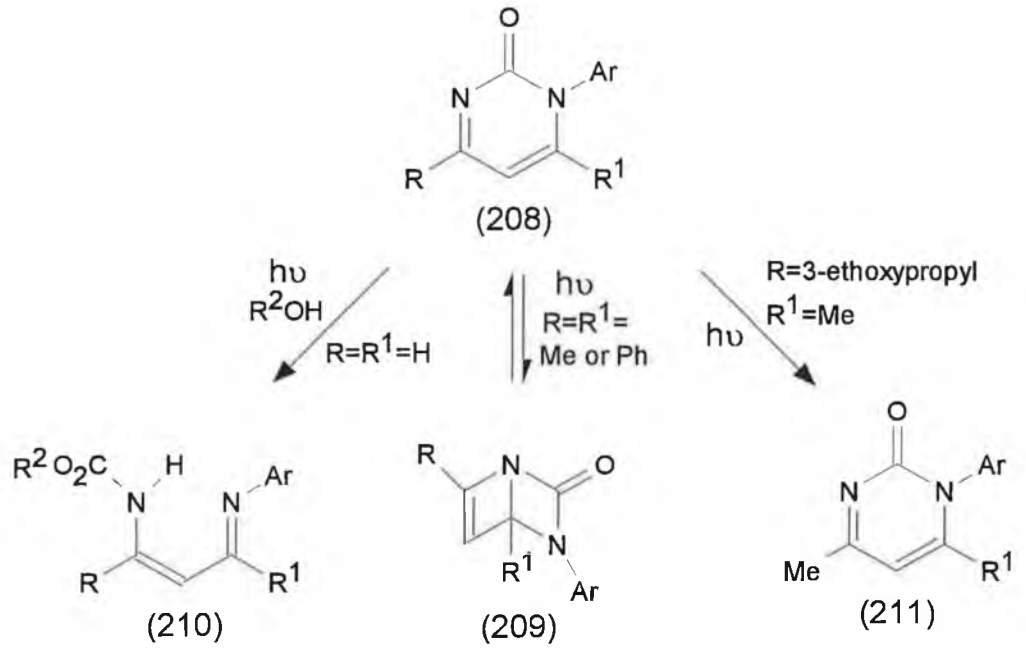
A similar zwitterionic intermediate has been proposed for the photochemical reactions of oxazinones (204) which are again believed to initially photoisomerise to their Dewar forms (205) which then undergo ring opening to the zwitterion (206)[137]. This may then ring close to ultimately yield

the starting material (204) or the photoisomer (207)[137] (where R=Ar), or, as in the case of the t-butyl derivative (204, R=t-butyl), may photofragment[138] (Scheme XVII).



SCHEME XVII

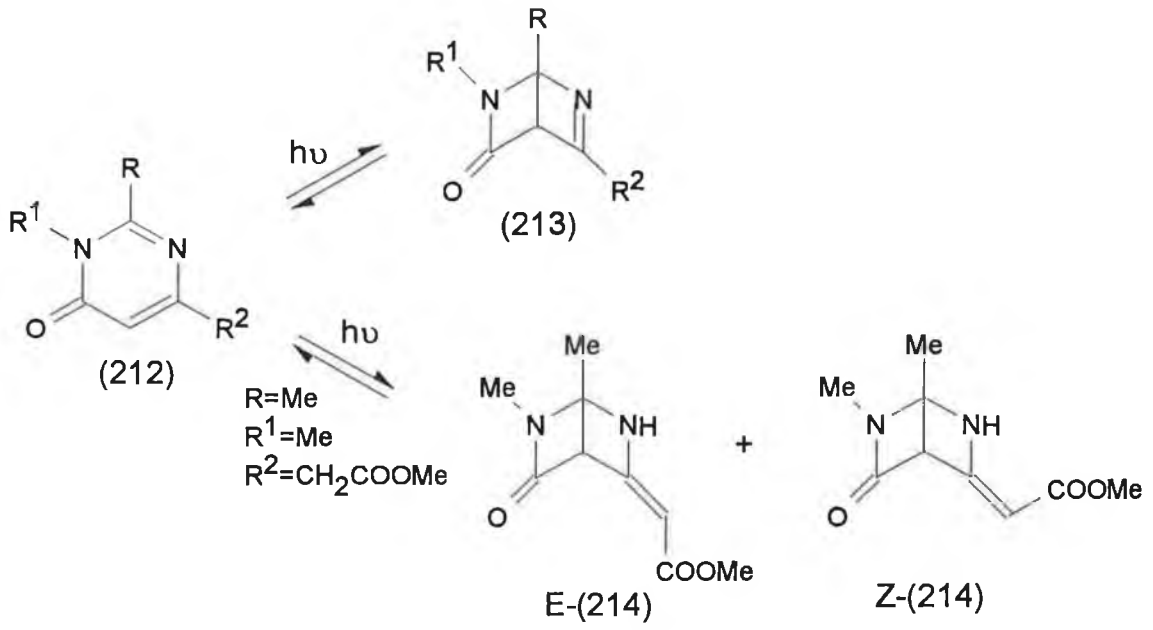
Pyrimidinones may also undergo rearrangement to their Dewar isomers. Nishio has studied the photochemical reactions of pyrimidin-2-ones and has found that their photochemical reactions are dependent on substitution at the 2- and 4- ring positions. Irradiation of *N*-aryl-2,4-dimethyl[139] (208, R=R^1=Me) or diphenyl[140] (208, R=R^1=Ph) pyrimidin-2-ones, yields the corresponding 2-oxo-1,3-diazabicyclohexenes (209) but irradiation of the unsubstituted pyrimidin-2-one (208, R=R^1=H) yields the ring opened product (210)[141], formed by cleavage of the bond α– to the carbonyl function (Type I cleavage) to form an isocyanate intermediate which subsequently may trap an alcohol molecule. The diazabicyclohexenes (209) form substituted quinolines on heating, via rearrangement and subsequent elimination of isocyanic acid[140]. 4-(3-Ethoxy-propyl)-pyrimidin-2-ones (208, R=$(CH_2)_3$OEt, R^1=Me) again form cyclised products (209) but also undergo a competing γ-hydrogen abstraction (Type II cleavage) to form the photoelimination product (211)[142].

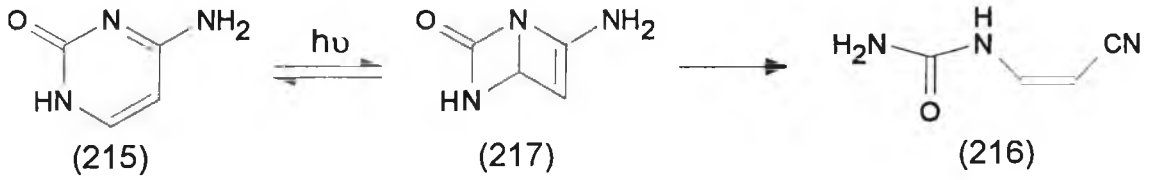


Yamazaki has also reported that pyrimidin-4-ones (212) form Dewar type intermediates (213) on irradiation[143-153]. Although these have proved difficult to isolate due to their facile thermal reversion to (212), a number have been isolated and characterised[143]. Irradiation of the 6-[(methoxycarbonyl)methyl]-derivative (212, $R=R^1=Me$, $R^2=CH_2COOMe$) yields two products, the E- and Z-isomers of the enamine isomer of the Dewar type pyrimidin-4-one (214, E- and Z-)[143]. The thermal reactions of the Dewar type intermediates of the pyrimidin-4-ones have been examined in methanol[144,145], methylamine/diethyl ether[146,147], methanol/sodium methoxide[145], liq. ammonia/diethyl ether[145,148], acetic acid[149,151], water[152,153] and hydrogen sulphide/water[153], and the products formed have been seen to depend greatly on the solvent used.

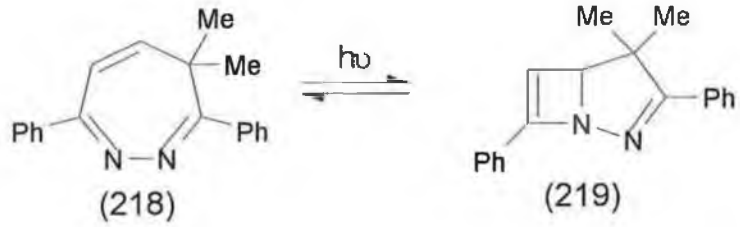
Formation of Dewar forms may also have significance in the photoreactions of the DNA nucleotide base cytosine (215)[154]. On irradiation cytosine (215) and some of its deivatives have been found to undergo photochemical isomerisation to ureidoacrylonitriles (216) again via a Dewar type intermediate (217) which subsequently undergoes ring opening to (216).

Further work needs to be done to establish if this process also occurs in the DNA of irradiated cells.



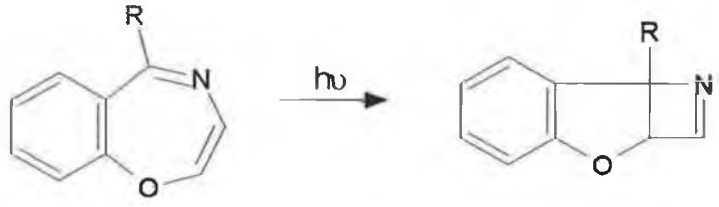


Diazepines undergo similar intramolecular 4π-electron electrocylic ring closures to those of the six membered nitrogen heterocycles, yielding pyrazole derivatives[155,156]. For example diazepine (218) yields pyrazole (219) on irradiation in methanol[155]. Similarly the bicyclic enimine (220), on irridiation, forms the novel tricyclic isomer (221)[157]. 1,4-Benzoxazepins (222) have been seen to undergo a comparable cyclization to the generally unstable derivatives of (223)[158].



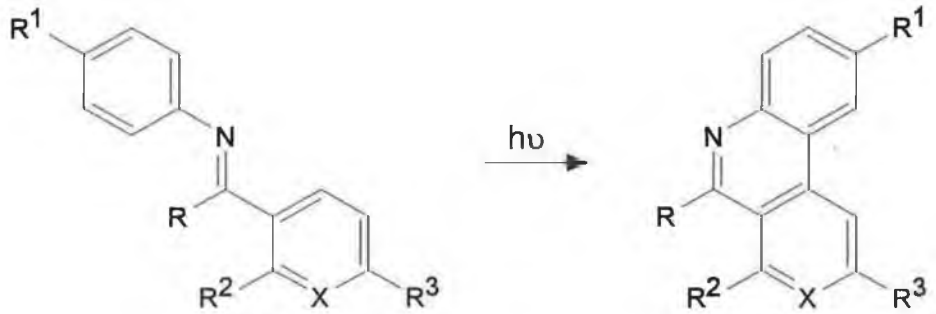
(218) (219)

(220) (221)



(222) (223)

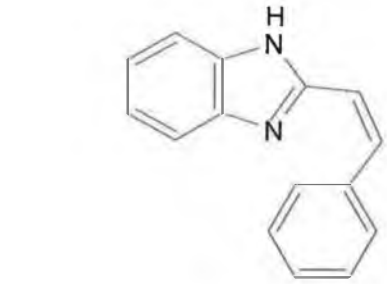
6π electron electrocyclic photocyclizations involving the carbon-nitrogen double bond with the formation of a new carbon-carbon bond are well known[3] and further examples have been reported[159-161]. For example arylimines (224) photocyclise to quinolines (225), in an analogous reaction to the stilbene-phenanthrene isomerisation, and the authors have reported that addition of boron trifluoride etherate promotes this photocyclization[159].



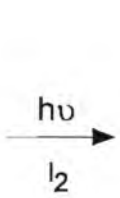
(224) (225)

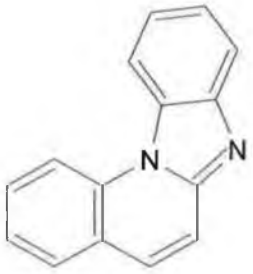
However it is only recently that reports of an analogous photocyclization

involving a terminal nitrogen atom, with the formation of a new carbon-nitogen bond, have been reported. Cooper and Irwin first reported that irradiation of the cis-olefin (226) in the presence of iodine yields quinoline (227)[162]. Glinka has shown that irradiation of the phenylbenzylideneacetone oxime (228) results in competing photocyclisation reactions to form the phenanthrene (229) and the quinoline (230)[163]. Irradiation in non polar solvents favours phenanthrene formation whilst irradiation in acidic methanol stongly favours quinoline formation.



(226)





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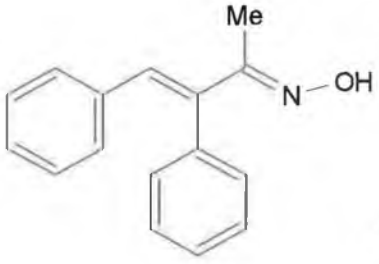

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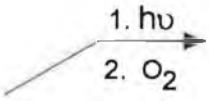

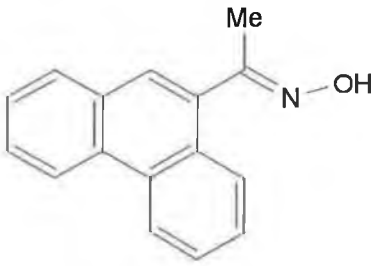

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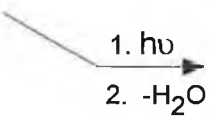
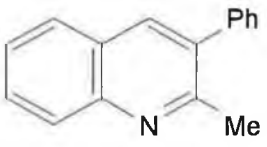
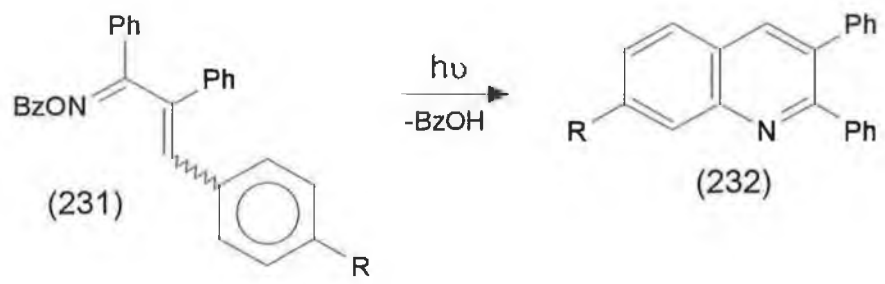




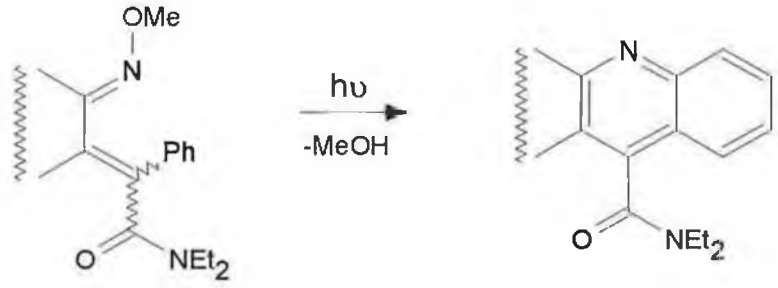
(230)

Similarly oxime benzoates (231) were also seen to photocyclise to form quinolines (232)[164], as were some γ-methoxyimino-α,β-unsaturated carboxamides (233), forming fused quinoline carboxamides (234)[165]. The

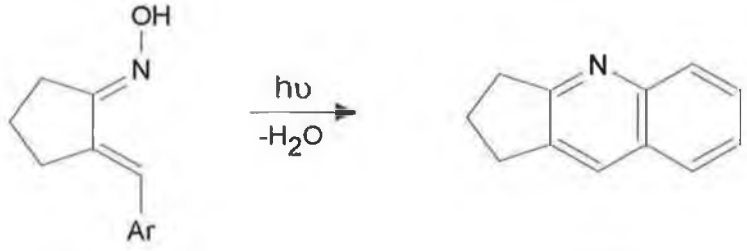
relative inefficiency of this photocyclization may be due to the facile E,Z-isomerisation in the molecules. In benzylidenecycloalkanone oximes, such as (235), the double bonds are fixed in the required cisoid conformation, and correspondingly the yields of the photocyclised products (236) are much improved[166]. These rearrangements may have some synthetic utility in the formation of substituted quinolines not readily attainable by normal synthetic methods.



(231) (232)

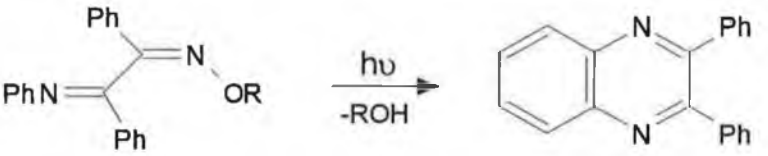


(233) (234)



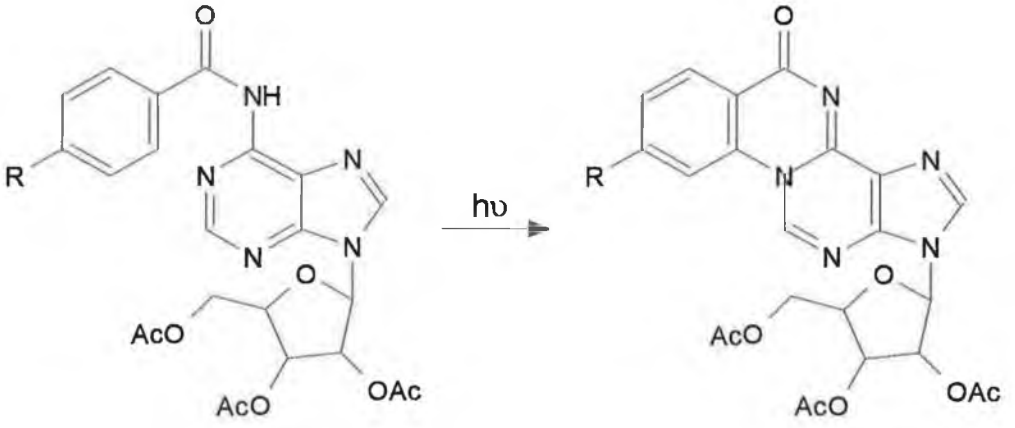
(235) (236)

A photocyclization similar to the above has been reported for some 1,4-diaza-1,3-dienes (237) to form quinoxaline derivatives (238) on irradiation[161].

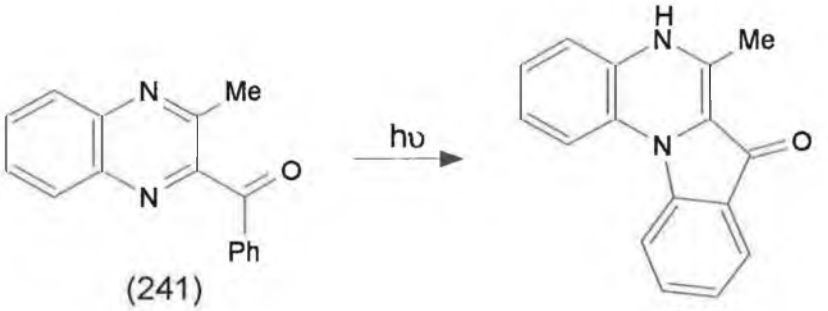


(237, R=Ac or Bz) (238)

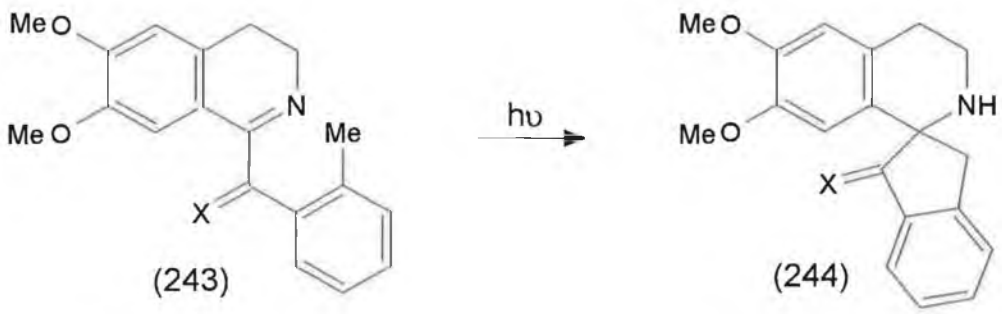
Photocyclisations involving carbon-nitrogen bond formations have also been reported in the adenine derivative (239) to form (240)[167], and the quinoxaline (241) which rapidly forms (242) on irradiation[168]. However irradiation of the structurally similar (243, X=O), which bears an ortho methyl group only gives conversion to the spiro compound (244, X=O), in low yield[169]. Similarly (243, $X=CH_2$) gives (244, $X=CH_2$) on irradiation[170].



(239) (240)

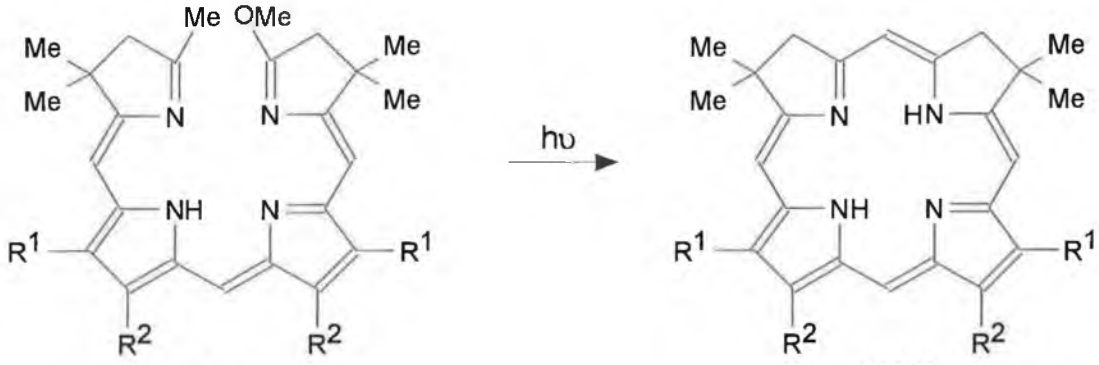


(241) (242)



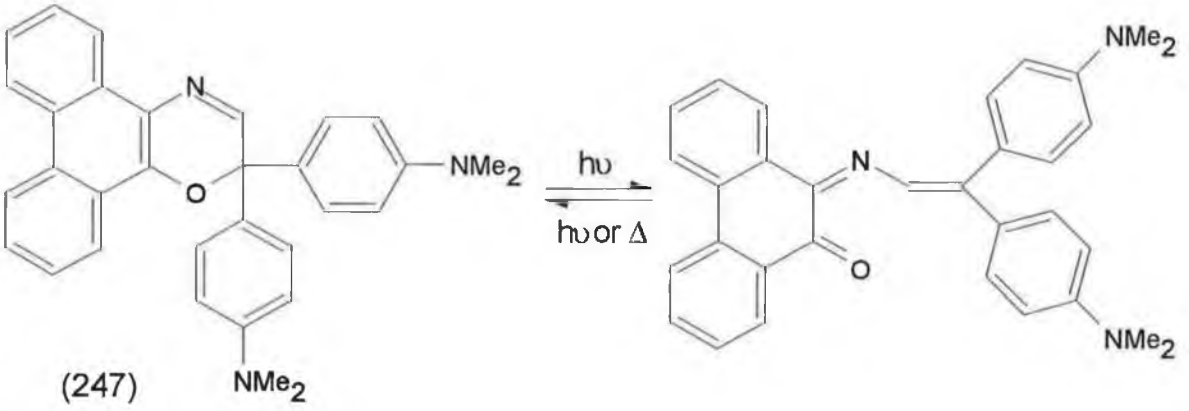
(243) (244)

Battersby and co-workers have utilised an 18π electron photochemical electrocyclization step, involving the carbon-nitrogen double bond, in the synthetic preparation of some chlorins[171-173]. For example irradiation of (245), in the presence of TFA and Hunig's base, gives chlorin (246) in good yield, presumably via a tautomerisation step[171].

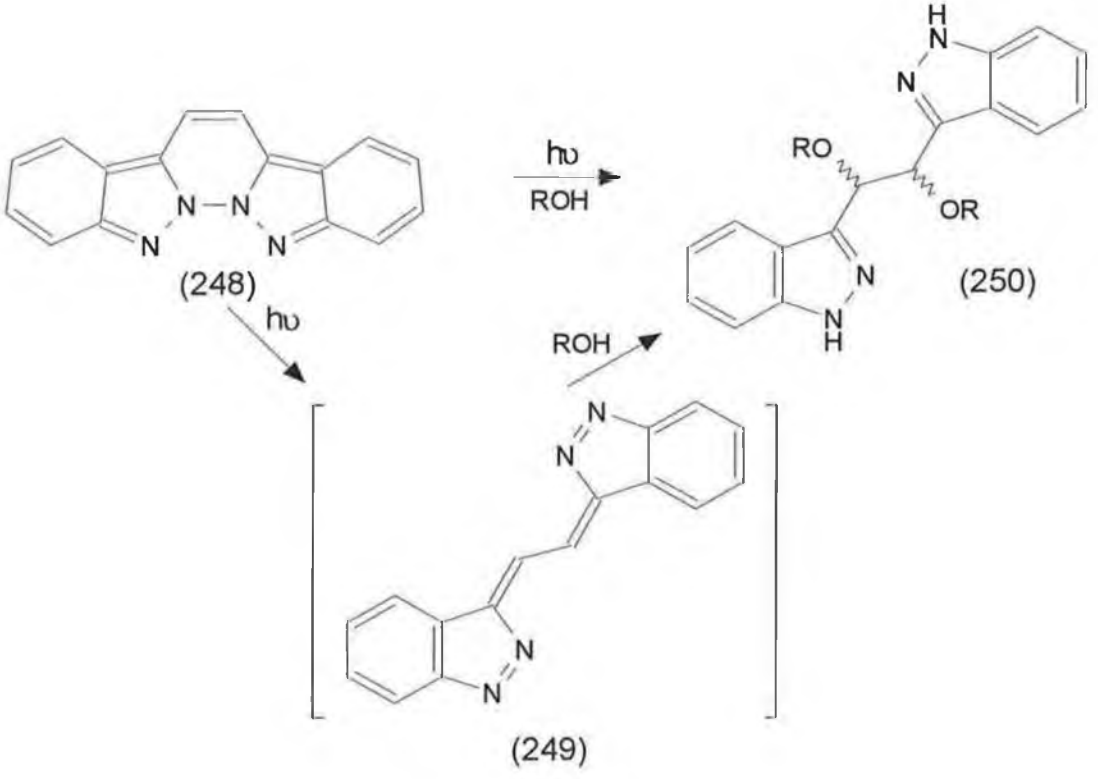


(245) (246)

Electrocyclic ring opening reactions may also occur on irradiation of certain compounds containing the carbon-nitrogen double bond and a number of examples of this type of photoreaction have been reported in the literature[174-177]. For example irradiation of the oxazine (247) leads to a reversible photochromic reaction involving an electrocyclic ring opening step[174]. The bis-indazolopyridazine (248) undergoes ring opening on irradiation in alcoholic solution, to the proposed intermediate (249), followed by addition of solvent to yield (250)[175].



(247)

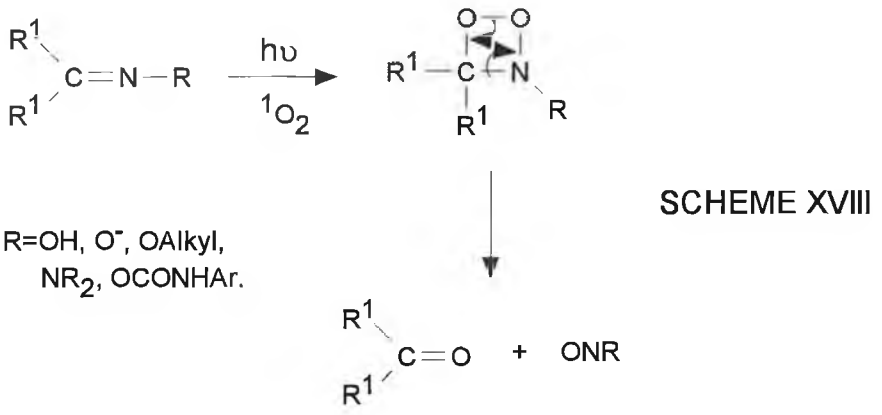


(249)

1.12 Photooxygenation

The principal reactions of the carbon-nitrogen double bond with singlet oxygen can be divided into two groups; the [2+2] addition of oxygen across the double bond followed by cleavage of the resulting carbon-nitrogen single bond to yield the parent ketone, and the [4+2] addition of oxygen to nitrogen containing heterocyclic compounds containing a carbon-carbon double bond α to the carbon-nitrogen double bond.

A number of workers have examined the reactions with singlet oxygen of compounds containing non-cyclic carbon-nitrogen double bonds and have found that the reaction depends on the nature of the substituent on the nitrogen atom[178-181]. The general reaction involves [2+2] addition of singlet oxygen across the carbon-nitrogen double bond followed by cleavage to the corresponding ketone and nitroso compounds (Scheme XVIII).

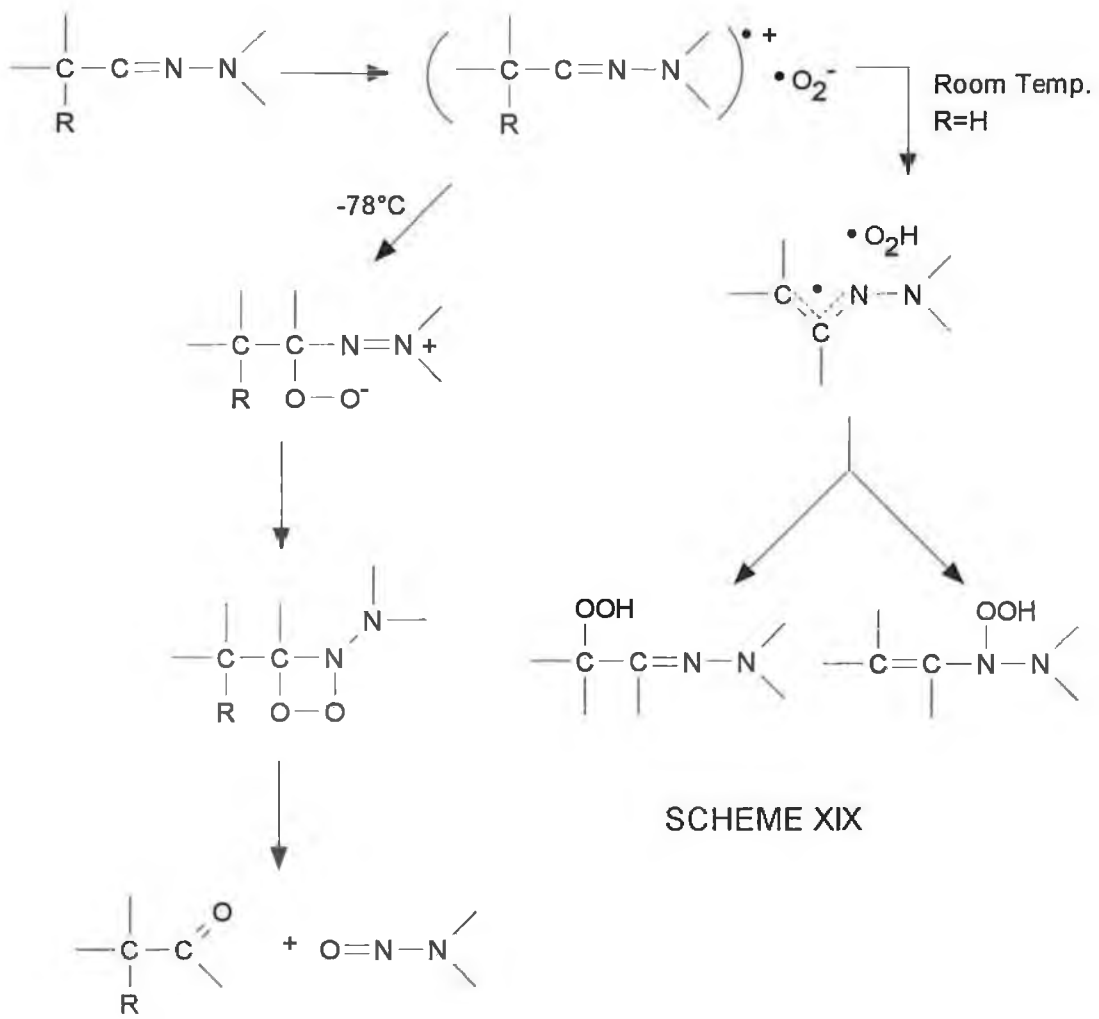


SCHEME XVIII

Oximes such as those of *p*-tolualdehyde and *p*-methylacetophenone are, in general, unreactive to singlet oxygen[178] although a small amount of parent ketone has been isolated from the irradiation of benzophenone oxime[179] and prolonged irradiation (>100 hrs.) of cyclohexanone oxime[180] with singlet oxygen. However oximate anions, which are more electron rich than oximes, undergo relatively rapid cleavage to the parent ketone. Thus dye-sensitised photooxygenation of *p*-tolualdehyde oxime or *p*-methylacetophenone oxime in the presence of base yields *p*-tolualdehyde and *p*-methylacetophenone respectively[178]. Few oxime ethers have been studied but benzophenone oxime O-methyl ether[179] and cyclohexanone oxime O-methyl ether[180] do yield the expected ketones on photooxygenation, slightly more rapidly than the corresponding oximes, as do a variety of oxime carbamates[180].

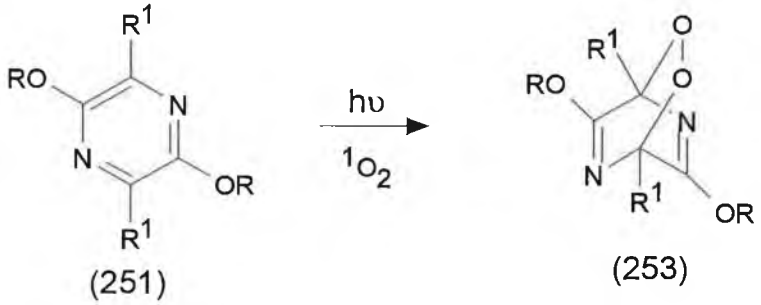
In the case of hydrazones photooxygenation products depend on the temperature of photolysis. At reduced temperature (-78°C) N,N-disubstituted

hydrazones are quite readily photooxygenated with singlet oxygen to yield the corresponding ketones[178,181]. However at room temperature, hydrazones bearing an α-C-H bond to the hydrazone carbon undergo α-oxidation to yield a variety of products depending on the nature of substituents and solvent[181], whilst those bearing no α-C-H bond do not undergo photooxidation reactions[178]. Erden and Keefe and co-workers have proposed that an exothermic stage is required prior to cleavage which would become progressively disfavoured at higher temperatures compared to the rate of α-oxidation reactions[178]. They have suggested a general scheme to encompass these results (Scheme XIX).

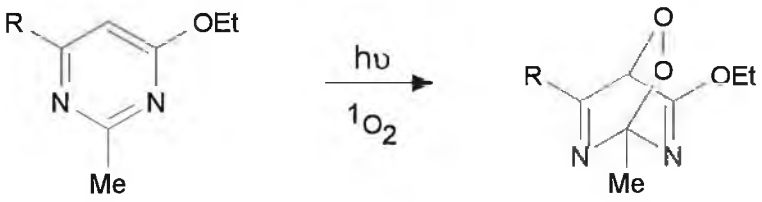


SCHEME XIX

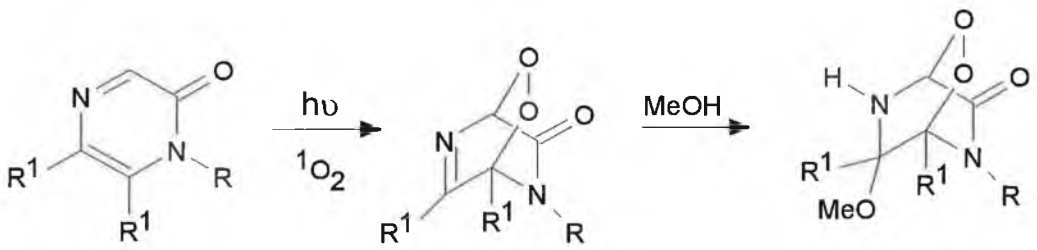
There have been a number of reports of [4+2] addition of singlet oxygen to nitrogen containing heterocycles to give endoperoxides. Markham and Sammes first reported that methylene blue sensitised oxygenation of pyrazines (251) and pyrimidines (252) yields the corresponding 1:1 adducts, the stable (253) and unstable (254) respectively[182].



(251) (253)



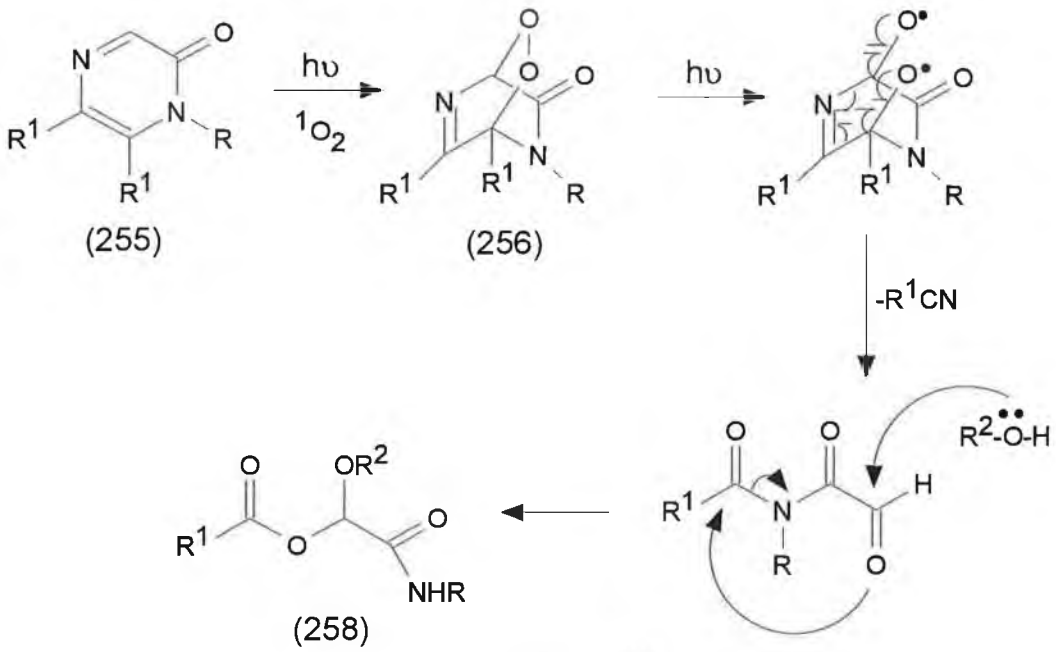
(252) (254)



(255) (256) (257)

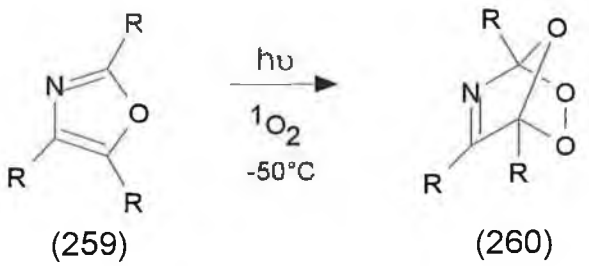
Nishio and co-workers have reported analogous reactions for pyrazin-2-ones[183-185]. Methylene Blue sensitised oxygenation of N-substituted pyrazin-2-ones (255, R=Me or Et) in dichloromethane results in the formation of the [4+2] cycloadduct (256) whilst irradiation in methanol yields the endoperoxide (257) formed by addition of methanol across the carbon-nitrogen double bond of (256)[183]. However photooxygenation of the N-unsubstituted pyrazin-2-ones

(255, R=H), under the same conditions, leads to complex mixtures of products[184]. Irradiation in the absence of sensitiser yields acetamide derivatives (258)[185]. Formation of these derivatives can be rationalised by initial formation of endoperoxide (256) with the pyrazin-2-one acting as its own sensitiser. This is followed by oxygen-oxygen bond scission, elimination of a nitrile derivative and addition of alcohol and rearrangement (Scheme XX).



SCHEME XX

A similar [4+2] addition reaction to those of the six membered hetetrocycles has been reported for the oxazoles (259) which form the unstable endoperoxide adducts (260) on Rose Bengal sensitised oxygenation at -50°C[186].



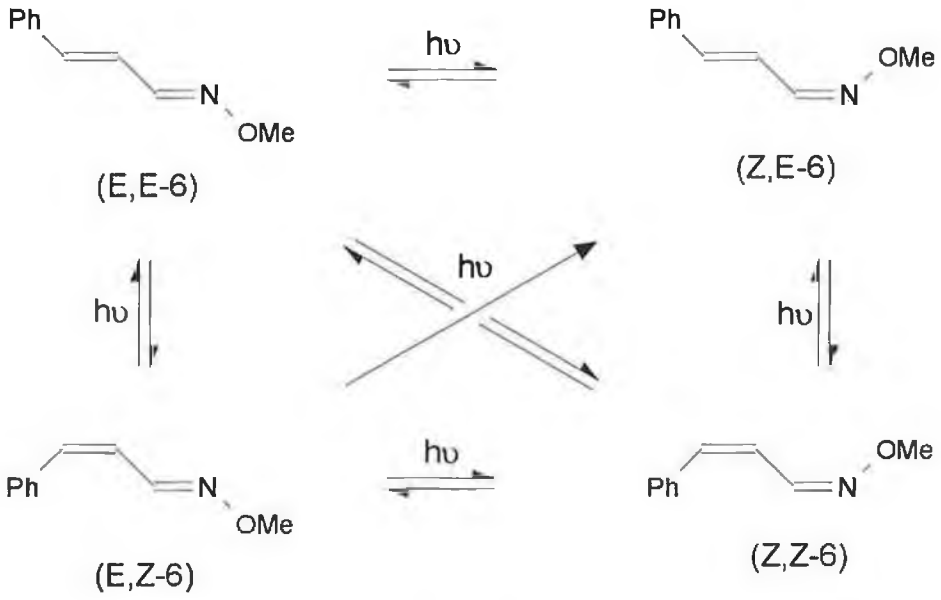
2.A: The Photochemistry of 2-Benzylidenecyclopentanone Oxime Ethers

2.A.1 Introduction

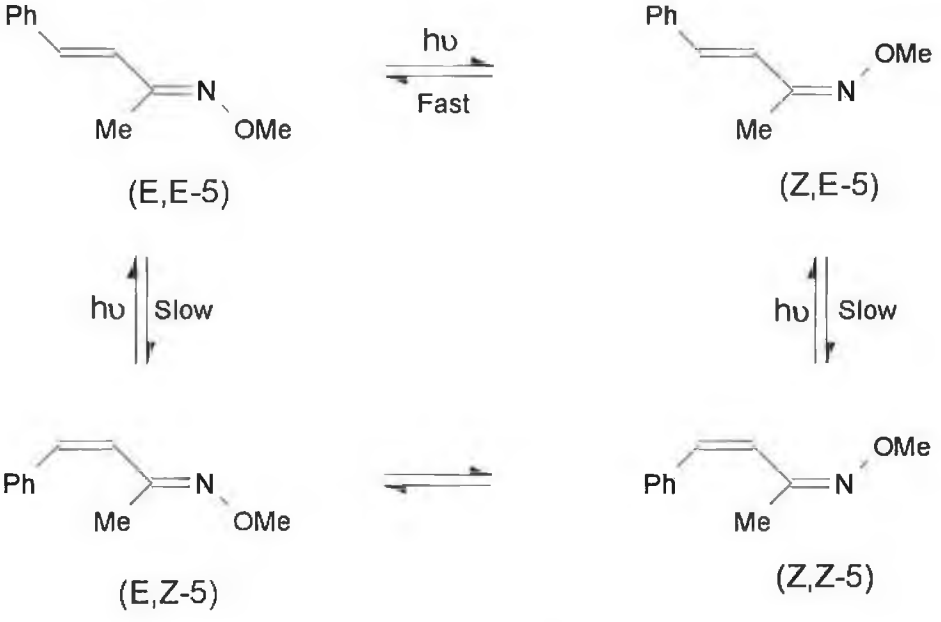
Unlike the photochemistry of 1,3-dienes[187,188], the photochemistry of α,β-unsaturated compounds containing the carbon-nitrogen double bond has not been the subject of extensive investigation. Tokumaru and co-workers have investigated the photochemistry of the benzylideneacetaldehyde oxime O-methyl ether system (E,E-6)[15-16]. Direct irradiation leads to the establishment of a photostationary state of the four isomers (Scheme XXI), the composition of which is the same irrespective of starting isomer[15]. Determination of the quantum yields shows that carbon-nitrogen, carbon-carbon and concurrent carbon-nitrogen \ carbon-carbon double bond isomerisation takes place but the isomerizations were found not to occur via a single common intermediate (Figure 3a, page 8). However measurement of the quantum yields on triplet sensitised (2-acetylnaphthalene) irradiation of the four isomers of (6) shows that here isomerisation must take place via a common intermediate, the quantum yields for the formation of any given isomer being almost the same irrespective of the isomer irradiated (Figure 3b, page 8)[16].

An investigation of the photochemistry of the structurally similar benzylideneacetone oxime O-methyl ether (5) found that, again, E-Z isomerisation occurred around both carbon-carbon and carbon-nitrogen double bonds (Scheme XXII)[14]. Direct irradiation of the E,E isomer (E,E-5) led to the Z,E isomer (Z,E-5) being formed as the sole photoproduct during the early stages of the reaction. Prolonged irradiation of (E,E-5) also led to formation of the Z,Z and E,Z isomers, (Z,Z-5) and (E,Z-5) respectively. Isomerisation around the carbon-nitrogen double bond was therefore concluded to be more efficient than isomerisation around the carbon nitrogen double bond in the molecule. The same photostationary state product ratio was reached irrespective of whether (E,E-5) or (Z,E-5) was irradiated. Triplet (*p*-methoxyacetophenone) sensitised irradiation also led to more efficient

isomerisation around the carbon-nitrogen double bond, accompanied by the slower isomerisation around the carbon-carbon double bond.



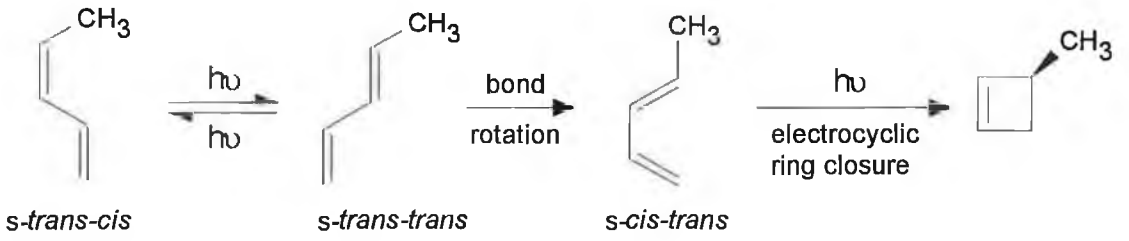
SCHEME XXI



SCHEME XXII

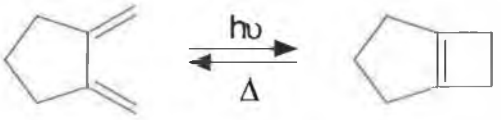
Unlike in the transoid configuration, buta-1,3-dienes in the cisoid

conformation undergo electrocyclic ring closure to yield cyclobutenes on irradiation (Scheme XXIII)[188].



SCHEME XXIII

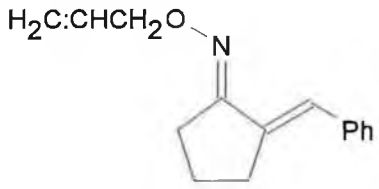
Constraining the buta-1,3-diene chromophore in the cisoid conformation facilitates the cyclisation. Thus 1,2-dimethylenecyclopentane (261) yields the bicycloheptene (262) in almost quantitative yield[189].



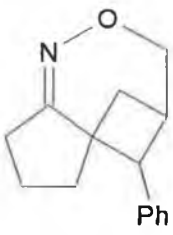
(261) (262)

It was therefore of interest to study the effects of irradiation on a system containing an α,β-unsaturated carbon-nitrogen double bond constrained in the cisoid configuration. 2-Benzylidenecyclopentanone oxime O-allyl ether (263) was chosen as the compound for initial photochemical investigation for a number of reasons. Oxime ethers show a high degree of configurational stability and thus allow easier separation and characterisation of isomers[3]. The benzylidene derivative of cyclopentanone is readily prepared by condensation of benzaldehyde and cyclopentanone, and contains a similar α,β-unsaturated backbone to that of the conformationally mobile benzlideneacetone oxime ether (5) studied previously[14]. The oxime O-allyl ether was chosen so as to investigate any possible bond forming interaction

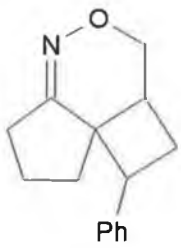
(such as [2+2] addition to form (264) or (265)) between the excited α,β-unsaturated chromophore and the carbon-carbon double bond of the allyl group.



(263)



(264)



(265)

2.A.2 Synthesis of 2-Benzylidene Cyclopentanone Oxime O-Allyl Ether (263)

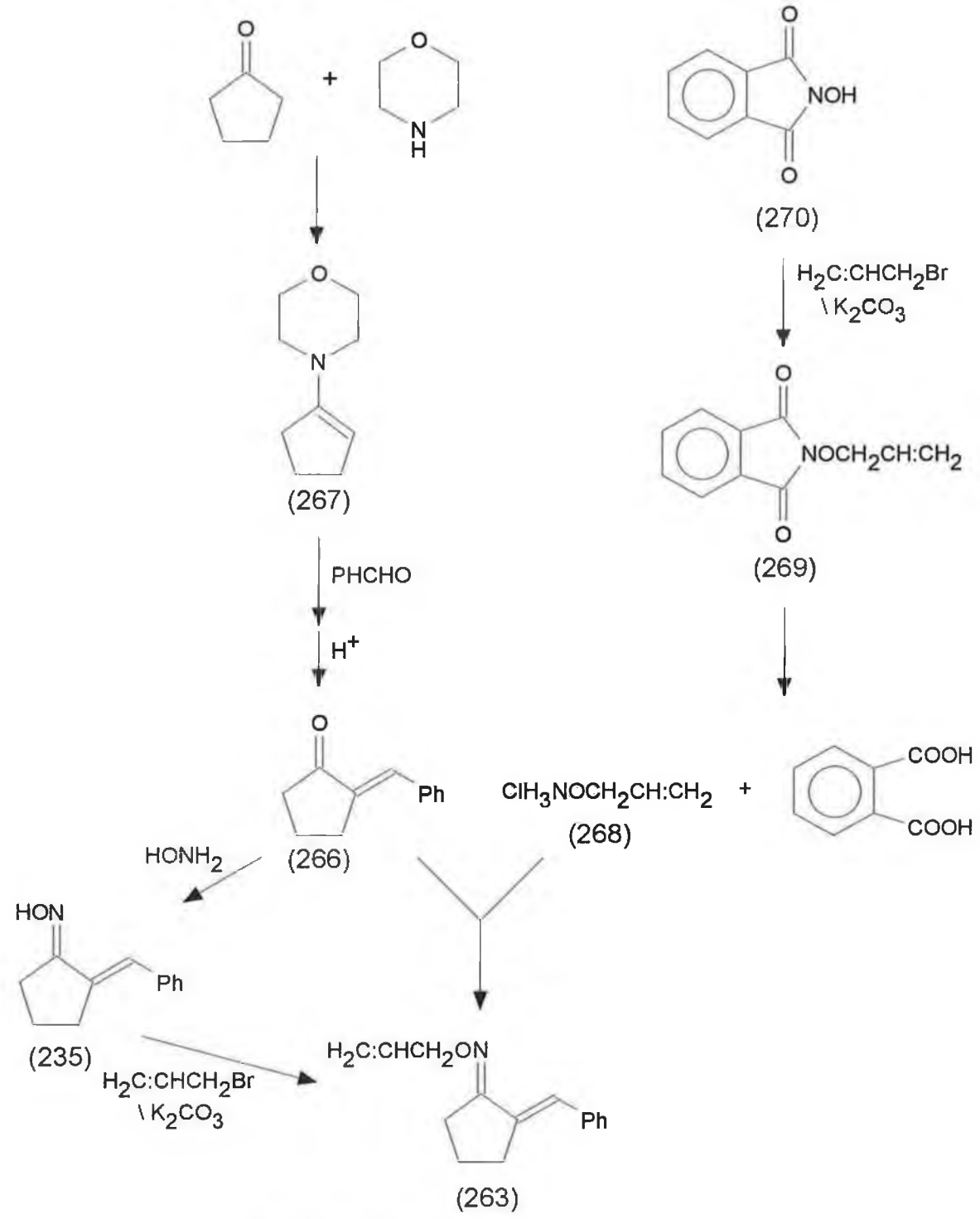
The synthesis of benzylidenecyclopentanone oxime O-allyl ether (263) is outlined in Scheme (XXIV). Benzylidenecyclopentanone (266) was prepared by initial preparation (without isolation) of the morpholine-enamine of cyclopentanone (267) followed by condensation with benzaldehyde, with azeotropic removal of water, using toluene as solvent. Subsequent acid hydrolysis and extraction yielded benzylidenecyclopentanone (266) in ~63% yield. This method is similar to that of Birkofer et. al.[190], with the exceptions that the enamine was not isolated and that toluene rather than benzene was used as solvent. Enone (266) has previously been prepared by addition of benzaldehyde to an ethanolic solution of cylopentanone containing sodium hydroxide[191] or sodium *tert*-amylate[192] as base. However these methods have disadvantages. Use of sodium hydroxide tends to lead to better formation of 2,5-dibenzylidenecyclopentanone[191a], which was not formed to any great extent by the enamine method. Use of sodium *tert*-amylate was not reported to give the dibenzylidene derivative but lower yields of (266) were recorded (~45%)[192].

It was originally intended to prepare the oxime O-allyl ether of (266) from

the corresponding oxime (235) followed by O-allylation using allyl bromide. The oxime (235) was prepared by a general procedure for the preparation of oximes of water insoluble ketones by reaction with hydroxylamine hydrochloride using pyridine as base[193]. On following the oximation reaction by TLC, two products were seen to be formed, one of which was greatly in excess of the other. On recrystallisation only the major component remained, identified as benzylidenecyclopentanone oxime (235). Since two geomerical isomers may be formed on oximation of cyclopentanone it is believed that the second, unisolated, component was the other isomer.

Allylation of the oxime (235) however proved difficult. Reaction of the oxime with allyl bromide using potassium carbonate as base gave only a poor yield of the oxime ether (263) (~25%). Use of other bases such as sodium hydroxide proved equally inefficient probably due to the low solubility of the sodium salt of the oxime (235) (the sodium salt precipitates from solution on formation). It was therefore decided to prepare allyloxyamine hydrochloride (268) and react this directly with benzylidenecyclopentanone (266) in the hope of achieving greater yield of the oxime ether (263).

Major and Hedrick had previously reported the preparation of N-methoxy- and N-ethoxyamines by the acid hydrolysis of the corresponding N-alkoxyphthalimides[194] and it was decided to adapt this method for the preparation of allyloxyamine hydrochloride (268). N-allyloxyphthalimide (269) was prepared by allylation of N-hydroxyphthalimide (270) with allyl bromide using potassium carbonate as base. Acid hydrolysis was achieved by heating the phthalimide product (269) under reflux in 6M hydrochloric acid. Although this formed the desired amine hydrochloride (268) it proved difficult to purify the product due to its hygroscopicity. Attempted recrystallisation from ethanol was not very successful, with poor recovery of product (268).

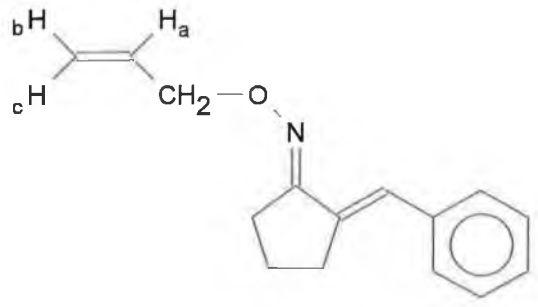


SCHEME XXIV

Consequently the melting point determined was lower than that previously recorded in the literature[195] and it proved impossible to record an infrared

spectrum of (268). However the proton NMR spectrum confirmed the proposed structure and use of the crude amine hydrochloride (268) for the preparation of the oxime O-allyl ether (263) of benzylidenecyclopentanone (266) was found to yield the expected product. The preparation of allyloxyamine hydrochloride had previously been reported from the reaction of allyl bromide with $KON(SO_3K)_2$[195].

Preparation of the oxime ether (263) was then carried out using conditions similar to those for the preparation of the oxime (235) of benzylidenecyclopentanone (266), by reaction of one equivalent each of benzylidenecyclopentanone (266) and allyloxyamine hydrochloride (268) in ethanol using pyridine as base. The yield from this reaction proved far higher than that for the O-allylation of benzylidenecyclopentanone oxime (235). On following the reaction by TLC only one product was seen. It had been expected that, since two oxime ether isomers were possible, both would be formed to a greater or lesser extent on oximation. However only one isomer, subsequently identified as the E,E-isomer of benzylidenecyclopentanone oxime O-allyl ether (E,E-263), by NMR, IR and microanalysis, was isolated. The product, (E,E-263), was purified by recrystallisation. The formation of only one isomer may be explained by the greater steric hindrance to the formation of the corresponding Z-isomer (Z,E-263) arrising from the more bulky allyl group.



(E,E-263)

The proton and carbon-13 NMR spectra agreed with the proposed structure. The proton NMR spectum shows three signals in the range δ 1.86-2.79ppm corresponding to the three methylene groups of the cyclopentane ring of (E,E-263). The signal at δ 2.79ppm, as well as showing coupling to the other methylene group at δ 1.86ppm, also shows a smaller, long range, coupling to the benzylidene group vinylic proton, indicating that this signal corresponds to the methylene group adjacent to the carbon-carbon double bond. In the range δ 4.69 to 6.08ppm four signals from the protons of the allyl group appear. The multiplet at δ 4.69ppm is from the protons of the methylene group attached to the oximino-oxygen atom. Three multiplets appear in the range δ 5.25-6.08ppm: a doublet of multiplets at δ 5.25ppm from the proton H_b (with the *cis*-coupling constant to H_a of 10.5Hz), a doublet of multiplets at δ 5.35ppm from the proton H_c (with the larger *trans*-coupling constant to H_a of 17.2Hz) and a multiplet at δ 6.08ppm from the proton H_a. The signals in the range δ 7.26-7.30ppm correspond to aromatic protons and the benzylidene group vinylic proton. The carbon-13 spectum shows three upfield signals in the range δ 22.64-31.38ppm due to the saturated carbons of the cyclopentane ring, a signal at δ 75.16ppm from the allylic carbon attached to the oximino oxygen atom, eight signals in the range δ 117.36-137.24ppm due to vinylic and aromatic carbons and a signal at δ 162.69ppm from the oximino carbon atom.

Benzylidenecyclopentanone (266) formed on condensation has a melting range corresponding to that of the E- rather than the Z- isomer[196], and it seems unlikely that the carbon-carbon double bond underwent isomerisation during the oximation reaction step. It is most likely that, since only one product is formed on reaction of (266) with allyloxyamine hydrochloride (268), that the product has the E- configuration around the carbon-nitrogen double bond due to the greater steric hindrance to formation of the corresponding Z-isomer. Confirmation of the E,E- configuration for this isomer became possible at a later

stage of the project from analysis of the spectral data of all four geometrical isomers of (263).

2.A.3 Photochemistry of E,E-2-Benzylidenecyclopentanone Oxime O-Allyl Ether (E,E-263) in Ethyl Acetate

2.A.3.1 Photochemistry

E,E-benzylidenecyclopentanone oxime O-allyl ether (E,E-263) was irradiated, using ethyl acetate as solvent, with Pyrex filtered light (λ>300nm). The photochemical reaction was followed by both Thin Layer Chromatography (TLC) and Gas Chromatography (GC). However TLC proved less useful since it failed to separate all of the products seen to be formed by GC analysis. Rapid formation of one photochemical product (PP1), accompanied by slower formation of two other photoproducts, (PP2) and (PP3), was noted. On prolonged irradiation a photostationary state was achieved.

Preparative separation of the starting material and photoproducts proved difficult. Although GC gave good separation, no preparative GC was available and an alternative method had to be used. As with the analytical TLC, preparative RCC, (radial centrifugal chromatography) using a Chromatotron system, failed to separate two of the photochemical products formed, (PP2) and (PP3). Good separation using HPLC also proved difficult, and only one of the components of the photolysis mixture (PP3) could be separated from the others satisfactorily. Fortunately, the component (PP3) that could be separated from the others by HPLC was one of the two that could not be separated by TLC and so a separation method combining the two techniques was used. The starting material (E,E-263) and one of the photoproducts (PP2) were thus isolated by use of the Chromatotron system, whilst the remaining two components of the

photolysis mixture, (PP1) and (PP3), contained in the third Chromatotron fraction, were subsequently isolated by use of preparative HPLC.

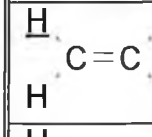
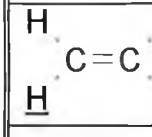
From the spectra and microanalytical data recorded for the three photoproducts, it was clear that they were all geometrically isomeric with the starting material, *i.e.* they were the three isomers (E,Z-263), (Z,E-263), and (Z,Z-263). The proton spectra of the four isomers are shown in Figures 6-9 and summarised in Table 1. Since the three photoproducts, (PP1)-(PP3), were oils, assignment of configuration by X-ray crystal structure determination was impossible and an alternative procedure had to be employed.

All of the spectra showed signals in the range δ 1.7-2.8ppm corresponding to the protons attached to the saturated carbons of the cyclopentane ring. However in both the second and third photoproducts, (PP2) and (PP3), the signals due to the protons adjacent to each of the double bonds had merged. A merging of the signals was noted for two of the protons of the allyl group in (PP3). However the most striking difference between the spectra was the chemical shift of the benzylidene group vinylic proton (which could be identified in each case by its long range coupling to the methylene group of the cyclopentane ring in the COSY spectrum and by the concurrence of the coupling constants of the two groups). In the E,E-isomer (E,E-263) the signal for the benzylidene group vinylic proton was located at δ 7.30ppm amongst a signal from aromatic protons. However the signal for the benzylidene group vinylic proton of the first photoproduct (PP1) showed a downfield shift to δ 8.11ppm. The second and third photoproducts, (PP2) and (PP3), both showed an upfield shift of this proton signal to around δ 6.7ppm. This could indicate that both of these isomers have the same configuration around the carbon-carbon double bond, and therefore, since the starting isomer (E,E-5) had the E-configuration around the carbon-carbon-double bond, that the second and third photoproducts, (PP2) and (PP3), have the Z-configuration around the

carbon-carbon double bond. However such an assignment would be very speculative.

Table 1

Chemical Shifts of the Protons of the Four Geometrical Isomers of Benzylidene-cyclopentanone Oxime O-Allyl Ether (263).

	E,E-263	Z,E-263 (PP1)	E,Z-263 (PP2)	Z,Z-263 (PP3)
$CH_2\underline{CH_2}CH_2$	1.86ppm	1.73	1.83	1.89
$\underline{CH_2}C{=}N$	2.63	2.45	2.70	2.66
$\underline{CH_2}C{=}C$	2.79	2.69		
$OC\underline{H_2}$	4.96	4.60	4.63	4.25
	5.25	5.17	5.27	4.92
	5.35	5.30	5.35	
$CH_2{=}C\underline{H}$-	6.08	6.00	6.08	5.36
Benzylidene-vinylic proton	7.42	8.11	6.62	6.72
Aromatic protons	7.26 (2H), 7.36 (2H) and 7.42 (1H)	7.18 (1H) and 7.29 (4H)	7.29 (3H) and 7.99 (2H)	7.27 (5H)

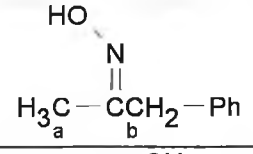
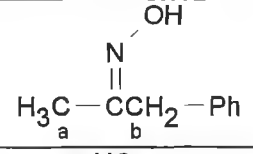
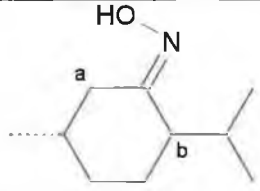
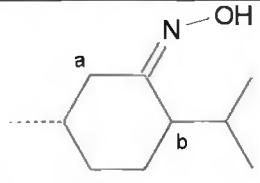
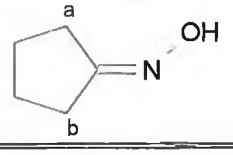
2.A.3.2 Determination of the Configurations of the Four Geometrical Isomers of 2-Benzylidenecyclopentanone Oxime O-Allyl Ether (263)

Little work has been done on the assignments of configurations of oximes, though a number of general NMR studies have been carried out with a

view to establishing trends in the ^{13}C and ^{15}N NMR spectra of oximes[197-200]. Hawkes et al. recorded the ^{13}C-NMR spectra of a range of ketoximes and found that the chemical shifts of the carbons α to the oximo-carbon atom vary quite significantly depending on the orientation of the substituent at nitrogen on the carbon-nitrogen double bond[197]. Thus when the oximino-oxygen atom was orientated towards an α-carbon atom, the chemical shift of the α-carbon was found to be between 3 and 9ppm lower than in the opposite orientation. Some examples of this are given in Table 2.

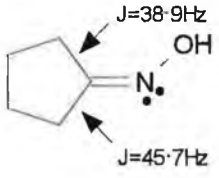
Table 2

^{13}C Chemical Shifts of the α-Carbon Atoms of some Oximes[197].

	C_a (ppm)	C_b (ppm)
	13.0	28.9
	18.9	21.7
	31.9	48.8
	35.2	40.0
	27.1	30.6

Other researchers found that the signals of the α-carbon atoms of the

Z- isomers of oximes are shifted significantly downfield on addition of $Eu(dpm)_3$ shift reagent[198]. The E- isomers are either unaffected or experience upfield shifts. Krivdin and co-workers have measured the carbon-carbon coupling constants between the oximino carbon and the α-carbon of a series of oximes. They have found that, when the oxime has the α-carbon syn to the lone pair of the oximino nitrogen, the coupling constants are more than 6Hz greater than those with the anti configuration[199]. For example the α-carbon of cyclopentanone oxime (271) syn to the nitrogen lone pair has a coupling constant of 45.7Hz compared with 38.9Hz for the α-carbon anti to the nitrogen lone pair. However the measuring of carbon-carbon coupling constants (INADEQUATE Spectroscopy) has drawbacks due to the the low natural abundance of the ^{13}C isotope. It therefore requires very high sample concentration and long accumulation times.



(271)

The assignment of the configurations of the four geometrical isomers of (263) was achieved using nuclear Overhauser effect (NOE) difference NMR spectroscopy. The NOE experiment involves the saturation of one proton resonance of a compound by applying a decoupling field at that proton's resonance frequency. As a result of dipolar interactions, the populations of the energy levels of other protons in close proximity, though not necessarily coupled, may be altered. This may cause an increase or decrease in their signal intensity. If a proton spectrum is recorded immediately after saturation of the proton resonance, and the original spectrum is then subtracted, the change in signal intensities may be seen. The maximum possible NOE

enhancement between two protons is 50%. There are however two general principles which must be borne in mind in relation to the application of NOE spectrocopy: i) the observation of an NOE enhancement between two protons does not, on its own, provide sufficient evidence that they are 'close' (NOE enhancements are dependent on the other sources of relaxation open to a proton) and ii) the absence of an NOE enhancement between two protons does not, on its own, provide sufficient evidence that they are 'far apart' (indirect negative effects may be in operation which may cancel out any direct, positive, NOE)[201]. Therefore determination of the configurations of the four isomers of (263) requires NOE difference spectra to be recorded for all four isomers.

NOE Enhancements in E,E-2-Benzylidenecyclopentanone Oxime O-Allyl Ether (E,E-263)

All of the proton resonances of (E,E-263) (shown in Table 1) were successively saturated, and the difference spectra were recorded. No NOE enhancement of any signal was noted on saturation of the signals at δ 1.86, 2.63, 4.96, 5.25, 5.35, 6.08 or 7.26ppm except for those protons directly coupled to that saturated. However saturation of the signal at δ 2.79ppm (the methylene group adjacent to the carbon-carbon double bond) gave a 14.2% enhancement of the aromatic protons (believed to be the *ortho*-protons) at δ 7.42ppm. When the reverse was carried out, and the aromatic protons at δ 7.42ppm were saturated, an NOE enhancement of 10.8% was seen for the protons at 2.79ppm (Figure 6).

NOE Enhancements in Z,E-2-Benzylidenecyclopentanone Oxime O-Allyl Ether (PP1)

As with (E,E-263), all of the proton resonances of (PP1) (shown in Table 1) were successively saturated and the difference spectra were recorded. No

NOE enhancement of any signal was noted on saturation of the signals at δ 1.73, 2.45, 5.17, 5.30, 6.00, 7.18 or 8.11ppm except for those protons directly coupled to that saturated. As for the E,E-isomer, saturation of the signal from the methylene protons adjacent to the carbon-carbon double bond (δ 2.69ppm), gave a 15.5% enhancement of the aromatic *ortho*-protons at δ 7.29ppm. The reverse was also seen, and a 7.3% enhancement of the methylene group protons at δ 2.69ppm was seen on saturation of the signal at δ 7.29ppm. In this isomer an extra, small, NOE enhancement was also noted. Saturation of the signal from the vinylic proton (at δ 8.11ppm) leads to a 1.7% enhancement of the proton signal at δ 4.60ppm (the allylic methylene group protons). However the reverse enhancement was found to be very low (<1%) and was regarded as being unreliable (Figure 7).

NOE Enhancements in E,Z-2-Benzylidenecyclopentanone Oxime O-Allyl Ether (PP2)

As with the previous isomers, all of the proton resonances of (PP2) (shown in Table 1) were successively saturated and the difference spectra were recorded. No NOE enhancement of any signal was noted on saturation of the signals at δ 1.83, 4.63, 5.27, 5.35, 6.08, 7.29 and 7.99ppm, except for those protons directly coupled to that saturated. Unlike the previous two isomers no enhancement of the signals of the aromatic *ortho*-protons was seen on saturation of the methylene protons adjacent to the carbon-carbon double bond (δ 2.70ppm). Instead a 5.6% enhancement of the signal of the benzylidene group vinylic proton (at δ 6.62) was recorded. Saturation of the resonance of the benzylidene group vinylic proton led to a 7.0% enhancement of the ring methylene signal (Figure 8).

NOE Enhancements in Z,Z-2-Benzylidenecyclopetanone Oxime O-Allyl Ether (PP3)

Again, all of the proton resonances of (PP3) (shown in Table 1) were successively saturated and the difference spectra were recorded. No NOE enhancement of any signal was noted on saturation of the signals at δ 1.89, 4.92, 5.36 and 7.27ppm, except for protons coupled to that saturated, as with the other geometrical isomers. Like the previous photoproduct (PP2) and unlike the starting isomer (E,E-5) and first photoproduct (PP1), NOE enhancements were seen between the benzylidene group vinylic proton and the methylene group protons adjacent to the carbon-carbon double bond. Thus saturation of the methylene group signal at δ 2.66ppm gave a 5.4% enhancement of the benzylidene group vinylic proton at δ 6.72ppm, whilst saturation of the benzylidene proton led to a reverse enhancement, of 5.7%, of the signal from the methylene group protons. Unlike any of the other isomers a small enhancement of the allylic methylene group signal intensity (at δ 4.25ppm) was noted on saturation of the aromatic protons at δ 7.27ppm. The reverse enhancements of the aromatic protons on saturating the signal at δ 4.25ppm were, however, less than 1% and could not be regarded as significant (Figure 9).

2.A.3.3 Discussion

A summary of the NOE enhancements is shown in Figure 10. Taken for each isomer separately, it is difficult to attach much significance to the NOE's recorded. However taken as a group, the results show much significance in the assignment of the configurations of the starting isomer (E,E-263) and the photoproducts. Both the starting isomer and (PP1) showed strong, two way, enhancements between the aromatic *ortho*-protons and the ring methylene protons. This indicated that the carbon-carbon double bond had the E-

configuration in each of these two isomers bringing the aromatic and methylene group protons into close proximity. If the carbon-carbon double bond had the Z-configuration then no NOE enhancement would be expected between these protons and indeed, for (PP2) and (PP3), no enhancement was noted. Both (PP2) and (PP3) showed NOE enhancements between the benzylidene proton and the ring methylene protons. No NOE enhancements between these two groups were recorded for the starting isomer (263) or for (PP1). This indicateted that the carbon-carbon double bond must be in the Z-configuration for (PP2) and (PP3).

Establishing the configurations of the carbon-nitrogen double bonds was more difficult since the NOE's recorded for the allyl group were much smaller. The low intensity of these NOE's is not surprising since the O-allyl group is mobile and not fixed in a conformation that would leave it permanently close to the other protons present in the molecule. For photoproduct (PP1) a small NOE enhancement was recorded for the allylic methylene protons on saturation of benzylidene vinylic proton whilst no such saturation was seen in any of the other isomers. Therefore (PP1) was believed to have the Z-configuration around the carbon-nitrogen double bond and was believed to be the Z,E-isomer of 2-benzylidenecyclopentanone oxime O-methyl ether (Z,E-263). Consequently the starting material which also has the E-configuration around the carbon-carbon double bond was confirmed to be the E,E-isomer of (263). Photoproduct (PP3) shows a small NOE enhancement of the allylic methylene protons on saturation of the aromatic *ortho*-protons and no such enhancement was seen in any of the other isomers. It was therefore believed that (PP3) is the Z,Z-isomer of 2-benzylidenecyclopentanone oxime O-methyl ether (Z,Z-263). Photoproduct (PP2), which had already been shown to have the Z-configuration around the carbon-carbon double bond, must therefore have been the E,Z-isomer (E,Z-263).

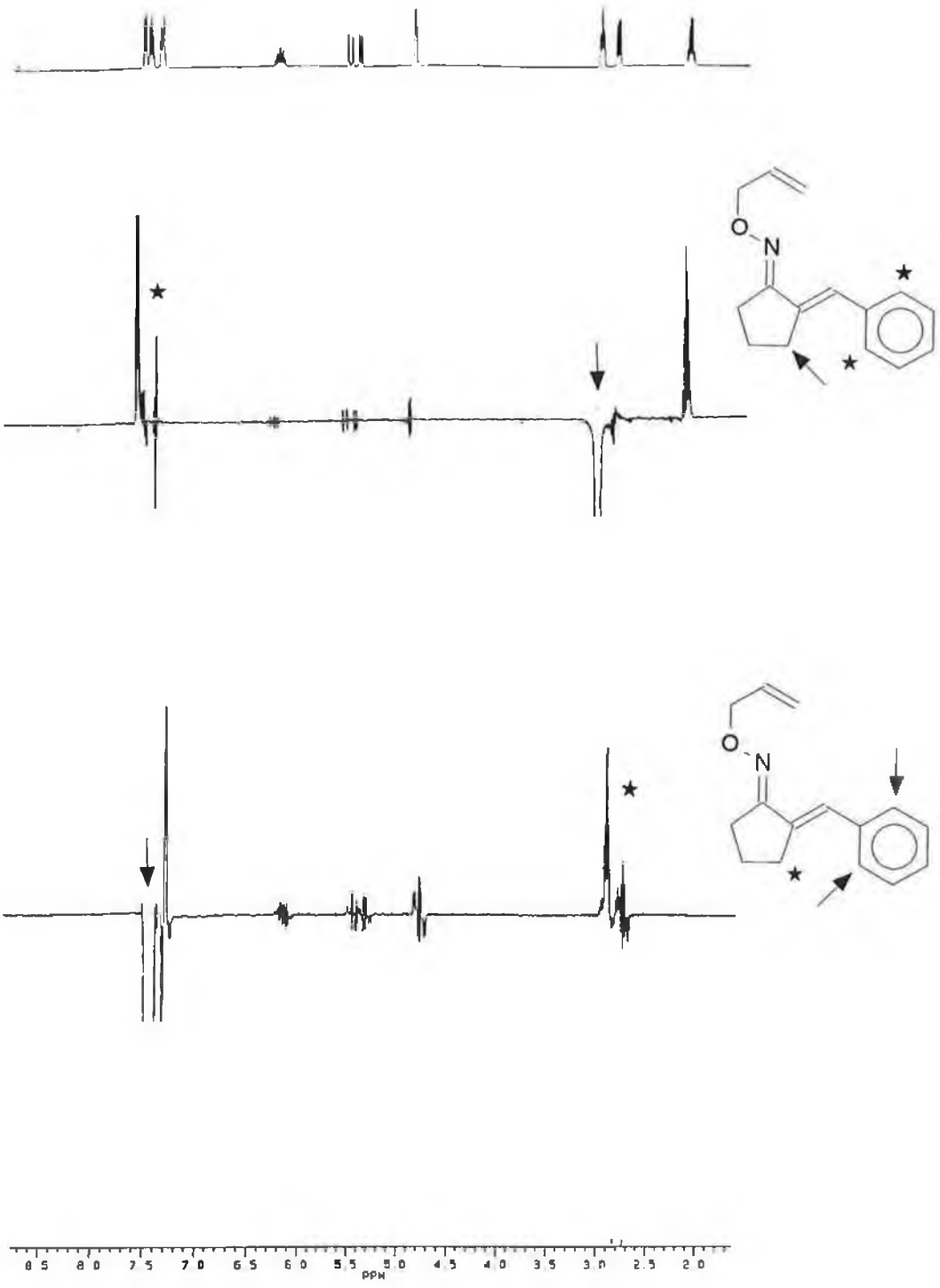


Fig. 6 *NOe enhancements in E,E-2-Benzylidenecyclopentanone oxime O-allyl ether (E,E-263).*

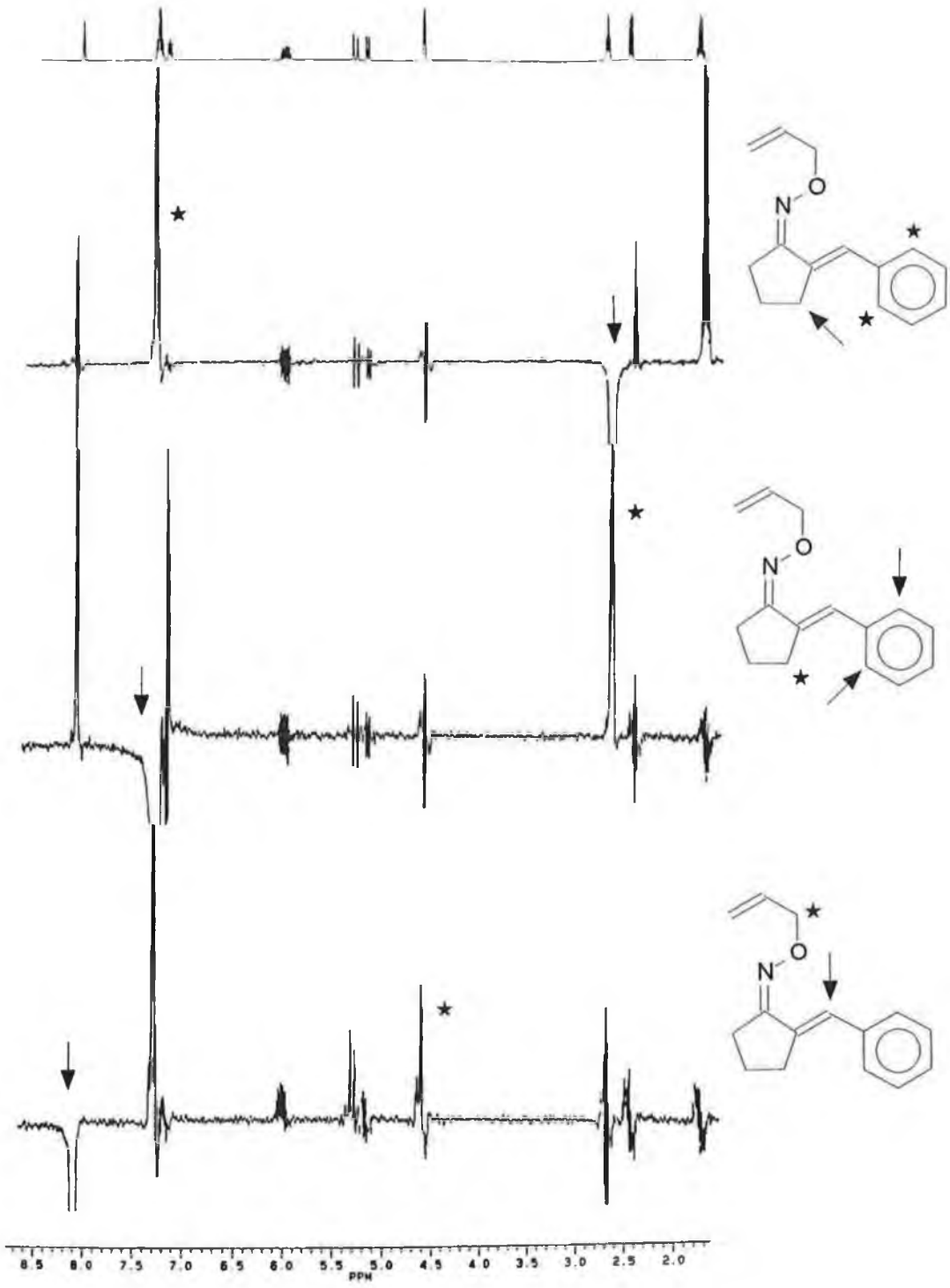


Fig. 7 *NOe enhancements in Z,E-2-Benzylidenecyclopentanone oxime O-allyl ether (Z,E-263).*

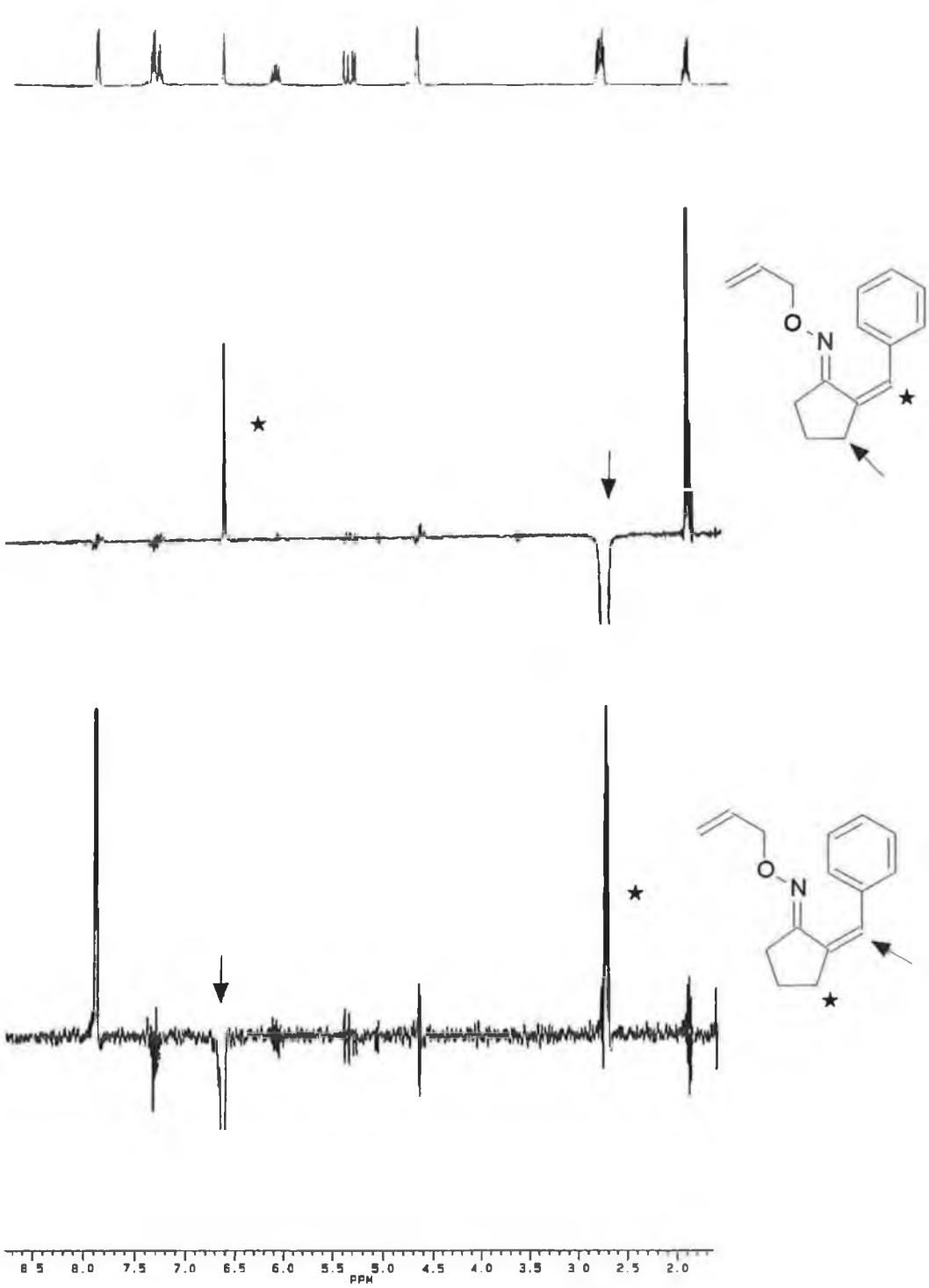


Fig. 8 *NOe enhancements in E,Z-2-Benzylidenecyclopentanone oxime O-allyl ether (E,Z-263).*

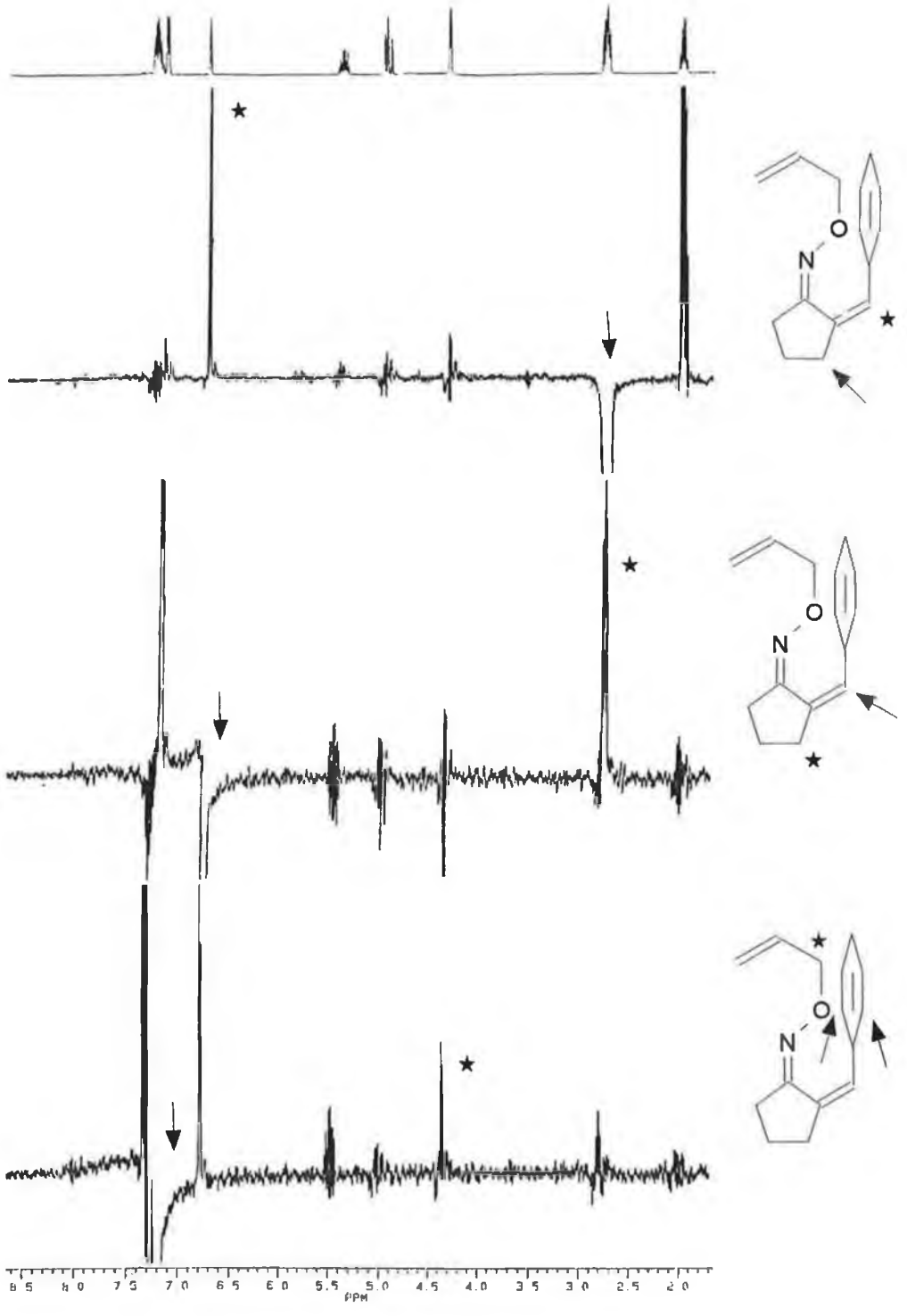


Fig. **9** *NOe enhancements in Z,Z-2-Benzylidenecyclopentanone oxime O-allyl ether (Z,Z-263).*

Further confirmation of these assignments of configuration around the carbon-nitrogen double bond was obtained by comparing the chemical shifts of the carbons α– to the oximino carbon for the four isomers of (263). The methylene α– carbon of (E,E-263) was found at δ 27.6ppm whilst that of the corresponding Z-isomer (Z,E-263) is located 4.9ppm further downfield at δ 32.5ppm. The methylene α carbon of (E,Z-263) is found at δ 29.6ppm whilst that of the corresponding Z-isomer (Z,Z-263) is located 1.8ppm further downfield at δ 31.4ppm. These results for the oxime ether (263) fitted the ^{13}C chemical shift pattern reported by Hawkes[197] for the E- and Z- isomers of oximes, although in the case of the isomers (E,Z-263) and (Z,Z-263) the difference in chemical shift was small. (It was difficult to give a definitive assignment to the other α carbon atoms in the four isomers since, being vinylic, they were found amongst the aromatic and other vinylic carbons. It could not be seen therefore whether Hawkes pattern also fitted these carbon resonances).

Having established the configurations of the three photoproducts formed on irradiation of (E,E-263), it was possible to examine the photochemistry of (E,E-263) in ethyl acetate more closely. The product formation profiles (by GC analysis) are shown in Figure 11. It can be seen that product formation involving isomerisation around the carbon-nitrogen double bond proceeds very rapidly, with the formation of the Z,E-isomer (Z,E-263) being detected at a very early stage in the photolysis. Formation of the E,Z isomer (E,Z-263) involving isomerisation around the carbon-carbon double bond, proceeds much more slowly, as does the formation of the Z,Z isomer (Z,Z-263). Rapid formation of product involving isomerisation around the carbon-nitrogen double bond accompanied by slower formation of product involving isomerisation around the carbon-carbon double bond on irradiation of (E,E-263) is similar to that seen on irradiation of benzylideneacetone oxime O-methyl ether (E,E-5)[14]. Therefore

constraining the α,β-unsaturated oxime ether system in the cisoid conformation does not appear to significantly affect the outcome of the photochemical isomerisations.

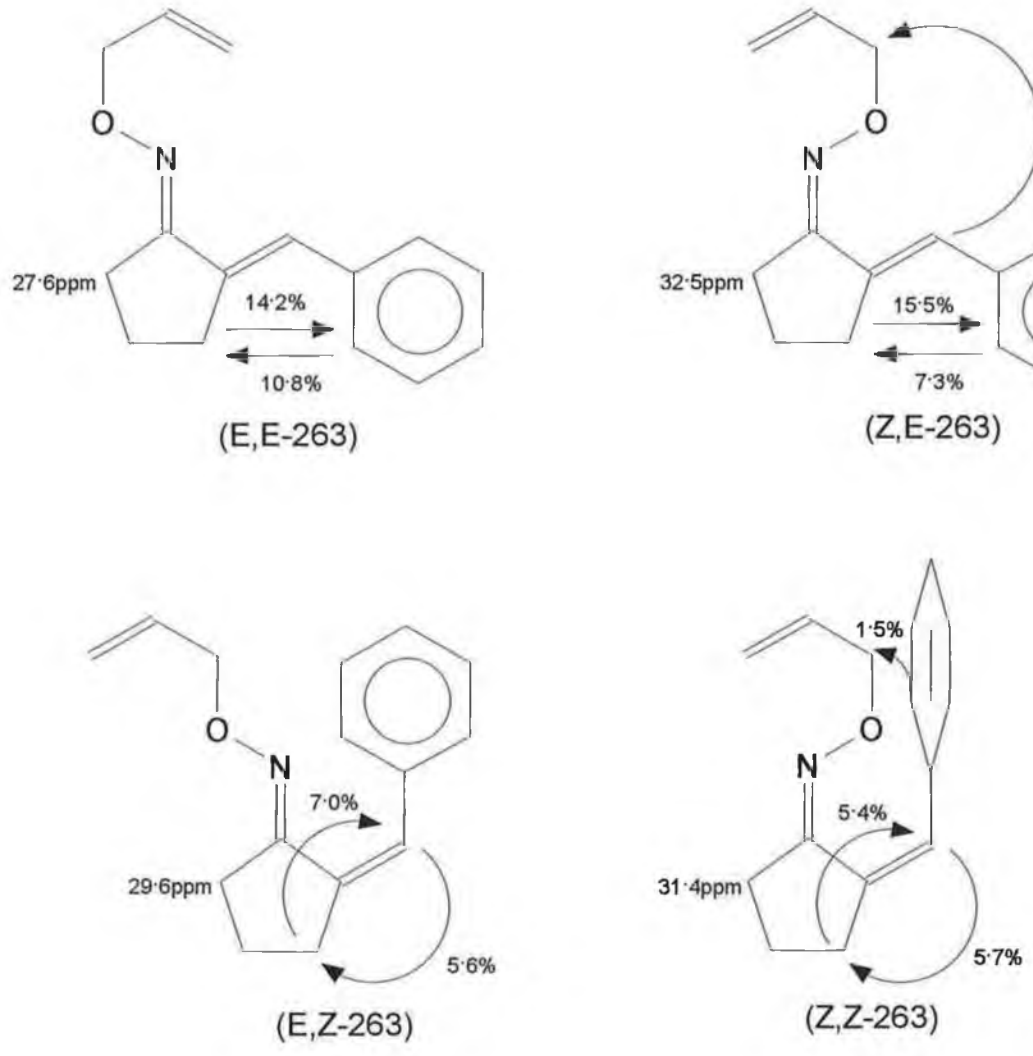
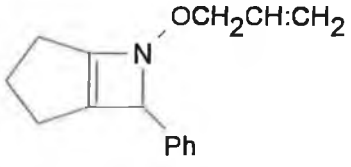


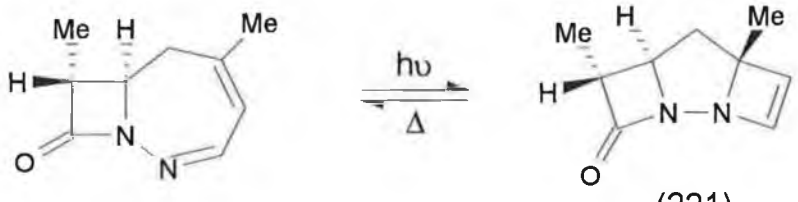
Fig.10 *Summary of the NMR data used in the configurational assignment of the isomers of 2-Benzylidenecyclopentanone oxime O-allyl ether (263). Percentage figures indicate the NOE enhancement of ^1H NMR signals on saturation of proton resonances. The chemical shift values of the methylene carbon atoms α to the oximino carbons are also shown.*

No other products were detected on irradiation of (E,E-263) in ethyl acetate. The absence of [2+2] addition products (264) or (265), involving addition of the allylic carbon-carbon double bond to the vinylic carbon-carbon double bond, is perhaps not surprising, with the energy absorbed by the α,β-unsaturated chromophore being used in the more facile isomerisation around the carbon-nitrogen and carbon-carbon double bonds. Formation of (264) or (265) could only occur for (Z,E-263) or (Z,Z-263) and would require appropriate conformational orientation of the allylic carbon-carbon double bond with respect to the benzylidene group.

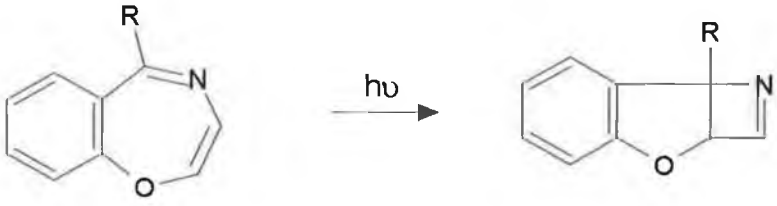
Likewise 4π-electron electrocyclic ring closure of the α,β–unsaturated carbon-carbon and carbon-nitrogen double bonds, to form (272), did not occur. Such closures are common in nitrogen containing heterocycles (see Electrocyclic Photorearrangements, page 51). For example the bicyclic enimine (220) and the 1,4-benzoxazepin (222) yield the ring closed products (221) and (223), respectively, on irradiation.



(272)



(220) (221)



(222) (223)

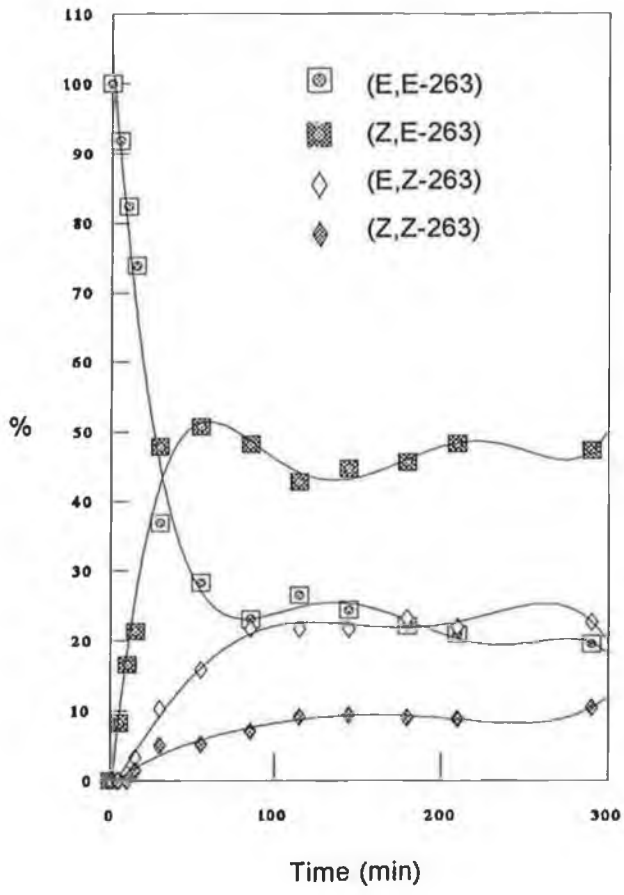


Fig.11 *Product formation on irradiation of E,E-2-benzylidenecyclopentanone oxime O-allyl ether (E,E-263) in Ethyl Acetate. Percentage figures represent fraction of each component compared to all components of the photolysis mixture.*

Lack of formation of any 4-π electron electrocyclic ring closed product on irradiation of (E,E-263) suggests that for such an electrocyclic process to occur the α,β-unsaturated carbon-nitrogen double bond must be contained within a ring system to prevent geometrical isomerisation from occurring.

2.A.4 Photochemistry of E,E-2-Benzylidenecyclopentanone Oxime O-Allyl Ether (E,E-263) in Methanol

Using the same conditions as for the irradiation in ethyl acetate, E,E-2-benzylidene cyclopentanone oxime O-allyl ether (E,E-263) was irradiated using methanol as solvent the reaction again being followed by TLC and GC. Formation of the Z,E isomer (Z,E-263) was again the most rapid photochemical process noted. Isomerisation around the carbon-carbon double bond, to give the E,Z isomer (E,Z-263), also occurred as did formation of the Z,Z isomer (Z,Z-263). However, in contrast to irradiation in ethyl acetate, the gradual formation of a fourth photoproduct (PP4) was noted (Figure 12). The concentration of this fourth product steadily increased on continued irradiation, at the expense of the four geometrical isomers of the oxime ether (263). Once this new photoproduct (PP4) was the major component of the photolysis mixture, irradiation was stopped. Separation of (PP4) from the four isomers of the oxime ether (263) proved straightforward since (PP4) had a much lower R_f value on TLC than any of the isomers of (263) allowing facile separation by preparative chromatography. On analysis of spectral data recorded for (PP4), it was established that the new photoproduct was 2,3-dihydro-1*H*-cyclopenta[b]quinoline (236). The ^{1}H-NMR spectra showed the absence of the allyl group signals in the range δ 4.2-6.0ppm that were present in the four oxime ether isomers of (263). The three upfield signals from the methylene groups of the five membered ring were still present, as in the four isomers of (263), although they had been shifted slightly downfield (~0.4ppm), and appeared as a quintet and two regular triplets. The aromatic region differed greatly from that of the four isomers of (263) and showed five well resolved signals with an integration for one proton each. These signals appeared as two triplets, two doublets and a singlet, although slightly broadened. The ^{13}C spectra showed twelve signals, three upfield corresponding to the methylene

group carbon atoms, and nine in the aromatic region of the spectra. The NMR spectra were consistent with the structure proposed and a check of the literature showed that the NMR spectra also agreed with those previously recorded for (236)[202] as did the melting point[203].

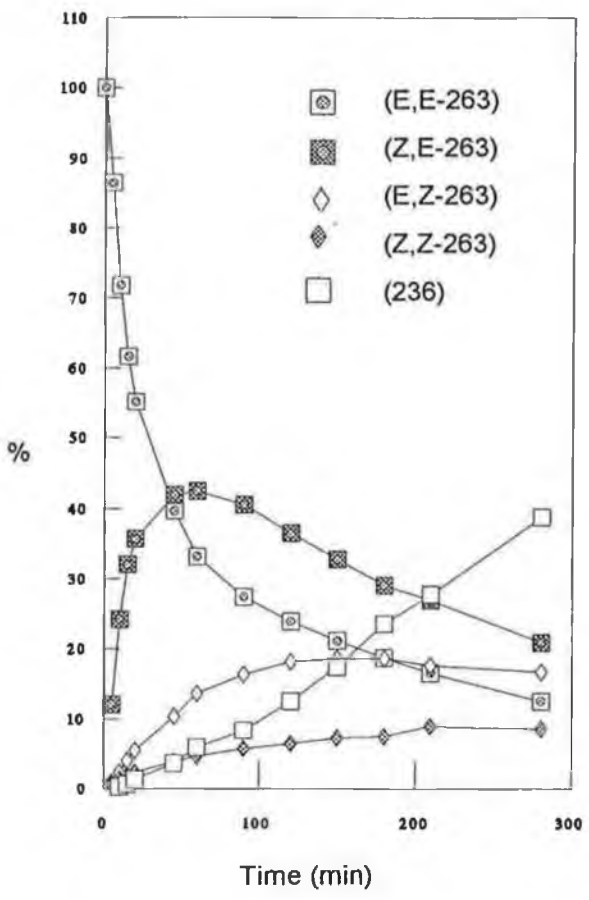
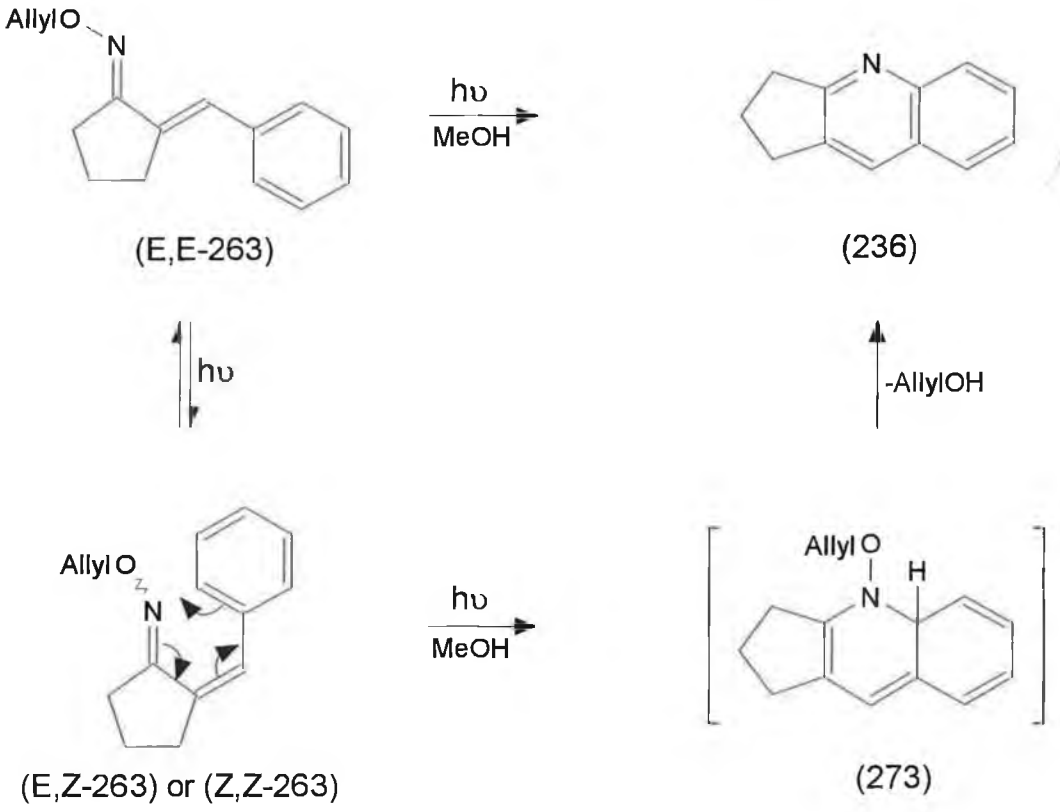


Fig.12 *Product formation on irradiation of E,E-2-benzylidenecyclopentanone oxime O-allyl ether (E,E-263) in Methanol. Percentage figures represent fraction of each component compared to all components of the photolysis mixture.*

Formation of 2,3-dihydro-1*H*-cyclopenta[b]quinoline (236) on irradiation of (E,E-263) can be accounted for by initial carbon-carbon double bond isomerisation followed by 6π-electron electrocyclic ring closure of (E,Z-263) or (Z,Z-263) to the non isolated heterocycle (273) followed by elimination of allyl alcohol to yield (236) (Scheme XXV).

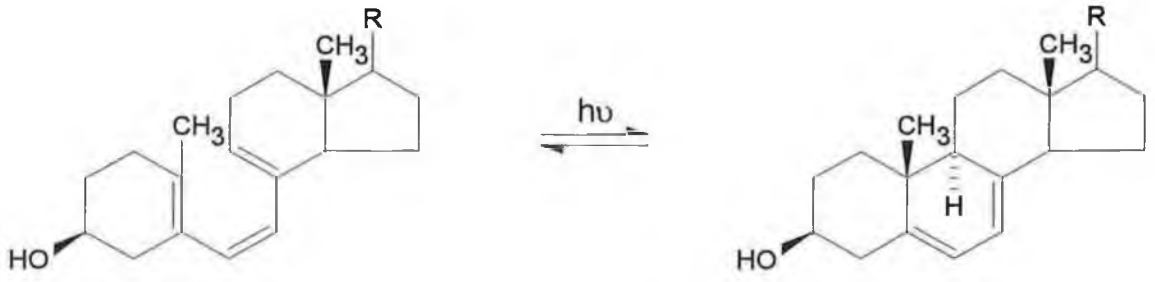


SCHEME XXV

The presence of the dihydro heterocyclic intermediate (273) was not detected. However since the aromatic quinoline (236) would be more favoured than the non aromatic (273) it seems likely that (273) undergoes elimination too rapidly for its presence to be detected. The presence of allyl alcohol amongst the products was also undetected. However the GC conditions used would not have been expected to separate allyl alcohol from the photolysis solvent (methanol), and any allyl alcohol present would have been lost during work up

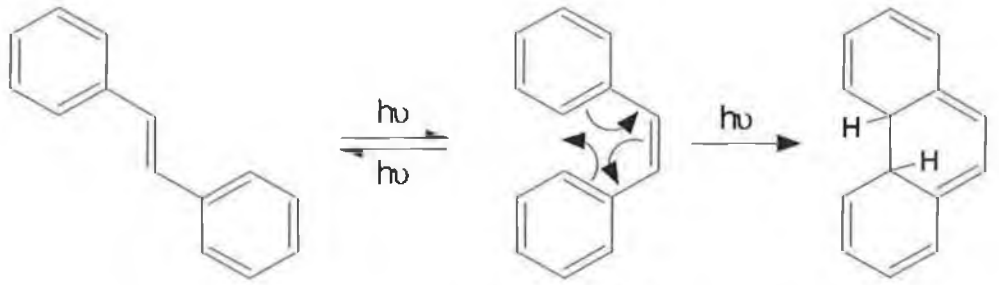
of the photolysis mixture.

Photochemical 6π-electron electrocyclic ring closure is a well established process[204]. Some of the first examples reported were in vitamin D chemistry[205]. For example previtamin D (274) undergoes electrocyclic ring closure to ergosterol (275).

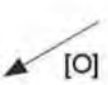


(274) (275)

Photochemical electrocyclic ring closures of the stilbene (276)-phenanthrene (277) type (Scheme XXVI) have been developed into a very useful general synthetic procedure[204].



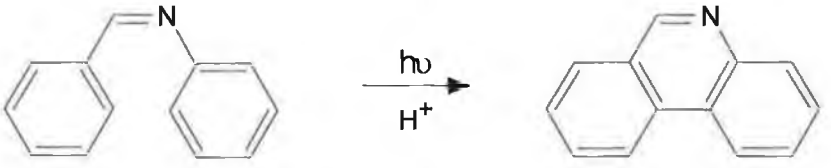
trans-(276) *cis*-(276)



SCHEME XXVI

(277)

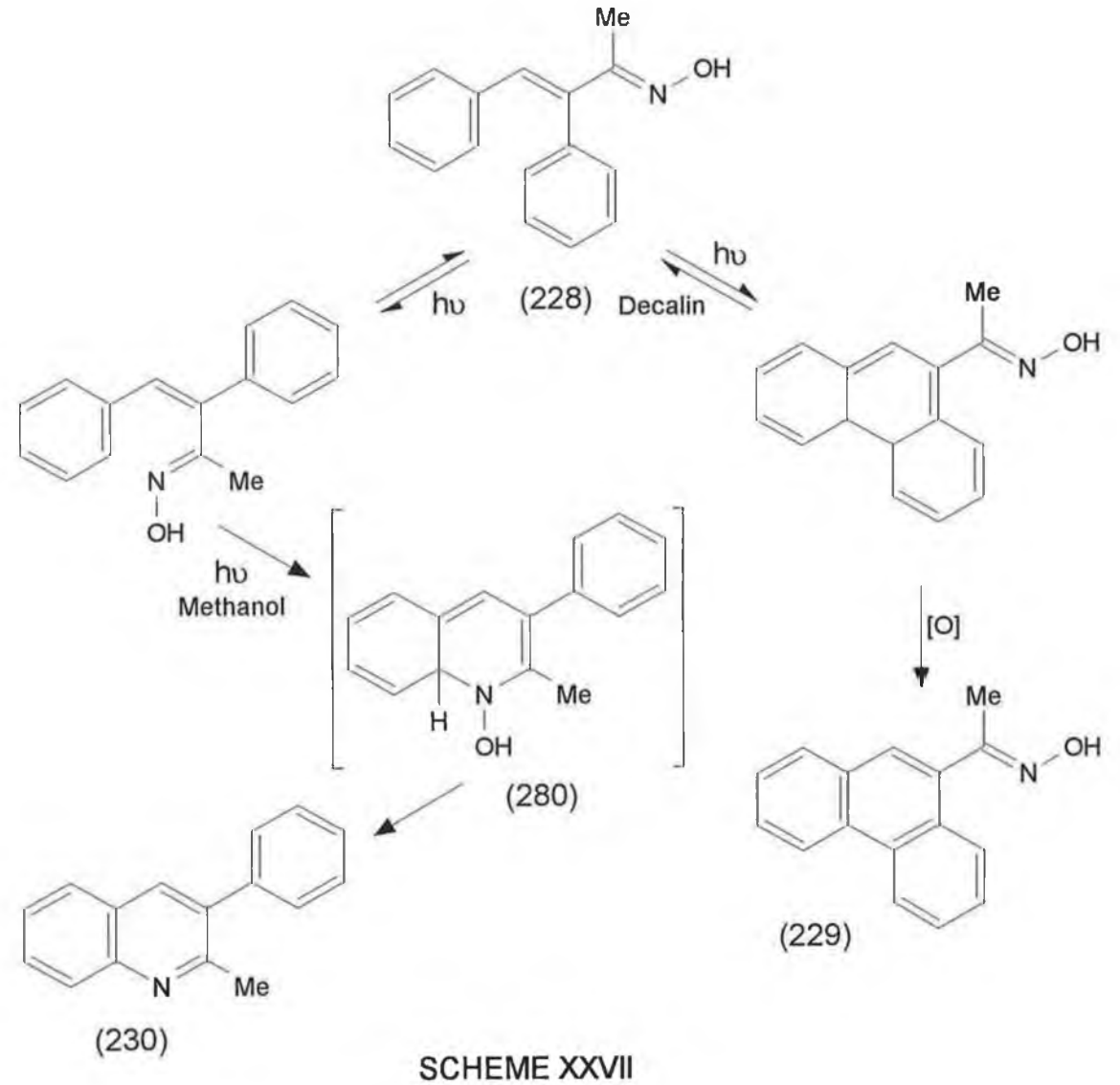
Photochemical 6π-electron electrocyclic ring closures involving a carbon-nitrogen double bond have also been reported in the literature[3]. In an analogous reaction to the stilbene-phenanthrene conversion, *N*-benzylidene-aniline (278) undegoes oxidative photocyclization to phenanthridine (279) in the presence of strong acid.



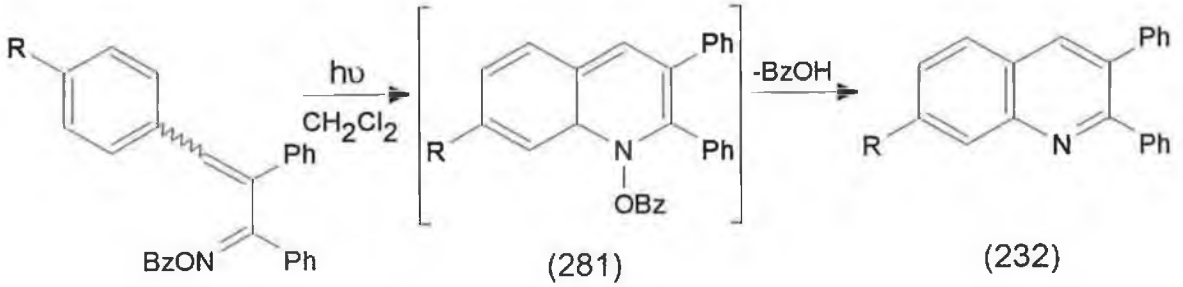
(278) (279)

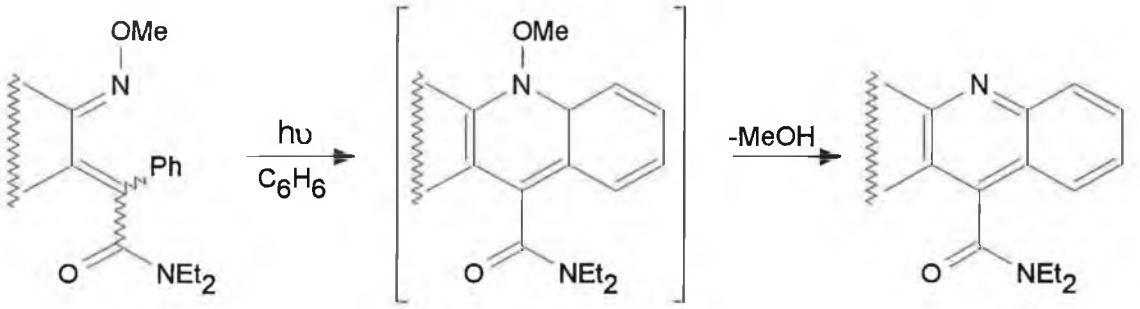
However photochemically induced 6π-electron electrocyclic ring closure involving a terminal nitrogen atom has been less well investigated and it is only relatively recently that reports have appeared in the literature[162-166]. Glinka has shown that irradiation of α-phenylbenzylideneacetone oxime (228) yields different products depending on solvent polarity (Scheme XXVII)[163]. In polar methanol, (228) undergoes electrocyclic ring closure to the terminal nitrogen followed by elimination to give the quinoline derivative (230). In non-polar decalin, (228) undergoes oxidative photocyclisation analogous to that of the stilbene-phenanthrene conversion to give the phenanthrene (229).

6π-Electron electrocyclic ring closure to quinolines has also been reported for the α,β-unsaturated oxime benzoates (231)[164] and carboxamides (233)[165], yielding quinolines (232) and (234) respectively. As was found with the 2-benzylidenecyclopentanone oxime O-allyl ether (263) system, in none of the three cases, (228), (231), or (233), were the expected intermediates, (280), (281) or (282) respectively, isolated.



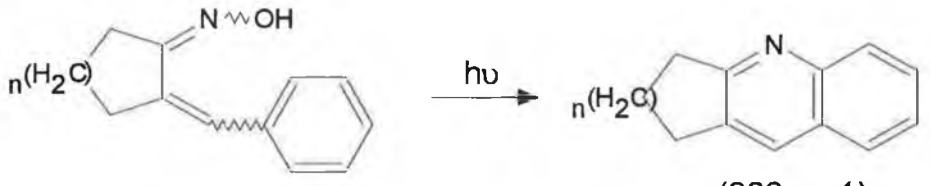
SCHEME XXVII





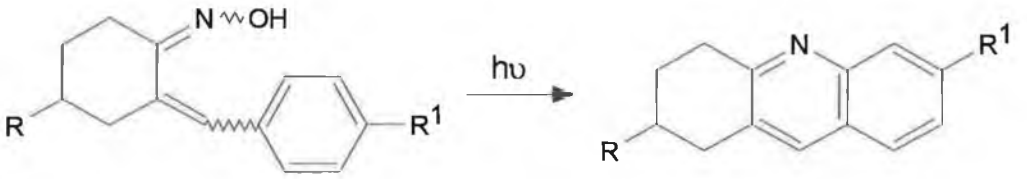
(233) (282) (234)

At the outset of the work on the 2-benzylidenecyclopentanone oxime O-allyl ether system (263), no examples of photocyclisation involving a benzylidenecyclopentanone oxime system had appeared in the literature. However Olsen has since shown that a variety of benzylidenecylcoalkanone oximes, (235) and (283)-(288), undergo 6π-electron electrocyclic ring closure to quinolines, (236), (289)-(294), on irradiation in methanol containing 1% sulphuric acid[166]. The photocyclisation reaction was found to proceed better for six and seven membered rings, (285) and (286), than for five and eight membered rings, (235) and (287), and was successful with methyl substitution on either ring, (286) and (287). The cyclisations were, however, unsuccessful using benzene or cyclohexane as solvent.



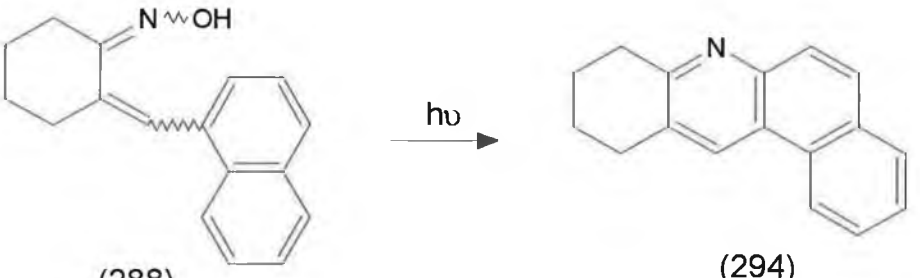
(235, n=1)
(283, n=2)
(284, n=3)
(285, n=4)

(236, n=1)
(289, n=2)
(290, n=3)
(291, n=4)



(286) a, R=H, R^1=CH_3
(287) b, R=CH_3, R^1=H

(292) a, R=H, R^1=CH_3
(293) b, R=CH_3, R^1=H



(288)

(294)

2.A.5 Effects of Solvent on the Photochemistry of E,E-2-Benzylidene-cyclopentanone Oxime O-Allyl Ether (263-E,E)

Having seen the formation of the quinoline derivative (236) on irradiation of (E,E-263) in methanol, which had not occured on irradiation of (E,E-263) in ethyl acetate, it was of interest to investigate the relationship between the formation of quinoline (236) and the polarity of the solvent used for irradiation. Other researchers, who have noted quinoline formation from α,β-unsaturated oxime derivatives, have found varying solvent effects dependent on the nature of the oxime group substituent[163-166]. Simple α,β-unsaturated oximes appear to require polar or acidic solvents to give cyclisation on irradiation[163,166]. Glinka showed that quinoline formation on irradiation of α-phenylbenzylideneacetone oxime (228) only occurred on irradiation in methanol, irradiation in nonpolar decalin did not lead to quinoline (230) formation but instead gave (229)[163]. This is similar to the findings of Olsen who failed to produce useful amounts of tetrahydroacridine (289) on irradiation of benzylidenecyclohexanone oxime (283) using either benzene or cyclohexane as solvent[166]. Irradiation of (283) in methanol gave good yields of

(289) whilst irradiation in methanol containing 1% sulphuric acid further enhanced the yields. However oxime benzoates (231) have been found to give quinolines (232) on irradiation in relatively non polar dichloromethane[164], whilst oxime acetates were found to give modest yields of quinolines on irradiation in hydrocarbon solvents[166].

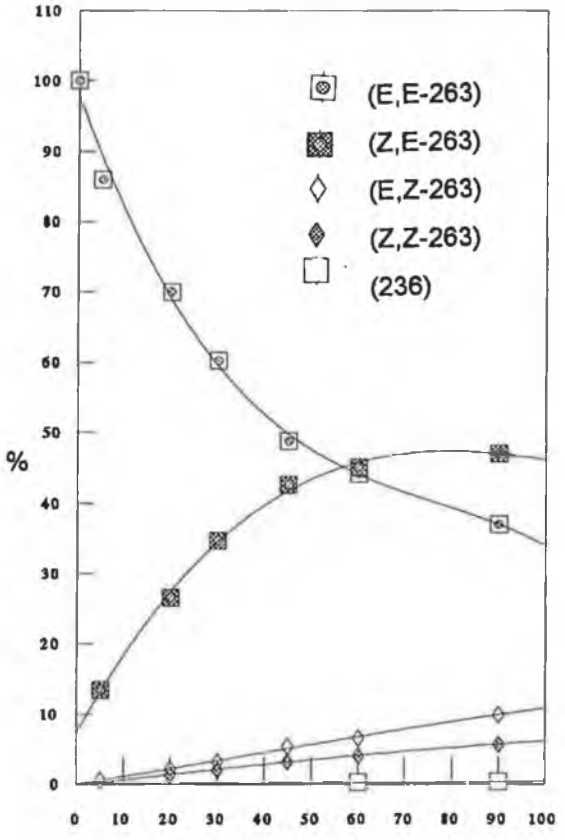


Fig.13 *Product formation on irradiation of E,E-2-benzylidenecyclopentanone oxime O-allyl ether (E,E-263) in acetonitrile. Percentage figures represent fraction of each component compared to all components of the photolysis mixture.*

The lack of quinoline formation on irradiation of the oxime ether (E,E-263) in relatively polar ethyl acetate is in contrast to the findings of Elferink and Bos who reported cyclisation to occur on irradiation of the oxime O-methyl ether (233) in non-polar benzene[165]. However this difference in reactivity may be due to the presence of the carboxamide function in (233).

Irradiation of E,E-2-benzylidenecyclopentanone oxime O-allyl ether (263) in acetonitrile, the reaction being followed by GC, showed similar initial results to irradiation in methanol and ethyl acetate, with rapid formation of the Z,E-isomer (Z,E-263) involving isomerisation around the carbon-nitrogen double bond accompanied by slower formation of the E,Z and Z,Z isomers (E,Z-263) and (Z,Z-263) involving isomerisation around the carbon-carbon double bond. However, in contrast to the reaction in ethyl acetate, traces of quinoline derivative (236) could be detected by GC on prolonged irradiation. The quinoline formation occurred much less rapidly than on irradiation in methanol. After ninety minutes of irradiation the concentration of (236) as a percentage of all components of the photolysis mixture was found to be only 0.3% in acetonitrile whereas in methanol the quinoline (236) had been found to account for 8.3% of the photolysis mixture after the same period of irradiation.

Due to the slight acidity of methanol it was possible that the formation of quinoline (236) on irradiation of (E,E-263) may have been facilitated by protonation at nitrogen in (263) by the protons present in the photolysis mixture. Therefore (E,E-263) was irradiated in methanol containing 1% potassium carbonate to ascertain if this would have any effect on the course of the photochemical reaction. Although the reaction was not followed by GC, TLC analysis did show the formation of quinoline (236). GC analysis after irradiation for 3 hours showed that the outcome of the photolysis of (E,E-263) in methanol had been unaffected by the presence of the potassium carbonate with quinoline (236) being a major component of the photolysis mixture. It can

therefore be concluded that whilst cyclisation of the oxime ether (263) to quinoline (236) requires highly polar solvents, it does not require acidic conditions.

2.A.6 The Nature of the Excited State for the Photochemical Isomerisation and Cyclisation of 2-Benzylidenecyclopentanone Oxime O-Allyl Ether (E,E-263)

Isolated carbon-nitrogen double bonds exhibit two bands in the ultraviolet region of the spectrum[2]. A high intensity band occurs between 170-180nm and has been attributed to π–π^* absorption, whilst a lower intensity band appears at longer wavelengths (230-260nm) and has been attributed to n–π^* absorption. Conjugation of the carbon-nitrogen double bond often causes the weak n–π^* absorption to be submerged by the more intense π–π^* band. The four geometrical isomers of 2-benzylidene-cyclopentanone oxime O-allyl ether (263) all exhibit strong absorption in the region of 300nm in their UV spectra. From its intensity it is clear that this band cannot be attributed to an n–π^* transition. Therefore it seems likely that the band at 300nm is the π–π^* band of the conjugated α,β-unsaturated system which has submerged the n–π^* transition of the carbon-nitrogen double bond. π–π^* Transitions usually exhibit a bathochromic shift (shift to longer wavelength) in polar solvents compared to non polar solvents. However in the case of (E,E-263) no such shifts in the absorption bands were noted on recording the UV spectrum in methanol, dichloromethane or heptane and therefore confirmation of the above assignments was not possible by this method.

Since n–π^* transitions are generally localised at the carbon-nitrogen double bond it is likely that 6π-electron electrocyclic ring closure of the α,β-unsaturated benzylidene system of (263) occurs from the π–π^* state. Electrocyclic ring closure of (263) was found to proceed on irradiation in

methanol, very slowly on irradiation in acetonitrile, but not on irradiation in the less polar ethyl acetate and therefore an alteration of the energies of the ground to excited state transitions must occur on changing solvent. Protic and polar solvents usually interact with the lone pair of nitrogen-containing molecules to form van der Waals complexes or hydrogen bonds which usually have the effect of increasing the energy of the n–π* transition (although in the case of the four geometrical isomers of (263) it is impossible to see if such wavelength shift has occurred since the n–π* transition is submerged by the stronger π–π* transition). Therefore the lack of cyclisation of the oxime ether system (263) in ethyl acetate may be due to (263) having a lowest energy n–π* transition in this solvent. On excitation to the slightly higher energy π–π* state, reaction from this state would have to compete with rapid internal conversion to the n–π* state, making cyclisation unfavourable. In methanol it is possible that (263) has a lowest energy π–π* state allowing cyclisation to occur. As has been proposed for the simpler acroleinimine (H_2C=CHCH=NH), isomerisation of the carbon-carbon double bond probaly occurs from the π–π* state, whilst isomerisation of the cabon-nitrogen double bond may probably occur from either n–π* or π–π* state[206].

2.A.7 Photochemistry of E,E-2-Benzylidenecyclopentanone Oxime O-Allyl Ether (E,E-263) in the Presence of Isoprene as Triplet Quencher

The determination of the multiplicities of the excited states from which (**E**,E-263) reacts to form its geometrical isomers (Z,E-263), (E,Z-263), and (Z,Z-263) and the cyclopentaquinoline (236) proved difficult by the use of triplet sensitisation experiments. Oxime ether (E,E-263) shows a very strong absorption band at λ 302nm (ε≈27,000). The commonly used triplet sensitisers (benzophenone, acetophenone, *p*-methoxyacetophenone) have strongest absorption bands in the region of 260nm with their absorbance decreasing in

the region of 300nm. The photolysis experiments carried out involved the use of Pyrex filtered light (λ>300nm). Therefore, since triplet sensitisation experiments require the triplet sensitiser used to absorb nearly all of the incident light, the concentration ratio of (E,E-263) to triplet sensitiser were found to be impractical. Even at shorter wavelengths the oxime ether (E,E-263) / triplet sensitiser ratio would still have been unfavourable and would have made following the course of the photochemical reaction difficult and unreliable.

However the multiplicity of the excited state for the photochemical transformations of (E,E-263) could be determined by using a triplet quenching method. On excitation a compound (A) may undergo decay to the ground state or undergo reaction (Scheme XXVIII). Alternatively, after excitation intersystem crossing may occur between the excited singlet state (A^s) and the excited triplet state (A^t). The compound in the excited triplet state may also subsequently undergo decay to the ground state or undergo reaction. When a triplet quencher (Q) is added to the photolysis mixture it may quench the excited state of the compound (A^t) and prevent reaction from occurring. Therefore, increasing the concentration of the triplet quencher in the presence of the compound under investigation should decrease the amount of product formed per unit time from the photochemical reaction if the reaction is proceeding via a triplet excited state, whilst reactions proceeding from the singlet excited state (A^s) should be unaffected by the presence of added quencher.

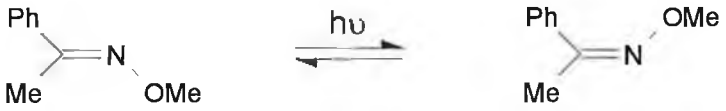
A series of samples for photochemical investigation was prepared, each containing a constant concentration of E,E-2-benzylidenecyclopentanone oxime O-allyl ether (E,E-263) (2.5×10^{-3}M), but with different concentrations of the triplet quencher isoprene ($H_2C=C(CH_3)CH=CH_2$), (0.0-1.0M). These samples were placed in stoppered quartz tubes, degassed and irradiated simultaneously using a carousel apparatus. The carousel apparatus has the

advantage of allowing a series of samples to be irradiated under identical conditions thus removing all other variables from the quenching experiment other than triplet quencher concentration. It was found by GC analysis that after irradiation all of the samples contained the same ratios of the four geometrical isomers of (263) and the cyclopentaquinoline derivative (236), irrespective of the isoprene concentration. Although it is possible that the (E,E-263) is reacting from its triplet state and that the isoprene is failing to act as an efficient triplet quencher, this seems unlikely since even the solution containing the highest concentration of isoprene (1.0M) had the same product composition as the solution of (E,E-263) containing no isoprene. The result therefore strongly suggests that both the E,Z photoisomerisation and the intramolecular cyclisation are occurring from the singlet excited state on direct irradiation.

$A + h\upsilon$	$\longrightarrow$	A^s	*excitation*
A^s	$\longrightarrow$	$A + h\upsilon'$	*fluorescence*
A^s	$\longrightarrow$	A	*internal conversion*
A^s	$\longrightarrow$	P	*product formation*
A^s	$\longrightarrow$	A^t	*intersystem crossing*
A^t	$\longrightarrow$	$A + h\upsilon''$	*phosphorescence*
A^t	$\longrightarrow$	P	*product formation*
$A^t + Q$	$\longrightarrow$	$A + Q^t$	*quenching*

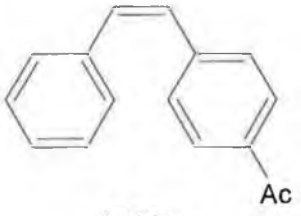
(SCHEME XXVIII)

This result agrees with the findings of Padwa for the simpler acetophenone oxime O-methyl ether system (295), where it was proposed that on direct irradiation, carbon-nitrogen double bond isomerisation occurred from the singlet excited state since the direct irradiation of (295) could not be quenched even with high concentrations of the triplet quencher piperylene[207].

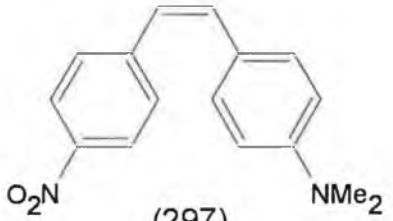


E-(295) Z-(295)

Other researchers who have reported photochemical 6π-electron electrocyclic ring closures in α,β-unsaturated systems containing a terminal carbon-nitrogen double bond have not investigated the multiplicity of the excited state from which cyclisation occurs. However in the analogous stilbene-phenanthrene photoconversion, cyclisation is also believed to proceed via an excited singlet rather than triplet state[204]. Irradiation of stilbene in the presence of azulene, an efficient quencher of triplet stilbene molecules, fails to prevent cyclisation from occurring[208]. On irradiation of 4-acetylstilbene (296) and 4-dimethyl-amino-4'-nitrostilbene (297), which contain groups which increase the probability of $S^1 \longrightarrow T^1$ transitions, E-Z isomerisation occurs normally but cyclisation to phenanthrenes does not occur[209,210].



(296)



(297)

2.A.8 Mode of Ring Closure

Potentially, electrocyclic ring closures may proceed via either of two pathways, although in the case of ring closure of the oxime ether (263) to the quinoline derivative (236) the intermediate products would be indistinguishable. The terminal groups (in the case of (263), the =CHPh and the =NOAllyl groups) may rotate in the same direction (in a *conrotatory* movement) or they may

rotate in opposite directions (in a *disrotatory* movement); these are shown in figure 14. Applying the frontier orbital approach, which predicts that a ground state electrocyclic reaction will occur from the highest occupied molecular orbital (HOMO), it can be seen from figure 14 for the (2π+2π+2π) system present in (263) that, in order for a bonding interaction to occur between the terminal lobes of the ψ_3 (HOMO) orbital, the reaction must proceed via disrotatory ring closure (Fig. 14a). However, on excitation, an electron will be promoted to the lowest unoccupied molecular orbital (LUMO) (ψ_4 in the case of a 6π-electron system) which then becomes the frontier orbital. Therefore in order for ring closure to proceed from the ψ_4 orbital, the cyclisation must proceed via the conrotatory mode, to allow a bonding interaction between the terminal lobes (Fig. 14b).

An alternative approach involves application of the 'aromatic transition state' concept, which does not depend on knowing the symmetries of the various molecular orbitals[211]. Here the transition state of the overlapping π orbitals is drawn putting in the + and - signs so as to minimise the number of sign changes in the participating orbitals. The transition state is then classified as being either a Möbius type, having an odd number of sign inversions, or a Hückel type, having an even number of sign inversions (sign inversions across the two lobes of p orbitals are not counted). For a photochemical reaction, systems containing (4n+2) electrons will be unfavourable if the transition state is of the Hückel type but will be favourable if the transition state is of the Möbius type (the rules are reversed for thermal reactions). For 6π-electron electrocyclic ring closures (these contain 4n+2 electrons, n=1) by the conrotatory mode, the transition state is of the Möbius type (containing an odd number (one) of sign inversions) (Fig. 15). Therefore the reaction would be predicted to be favourable.

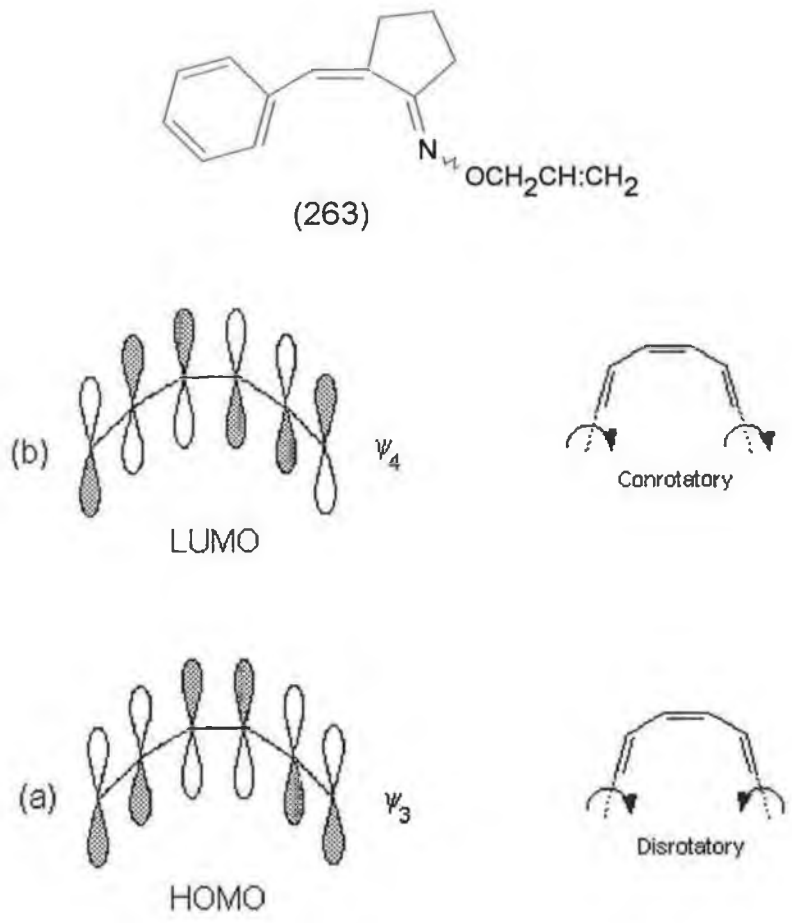


Fig. 14. *HOMO and LUMO orbitals for a (2π+2π+2π) system showing the conrotatory and disrotatory modes of ring closures.*

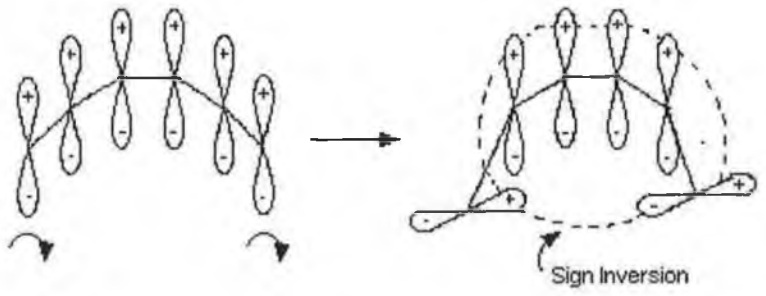
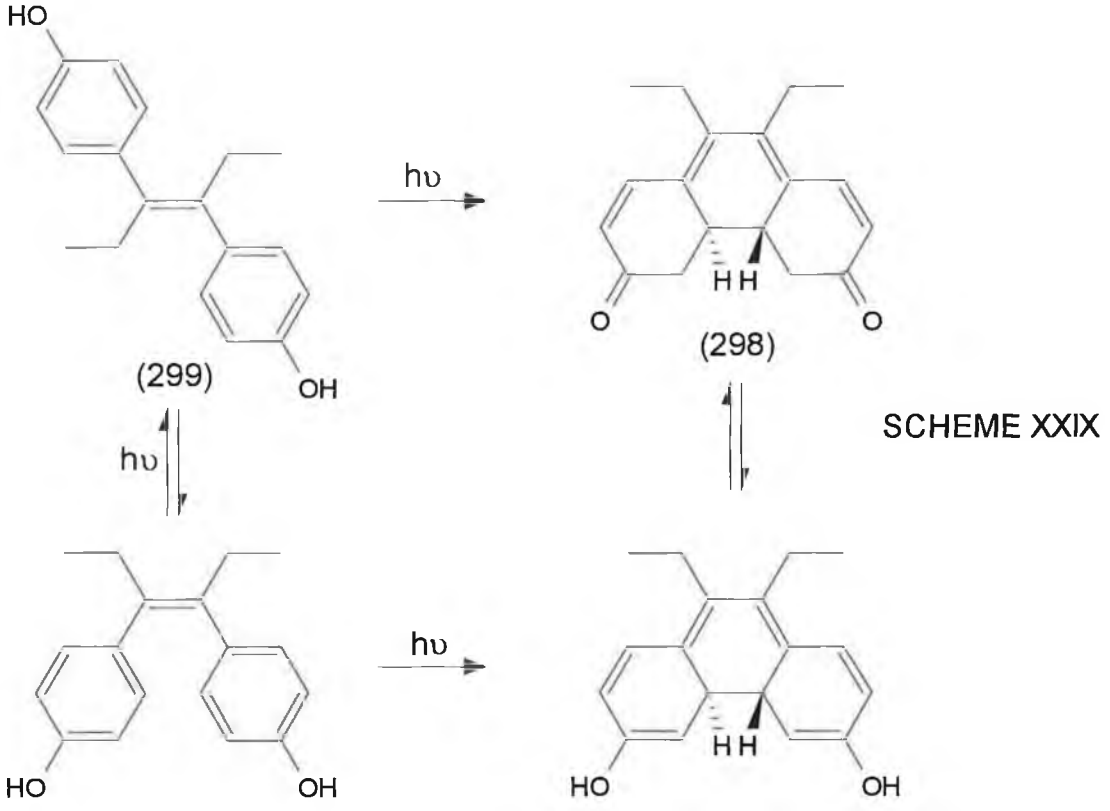


Fig. 15 *Transition state for a 6π-electron system following the conrotatory mode of ring closure.*

It had been postulated that cyclisation of stilbenes on irradiation may not result from an excited state but rather from a vibrationally excited (hot) ground state[212]. The stereochemistry of the dihydrophenanthrene intermediate would give proof of the state from which the cyclisation occurs since, if ring closure occured from the ground state, it would do so via the disrotatory mode and the dihydrophenanthrene intermediate formed would have *cis* stereochemistry. Cyclisation from the excited state would proceed via the conrotatory mode and therefore the dihydrophenanthrene would be expected to have *trans* stereochemistry. Generally the cyclised intermediates formed on 6π-electron electrocyclic ring closure cannot be isolated due to rapid oxidation or elimination, and so confirmation of the stereochemistry of the proposed intermediates proved difficult.



However Doyle and co-workers have isolated the dihydrophenanthrene (298) formed on irradiation of the diethylstilbestrol (299) followed by tautomerisation (Scheme XXIX) which has been shown by ^{1}H-NMR studies to have the *trans* stereochemistry indicating that 6π-electron electrocyclisations occurred from an excited, rather than a 'hot' ground, state[213].

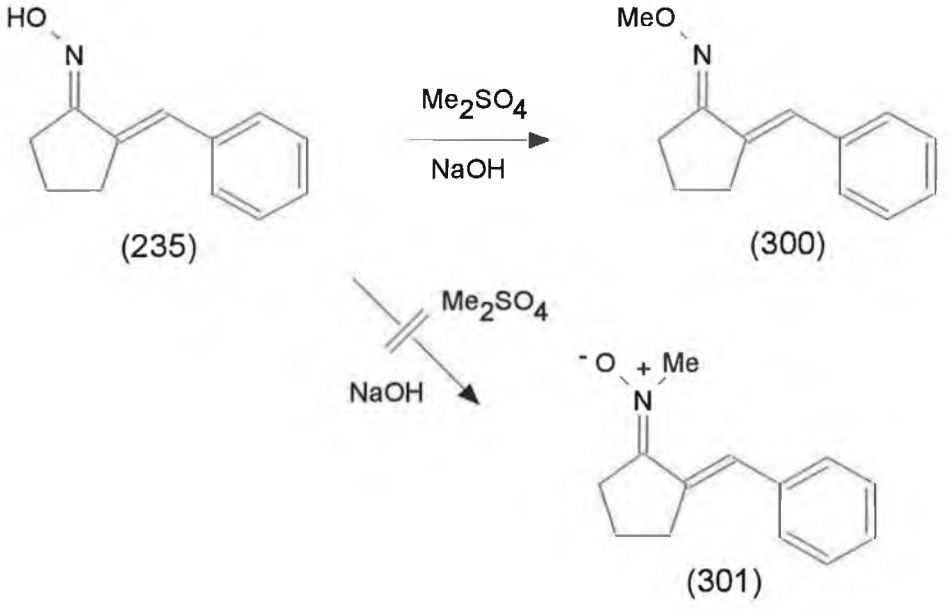
2.A.9 Photochemistry of 2-Benzylidenecyclopentaone Oxime O-Methyl Ether (300)

Having discovered the intramolecular photochemical cyclisation reaction of the α,β-unsaturated oxime O-allyl ether system (263) it was of interest to determine whether changing the oxime ether group might also change the reactivity of the system. It was decided to attempt the photolysis of the corresponding 2-benzylidenecyclopentanone oxime O-methyl ether (300), to see if the photocyclisation would still proceed and to investigate the comparative efficiencies of quinoline formation between the two compounds.

2-Benzylidenecyclopentanone oxime O-methyl ether (300) was prepared by methylating the previously prepared 2-benzylidenecyclopentanone oxime (235). Methyl iodide proved an inefficient methylating agent with mostly starting material (235) being recovered after reaction. However dimethyl sulphate proved far more efficient with a good yield of the desired oxime ether (300) being obtained (67%). It has previously been reported that methylation of oximes may lead to N-methylation as a competing side reaction, dependent on the nature of reagents, the reaction conditions and the configuration of the oxime[214]. However none of the equivalent N-methylated nitrone product (301) was isolated on methylation of (235).

2-Benzylidenecyclopentanone oxime O-methyl ether (300) was irradiated in methanol under conditions similar to those used for the corresponding oxime O-allyl ether (E,E-263). On following the reaction by TLC

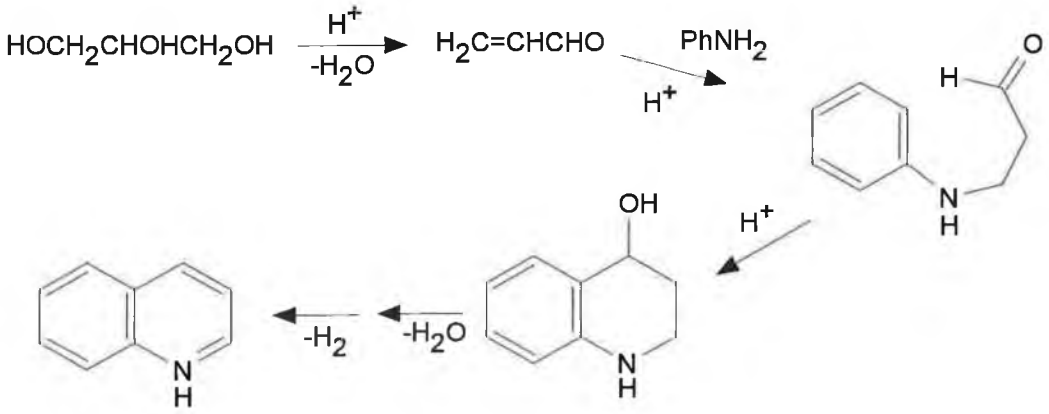
it was noted that initially two new spots were detected, whilst on further irradiation a new spot with the same R_f value as that of 2,3-dihydro-1*H*-cyclopenta[b]quinoline (236) was formed. As on irradiation of (E,E-263) the concentration of this grew until it was the major component of the photolysis mixture. Workup and comparison of spectral data confirmed that the product was indeed (236). No attempt was made to isolate the initially formed photoproducts since it was believed that these were the other geometrical isomers of (300). Some confirmation for this assumption can be gained from the fact that their concentrations increased initially but then levelled off and decreased on formation of (236). The yield of (236) on irradiation of the oxime O-methyl ether (300) (29%) was found to be slightly higher than on irradiation of the corresponding oxime O-allyl ether (E,E-263) (24%). However the course of the photochemical reaction appears to proceed very similarly for both (E,E-263) and (300).



2.B: The Scope of the Photocyclisation of Arylidene Cycloalkanone Oxime Ethers

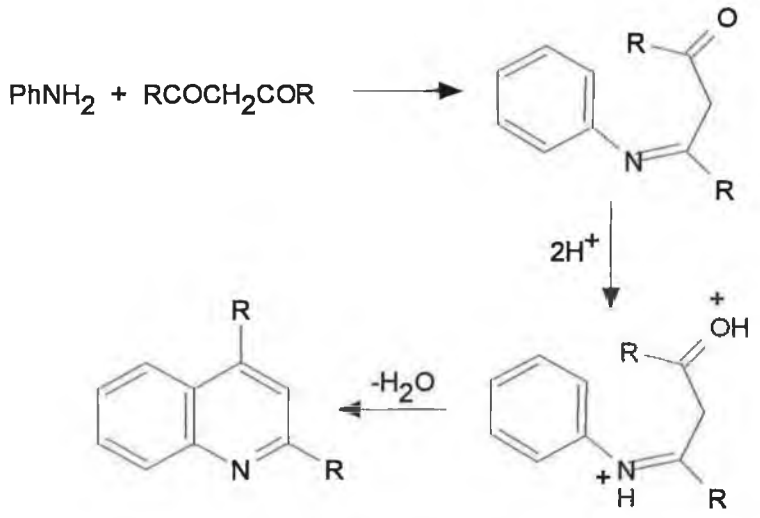
2.B.1 Scope of the Electrocyclisation of Arylidenecycloalkanone Oxime O-Methyl Ethers

Several methods are known for the synthesis of quinolines, the most common of which involve the construction of the heterocyclic ring on a substituted benzene derivative[215]. The *Skraup* synthesis involves the heating of an aniline with glycerol and sulphuric acid, which acts as a dehydrating agent and an acid catalyst. Although the mechanism has not been established it is believed that the glycerol is dehydrated to acrolein which then undergoes conjugate addition to the aniline, yielding an intermediate which subsequently undergoes cyclisation, oxidation and dehydration to give the quinoline (Scheme XXX). The *Doebner-von Miller* synthesis is a variation which involves the use of α,β-unsaturated aldehydes or ketones in place of glycerol to allow greater variation of the substitution pattern.



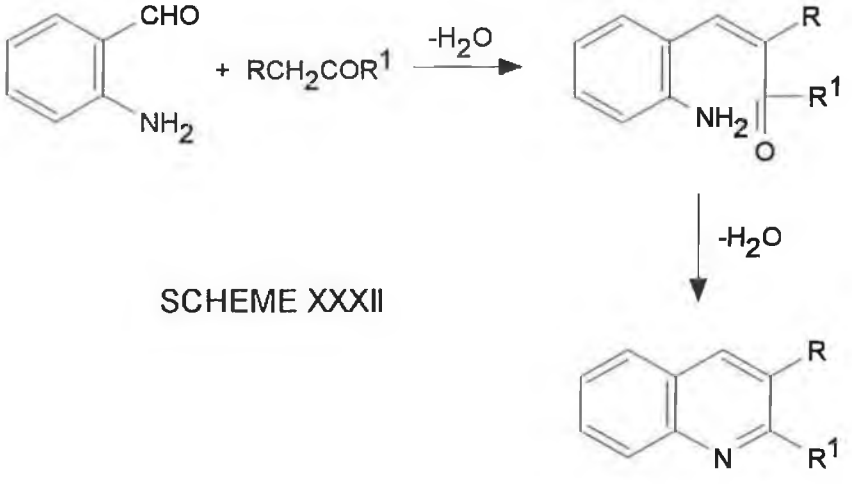
SCHEME XXX

The *Combes* synthesis involves the reaction of an aniline with a 1,3-diketone in the presence of acid to form a Schiff base which then undergoes diprotonation and dehydration to form the quinoline (Scheme XXXI).



SCHEME XXXI

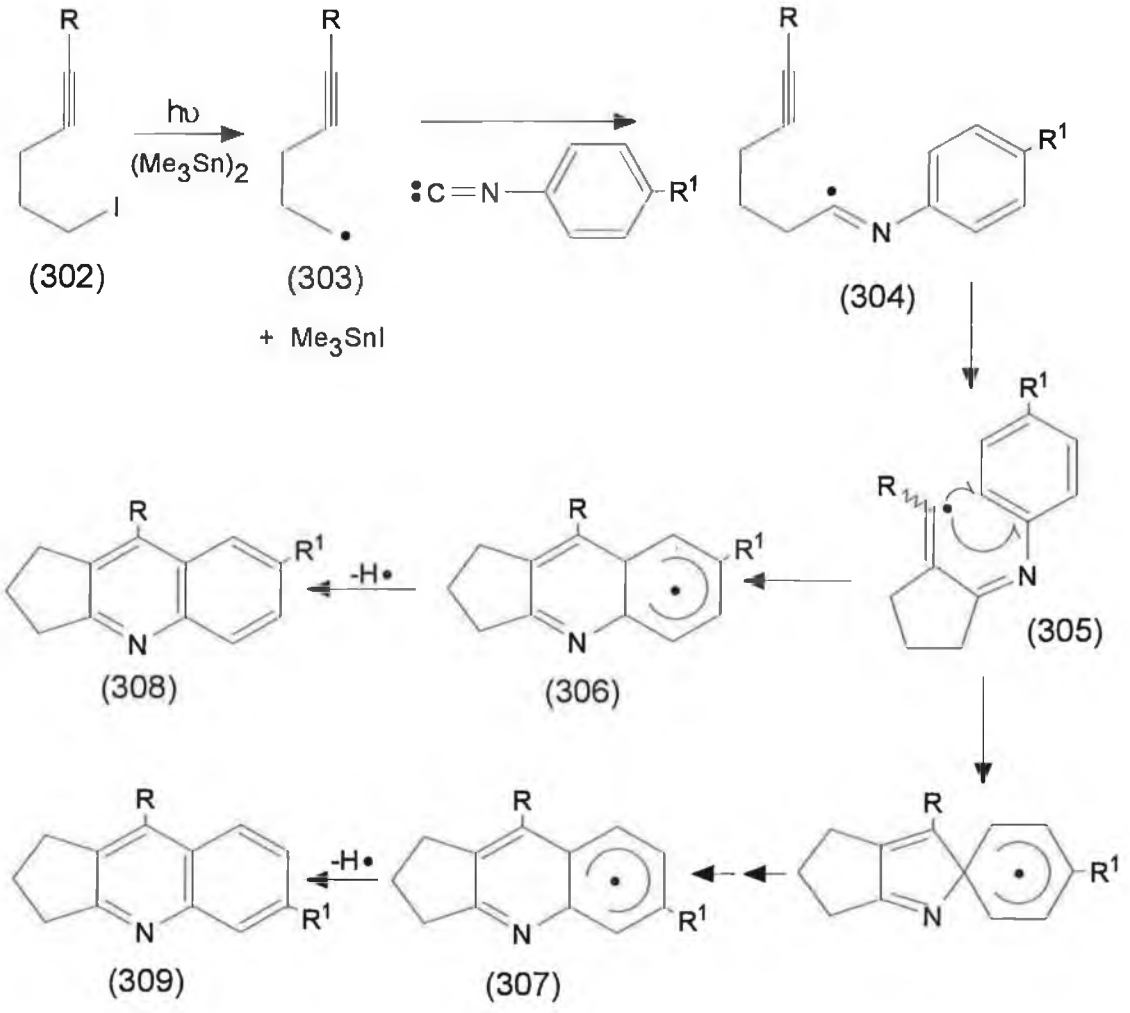
The *Friedländer* synthesis involves the addition of an α-methylene ketone to an *o*-aminobenzaldehyde in the presence of base (Scheme XXXII).



SCHEME XXXII

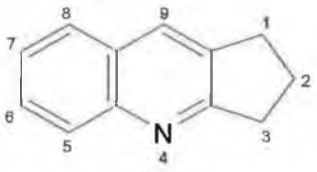
Curran and Liu have synthesised substituted cyclopenta[b]quinolines by a novel [4+1] radical annulation method using 5-iodo-1-pentynes and phenyl isocyanides (Scheme XXXIII)[202]. Reaction proceeds via initial radical generation either by direct photolytic cleavage of the 5-iodo-1-pentyne (302) or by cleavage of hexamethylditin which may subsequently generate radical (303). Addition of radical (303) to the isonitrile generates radical (304) which then

undergoes ring closure to (305), followed by cyclization to either of two positions on the aromatic ring. Radicals (306) and (307) may then undergo loss of a hydrogen radical to generate the cyclopenta[b]quinolines (308) and (309).



SCHEME XXXIII

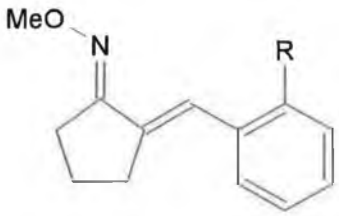
However adaptation of these methods to produce aromatically substituted 2,3-dihydro-1*H*-cyclopenta[b]quinolines proves difficult, particularly for substitution at the 6- and 8- positions.



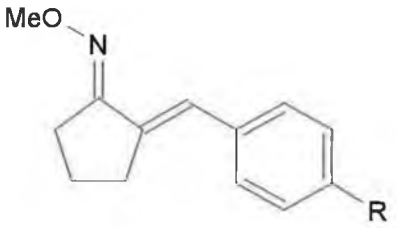
(236)

To prepare 6- or 8- substituted 2,3-dihydro-1*H*-cyclopenta[b]quinolines via the Doebner-von Miller or Combes synthesis would require the use of anilines bearing *meta* substituents. Consequently two different *ortho* positions would become available and cyclization would be expected to favour the formation of either the 6- or 8- isomer, or to produce a mixture of both the 6- and 8-substituted isomers. The radical annulation method of Curran and Liu produces a mixture of both the 6- and 7- isomers although the 7 substituted derivative is usually the major isomer[202]. Whilst the Friedländer method overcomes this problem, its use is limited by the difficulty in preparing *o*-aminocarbonyl compounds.

The photochemical cyclisation of benzylidenecyclopentanone oxime ethers therefore offers a potentially useful route to producing substituted cyclopenta[b]quinolines, particularly those bearing substituents at the 6- and 8-positions. Substituted arylidenecycloalkanones may be readily produced by condensation of the desired cycloalkanone with the appropriate aromatic aldehyde. It was therefore decided to investigate the photochemistry of a range of *ortho* and *para* substituted benzylidene cycloalkanone oxime ethers. Included in the study were compounds (310)-(317), the naphthylidene and furylidene cyclopentanone oxime ethers, (318) and (319), the cyclohexanone derivative (320) and 2-(diphenylmethylene)cyclopentanone oxime O-methyl ether (321).



(310, R=NO_2)



(311, R=NO_2)

(312, R=Cl)

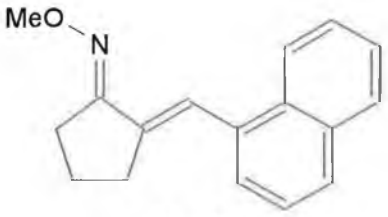
(313, R=Cl)

(314, R=MeO)

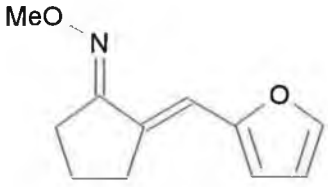
(315, R=MeO)

(316, R=Me)

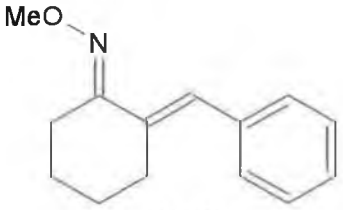
(317, R=Me)



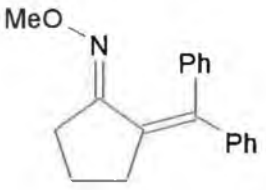
(318)



(319)



(320)



(321)

2.B.2 Preparation of Arylidenecycloalkanone Oxime O-Methyl Ethers (310)-(320)

Arylidenecyclopentanones (322a-j) were prepared by reaction of the desired aldehyde with the morpholine enamine of cyclopentanone (267). Benzylidenecyclohexanone (322k) was similarly prepared by reaction of the morpholine enamine of cyclohexanone (323) followed by reaction of this with benzaldehyde. Reaction times were significantly longer for preparation of the cyclohexanone derivatives (322k) and (323) than had been found for preparation of the corresponding cyclopentanone derivatives (267) and (266).

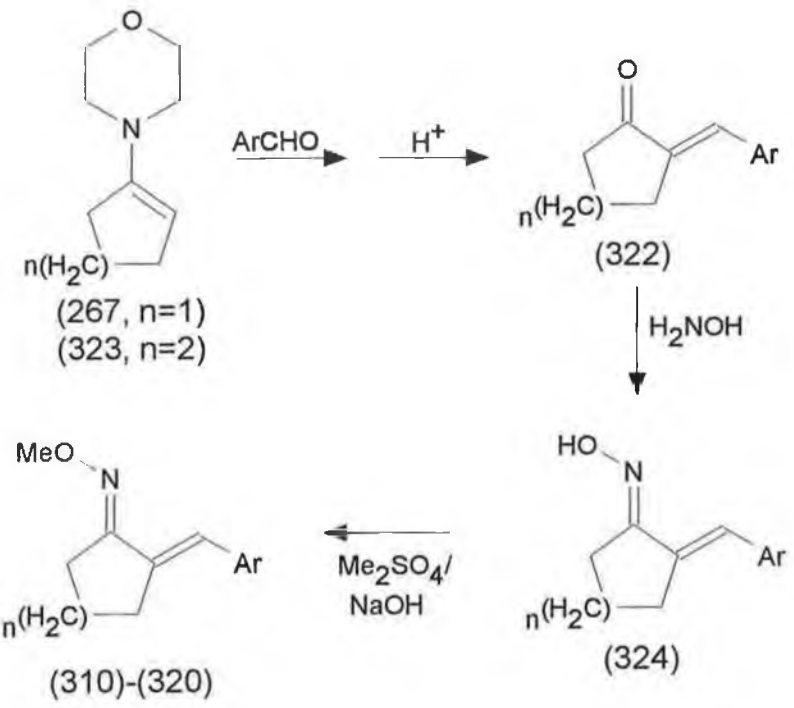
This was probably due to the less rigid cyclohexane ring present. All other derivatives (322a-j) were prepared in similar reaction times. The lowest yield recorded was for the furylidene derivative (322j) which yielded only 37% after work up of the reaction mixture. The low yield on reaction appeared to be due to decomposition of furaldehyde on reaction since less than the expected quantity of water was collected on reaction of the morpholine enamine of cyclopentanone (267) with furaldehyde.

The IR, ^{1}H and ^{13}C-NMR spectra of the arylidenecycloalkanones (322a-j) were asd expected for the proposed structures. The ^{13}C-NMR spectrum of benzylidenecyclohexanone (322k) shows one less carbon signal in the aromatic region than expected. However the ^{1}H spectrum agrees with the proposed structure and it is likely that two of the carbons present in (322k) have identical resonances, and appear as one signal.

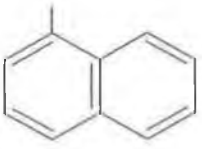
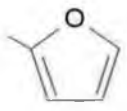
Oximes, (324a-j) and (283), were again prepared using hydroxylamine, and good yields were recorded for all derivatives. In none of the derivatives was the presence of two isomers detected after isolation and recrystallisation of the oxime product. Although no attempt was made to ascertain the configuration of the oximino function it is likely that, as with (235), the oxime group would form in the less hindered E- configuration.

The O-methyl ethers (310)-(320) of the oximes were prepared again using dimethyl sulphate. Yields were found to be acceptable and no nitrone products from N-methylation were isolated.

All of the arylidenecycloalkanone oxime ethers prepared, (310)-(320), show a strong absorption bands in the region 300nm ± 30nm. As with the oxime O-allyl ether (E,E-263) it is likely that these bands are from the π–π^* transition of the conjugated α,β-unsaturated system with the band from the n-π^* transition being submerged by the more intense π–π^* band.



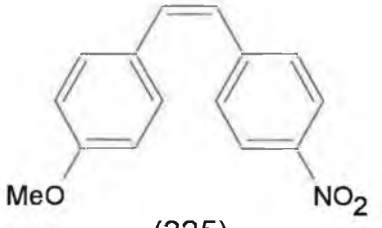
SCHEME XXXIV

(322a), (324a), (310)	n=1,	Ar=*o*-$NO_2C_6H_4$
(322b), (324b), (311)	n=1,	Ar=*p*-$NO_2C_6H_4$
(322c), (324c), (312)	n=1,	Ar=*o*-ClC_6H_4
(322d), (324d), (313)	n=1,	Ar=*p*-ClC_6H_4
(322e), (324e), (314)	n=1,	Ar=*o*-$MeOC_6H_4$
(322f), (324f), (315)	n=1,	Ar=*p*-$MeOC_6H_4$
(322g), (324g), (316)	n=1,	Ar=*o*-MeC_6H_4
(322h), (324h), (317)	n=1,	Ar=*p*-MeC_6H_4
(322i), (324i), (318)	n=1,	Ar= 
(322j), (324j), (319)	n=1,	Ar= 
(322k), (283), (320)	n=2,	Ar=C_6H_5

2.B.3 Photochemistry of 2-(o-Nitrobenzylidene)cyclopentanone Oxime O-Methyl Ether (310) and 2-(*p*-Nitrobenzylidene)cyclopentanone Oxime O-Methyl Ether (311)

Both 2-(*o*-nitrobenzylidene)cyclopentanone oxime O-methyl ether (310) and 2-(*p*-nitrobenzylidene)cyclopentanone oxime O-methyl ether (311) on irradiation gave rise to a large number of unisolated and uncharacterised products. Initially both compounds showed formation of two new spots on TLC, with TLC separations similar to those of the isomers of E,E-2-benzylidenecyclopentanone oxime O-allyl ether (263). However continued irradiation led to a steady increase in the number of products present in the photolysis mixture.

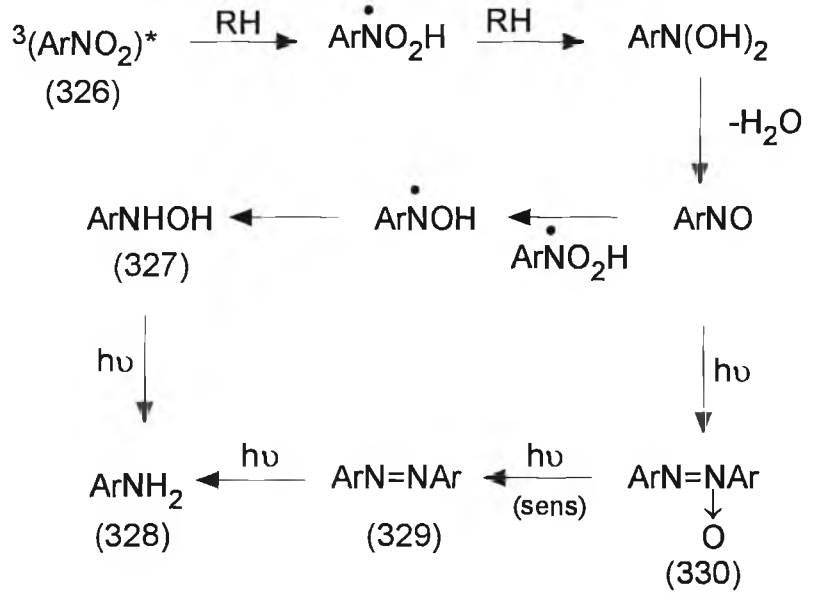
Kasha postulated that intersystem crossing between the S^1 and T^1 states occurs extremely efficiently in nitro substituted compounds[216]. In the stilbene-phenanthrene photoconversion, stilbenes bearing nitro substituents, such as (325), were found not to undergo cyclisation to phenanthrenes, and this has been attributed to this intersystem crossing[209]. It seems likely therefore that oxime ethers (310) and (311) would also undergo efficient intersystem crossing resulting in photochemical reaction from their triplet states and leading to formation of products from these states.



(325)

The photochemistry of aromatic nitro compounds is known to be quite complex[217]. The photoreactions of a nitro group can involve a number of reorganization and reduction stages involving intermediates which may

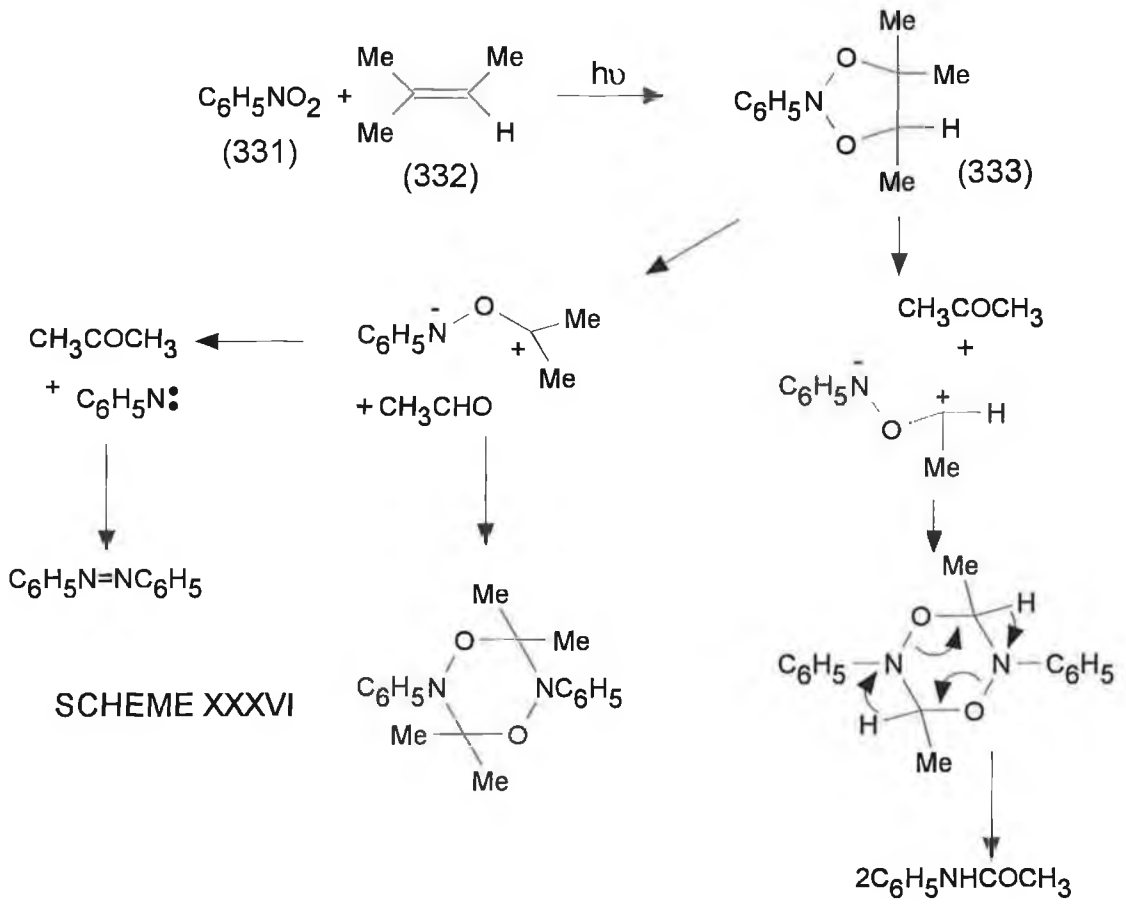
subsequently undergo secondary photoreactions or dark reactions. In hydroxylic solvents aromatic nitro compounds (326) are known to undergo photolytic reduction to yield hydroxylamines (327)[218] which may subsequently undergo further photochemical reaction to yield anilines (328) with minor amounts of azo- (329) and azoxy-benzenes (330), depending on the conditions (Scheme XXXV)[218]. Formation of hydroxylamines (327) has been accounted for by initial hydrogen abstraction by the lowest excited triplet state of the nitro compound followed by a series of dark radical reactions leading directly to the hydroxylamine (327)[217]. It is therefore possible that the numerous products formed on irradiation of the nitrobenzylidene-cyclopentanone oxime O-methyl ethers (310) and (311), may arise in part, from radical generation on photolysis.



SCHEME XXXV

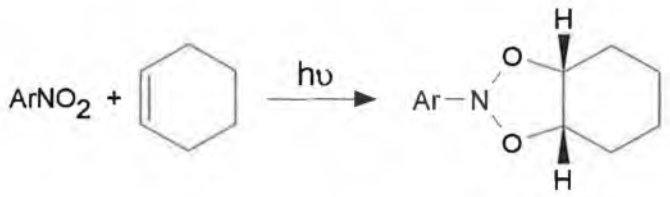
Aromatic nitro componds are also known to add across carbon-carbon double bonds to form 1,3,2-dioxazolidines, which may subsequently undergo photodecomposition mainly to carbonyl compounds and azobenzenes[217]. For example, a number of products are formed on irradiation of nitrobenzene (331) in the presence of 2-methylbut-2-ene (332) (Scheme XXXVI)[219]. Products

formed are believed to result from initial addition of the nitro group of nitrobenzene (331) to the carbon-carbon double bond of 2-methylbut-2-ene (332) to form the unisolated 1,3,2-dioxazolidine (333) which may then undergo fragmentation to give the isolated products. 1,3,2-Dioxazolidine (334) has been isolated at low temperatures on photoreaction of aromatic nitro derivatives with cyclohexene[220].



SCHEME XXXVI

It is possible therefore that some of the photochemical products formed on irradiation of *ortho*- and *para*-nitrobenzylidenecyclopentanone oxime O-methyl ethers (310) and (311) may have been due to intermolecular addition / fragmentation involving the nitro group of one molecule and the benzylidene carbon-carbon double bond of a second molecule.



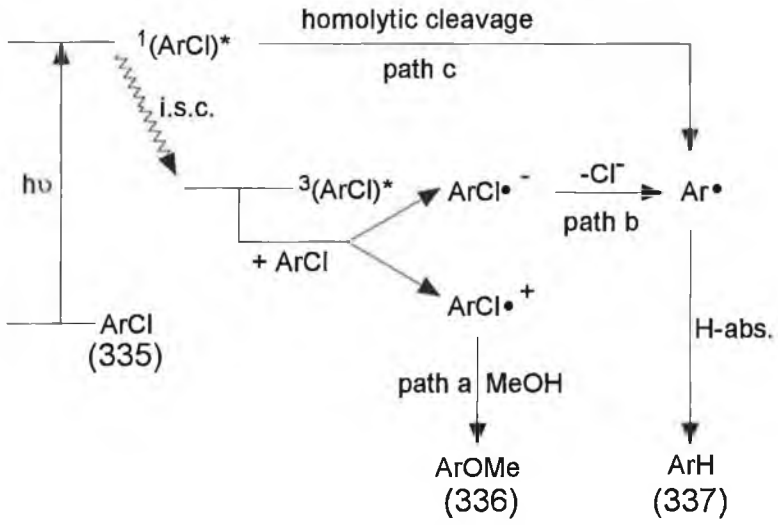
(334)

2.B.4 The Photochemistry of 2-(o-Chlorobenzylidene)cyclopentanone Oxime O-Methyl Ether (312) and 2-(*p*-Chlorobenzylidene)cyclopentanone Oxime O-Methyl Ether (313)

As on irradiation of the *ortho*- and *para*- nitro substituted derivatives of 2-benzylidenecyclopentanone oxime O-methyl ether (310) and (311), none of the expected quinoline derivatives were recovered on irradiation of 2-(*o*-chloro-benzylidene)cyclopentanone oxime O-methyl ether (312) or 2-(*p*-chloro-benzylidene)cyclopentanone oxime O-methyl ether (313). The photochemical reactions of (312) and (313) were followed by TLC and a steadily increasing number of photoproducts was noted for both (312) and (313), with no appreciable amounts of any one product being formed. Due to the complex nature of the photolysis mixtures no attempts were made to isolate the products formed.

The lack of cyclisation of (312) and (313) was in contrast to the oxime benzoates (231, R=H, Cl, MeO, Me) where the nature of the substituent appeared to have little effect on the cyclisation of (231) to quinolines (232). Soumillion and De Wolf have found that on irradiation in methanol, chloroaromatic compounds (335) form both photosubstituted (336) and photoreduced products (337)[221]. They have proposed that both of these processes may occur via excimer formation from the triplet excited state of the chloroaromatic compound (Scheme XXXVII). The substitution product (336) may then be formed via addition to the radical-cation (Scheme XXXVII, path a), whilst the reduction product (337) may be formed via loss of chlorine from the

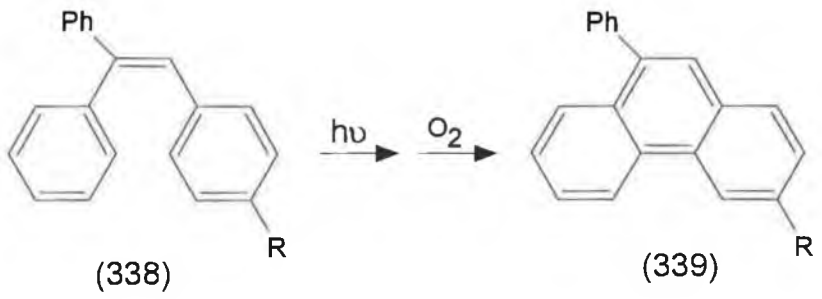
radical-anion followed by hydrogen abstraction (Scheme XXXVII, path b). Formation of the photoreduced product (337) is also believed to occur by homolytic cleavage of the singlet excited state of the aromatic chloride (Scheme XXXVII, path c).



SCHEME XXXVII

It has been reported that the presence of alkenes enhances the photoreactivity of chloroaromatic compounds towards reductive dehalogenation in methanol due to complexation between the alkene and the aromatic chloride[222].

In the stilbene-phenanthrene photocyclisation the presence of a chloro-substituent appears to decrease the rate of formation of photocyclised products. Although all the substituted triphenylethylenes (338, R=H, CH_3, OCH_3 and Cl) undergo cyclisation to the corresponding phenanthrenes (339), the chloro substituted derivative (338, R=Cl) was found to react slowest, whilst the presence of an electron releasing group on the aromatic ring (338, R=Me, MeO) increases reactivity over the unsubstituted derivative (338, R=H)[223]. It is therefore possible that the chloro-substituted derivatives, (312) and (313), are also lethargic towards 6π-electron photocyclisation, and that other more favourable product forming processes predominate.



(338) (339)

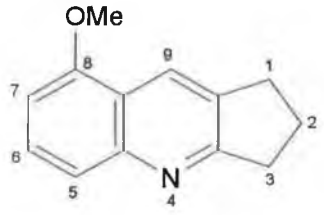
Therefore the large number of products formed on irradiation of the chloro-bezylidenecyclopentanone oxime ether derivatives (312) and (313) in methanol may be due to photoisomerisation to their four geometrical isomers accompanied by reductive dehalogenation or substitution of chlorine by methanol. These products could then possibly undergo photocyclisation to quinolines although, due to the complex nature of the photolysis mixture it proved difficult to detect their presence. The presence of the benzylidene carbon-carbon double bond may possibly enhance the reductive dehalogenation, whilst any generation of radicals or radical-cations could lead to the formation of complex mixtures of biaryls as has been noted with other chloroaromatic compounds[224].

2.B.5 The Photochemistry of 2-(*o*-Methoxybenzylidene)cyclopentanone Oxime O-Methyl Ether (314) and 2-(*p*-Methoxybenzylidene)cyclopentanone Oxime O-Methyl Ether (315)

2.B.5.1 2-(*o*-Methoxybenzylidene)cyclopentanone Oxime O-Methyl Ether (314)

On irradiation of (314) in methanol three new spots appeared on TLC after a short period of irradiation. On further irradiation one of these compounds became the major component of the photolysis mixture at the expense of the starting material and the other products formed. On isolation

and characterisation this product was found to be the previously unreported 8-methoxy-2,3-dihydro-1*H*-cyclopenta[b]quinoline (340).



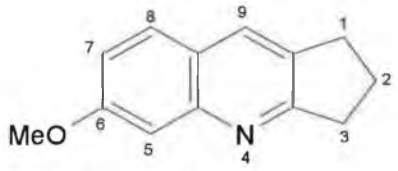
(340)

As required for (340), the ^{1}H-NMR spectrum showed four signals in the range δ 2.21-3.99ppm: a quintet (with an integration corresponding to two protons) at δ 2.21ppm corresponding to the central methylene group at C-2 of (340); two triplets at δ 3.09 and 3.15ppm (integration: two protons for each triplet) corresponding to the methylene groups at C-1 and C-3 and a singlet at δ 3.99ppm (integration: three protons) corresponding to the protons of the methoxy group. Four signals appeared in the aromatic region of the spectrum, an integrating for one proton, in agreement with the proposed structure: two doublets at δ 6.81 (*J*, 7.9Hz) and 7.61ppm (*J*, 8.4Hz) corresponding to the aromatic protons at C-5 and C-7, a triplet at δ 7.51ppm (*J*, 8.1Hz) corresponding to the proton at C-6 and a singlet at δ 8.3ppm corresponding to the uncoupled proton at C-9. Although $J_{5,6}$ and $J_{6,7}$ were not identical, the difference between them was small (0.5Hz) and the signal from the proton at C-6 appeared as a regular triplet instead of the doublet of doublets which might have been expected had the difference in coupling constants been greater.

The ^{13}C spectrum of (340) also agreed with the proposed structure with three signals in the range δ 23-35ppm corresponding to the three methylene group carbons (C-1, C-2 and C-3), a signal at δ 56ppm corresponding to the carbon of the methoxy group, and nine signals in the region δ 103-168ppm corresponding to the nine aromatic carbons present.

2.B.5.2 2-(*p*-Methoxybenzylidene)cyclopentanone Oxime O-Methyl Ether (315)

The photochemistry of the *para*-methoxy substituted derivative (315) was found to be quite similar to that of the *ortho* substituted derivative (314). Initial irradiation led to the formation of three new spots on TLC analysis whilst further irradiation led to the gradual disappearance of the starting material and all but one of the products formed. Isolation and characterisation of this product showed it to be 6-methoxy-2,3-dihydro-1*H*-cyclopenta[b]quinoline (341). The ^{1}H and ^{13}C-NMR spectra were found to agree with the proposed structure and with the spectra previously reported for (341) on preparation by the [4+1] radical annulation method[202].



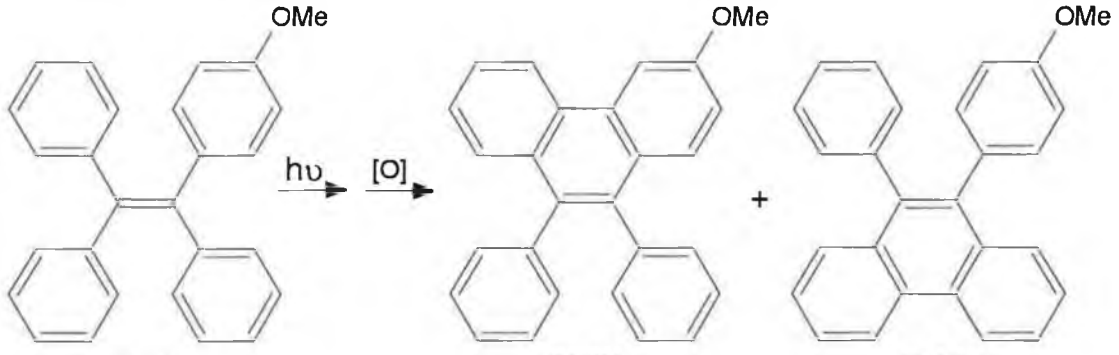
(341)

The ^{1}H-NMR of (341) is similar to that of the 8-methoxy derivative (340) in the region δ 2.20-3.93ppm, with a quintet at δ 2.20ppm corresponding to the methylene group protons at C-2, two triplets at δ 3.06 and 3.15ppm corresponding to the methylene group protons at C-1 and C-3, and a singlet at δ 3.93ppm correponding to the protons of the methoxy group. In the region δ 7.12-7.82ppm the proton signal pattern fitted that which would have been expected for the 6-substituted cyclopenta[b]quinoline (341), with four signals (integration for one proton each) corresponding to the four aromatic protons present in (341). A doublet of doublets occurred at δ 7.12ppm with coupling constants of 8.8Hz and 2.2Hz corresponding to the proton at C-7. A doublet was found at δ 7.37ppm corresponding to the proton at C-5 with a small *meta* coupling to the proton at C-7 of 2.2Hz. At δ 7.62ppm a doublet was found corresponding to the proton at C-8, coupled to that at C-7 ($J_{7,8}$, 8.8Hz) and at δ

7.82ppm a singlet was found, corresponding to the proton at C-9. The presence of *meta* coupling between the protons at C-5 and C-7 in (341) is interesting since it was not seen to occur in the 8-methoxy substituted derivative (340). The ^{13}C spectrum shows three signals between δ 23 and 35 ppm corresponding to the three methylene-group carbons, a signal at δ 56ppm corresponding to the methoxy group carbon, and nine signals in the range δ 103-168ppm corresponding to the nine aromatic carbons present in (341).

Discussion

Both the *ortho*- and *para*-methoxy benzylidenecyclopentanone oxime O-methyl ethers, (314) and (315) were converted on irradiation to the corresponding methoxy substituted quinoline derivatives, (340) and (341) respectively, faster than was found for formation of the unsubstituted derivative (236) on irradiation of the oxime ether (300). The isolated yields were also greater than for the unsubstituted derivative (48% and 53% for (340) and (341) respectively). This is consistent with the supposition that the presence of an electron releasing substituent on the aromatic ring increases the reactivity of the 6π-electron system towards electrocyclic ring closure. An effect similar to this has been seen in the methoxy substituted tetraphenylethylene (342)[225].



(342) (343) (344)

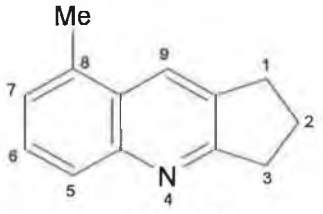
8·4 : 1

On irradiation, (342) undergoes cyclisation to form both 2-methoxy-9,10-diphenylphenanthrene (343) and 9-(*p*-methoxyphenyl)-10-phenylphenanthrene (344), but with a product ratio of 8.4:1 in favour of the methoxyphenanthrene (343).

2.B.6 The Photochemistry of 2-(o-Methylbenzylidene)cyclopentanone Oxime O-Methyl Ether (316) and 2-(*p*-Methylbenzylidene)cyclopentanone Oxime O-Methyl Ether (317)

2.B.6.1 2-(*o*-Methylbenzylidene)cyclopentanone Oxime O-Methyl Ether (316)

Irradiation of 2-(*o*-methylbenzylidene)cyclopentanone oxime O-methyl ether (316) in methanol led to the initial formation of three new spots on TLC, but further irradiation led to one of these becoming the major component of the photolysis mixture. On isolation and characterisation this product was found to be the previously unreported 8-methyl-2,3-dihydro-1*H*-cyclopenta[b]quinoline (345).



(345)

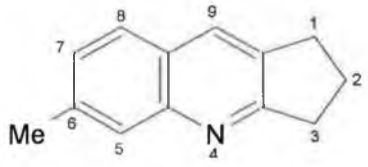
The NMR spectra of the product (345) agreed with the structure proposed . The ^{1}H-NMR spectrum showed four signals in the range δ 2.21-3.16ppm: a quintet at δ 2.21ppm (integration: two protons) corresponding to the central methylene group protons at C-2; a singlet at δ 2.65ppm (integration: three protons) corresponding to the methyl group protons; and two triplets

between δ 3.10 and 3.16ppm, with an integration corresponding to two protons each, from the methylene group protons at C-1 and C-3. As required for quinoline (345), four one proton signals appear in the aromatic region of the spectrum: two doublets at δ 7.28 (*J*, 7.4Hz) and 7.87ppm (*J*, 8.4Hz) from the aromatic protons at C-5 and C-7, a triplet at δ 7.50ppm (*J*, 7.9Hz) from the aromatic proton at C-6 and a singlet at δ 8.1ppm from the aromatic proton at C-9. As with the 8-methoxy derivative (340) the coupling constants $J_{4,5}$ and $J_{6,7}$ were not equivalent but the signal for the proton at C-6 still appeared as a regular triplet.

The ^{13}C-NMR spectrum shows four signals in the range δ 18-35ppm arising from the methylene carbons at C-1, C-2 and C-3 and the methyl group carbon. In the aromatic region nine signals appear between δ 126 and 167ppm from the nine aromatic carbons present in (345).

2.B.6.2 2-(*p*-Methylbenzylidene)cyclopentanone Oxime O-Methyl Ether (317)

The photochemistry of 2-(*p*-methylbenzylidene)cyclopentanone oxime O-methyl ether (317) in methanol follows a similar pattern to that of the *o*-methyl derivative (316). TLC analysis shows the initial formation of three new spots with one of these becoming the major component of the photolysis mixture. This product was found to be the previously unreported 6-methyl-2,3-dihydro-1*H*-cyclopenta[b]quinoline (346).



(346)

As with the other quinoline derivatives prepared, the ^{1}H-NMR spectum agreed with the proposed structure. In the region δ 2.20-3.15ppm the spectrum

of (346) is similar to that of the the 8-methyl substituted derivative (345) with four signals: a quintet at δ 2.20ppm corresponding to the protons from the central methylene group at C-2; a singlet at δ 2.54ppm from the methyl group protons; and two triplets between δ 3.07 and 3.15ppm from the methylene group protons at C-1 and C-3. The aromatic region of the spectrum showed four one proton signals: two doubets at δ 7.30 (*J*, 8.2Hz) and 7.63ppm (*J*, 8.2Hz) from the protons at C-7 and C-8 and two singlets between δ 7.79 and 7.85ppm from the aromatic protons at C-5 and C-9.

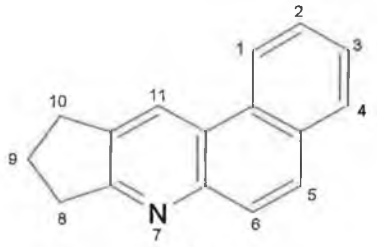
The ^{13}C-NMR spectrum shows four signals in the region δ 21-35ppm from the three methylene group carbons and the methyl group carbon. In the aromatic region of the spectrum nine signals appear in the range δ 125-168ppm corresponding to the nine aromatic carbons in (346).

Discussion

Both 2-(*o*-methylbenzylidene)cyclopentanone oxime O-methyl ether (316) and 2-(*p*-methylbenzylidene)cyclopentanone oxime O-methyl ether (317) underwent cyclisation more readily than the unsubstituted derivative (300). This again agrees with the expectation that the presence of an electron releasing substituent on the aromatic ring facilitates the cyclisation of the α,β-unsaturated oxime ethers to the quinoline derivatives. However the photochemical cyclisations of (316) and (317) to the quinoline derivatives (345) and (346) proceeded more slowly than those of the *ortho*- and *para*-methoxy derivatives (316) and (317). Therefore, since methoxy groups are more electron releasing than methyl groups, it appears that increasing the electron releasing ability of the substituent further facilitates the cyclisation.

2.B.7. The Photochemistry of 2-(1-Naphthylidene)cyclopentanone Oxime O-Methyl Ether (318)

2-(1-Naphthylidene)cyclopentanone oxime O-methyl ether (318) was irradiated in methanol under the standard conditions. On following the reaction by TLC three new spots had formed after a short period of irradiation, but after an irradiation time of only thirty minutes the spots corresponding to the starting material and two of the newly formed intermediates had disappeared leaving only one product remaining. Isolation and characterisation of the product showed it to be the previously unreported heterocycle 9,10-dihydro-8*H*-cyclopenta[b]benzo[*f*]quinoline (347)[226].

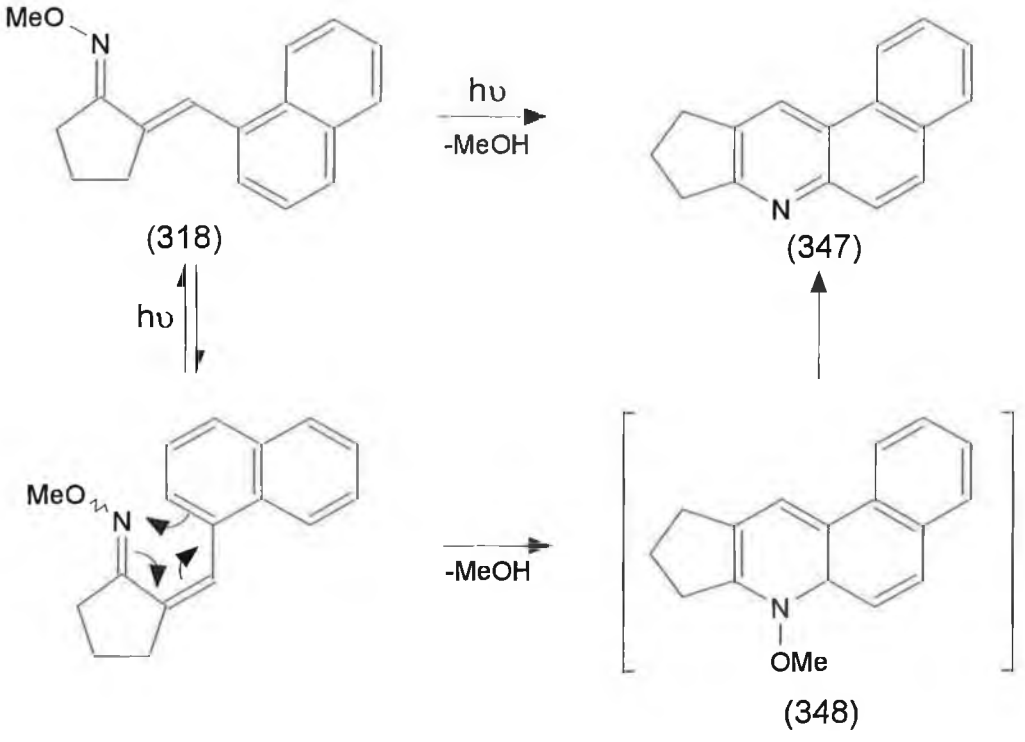


(347)

The ^{1}H and ^{13}C NMR spectra agreed with the structure proposed for (347). The proton NMR spectrum showed two signals in the range δ 2.27-3.22ppm: a quintet at δ 2.27ppm corresponding to the methylene group at C-9 and a multiplet at δ 3.20, which appeared as two overlapping triplets which corresponded to the two methylene groups at C-8 and C-10. The aromatic region of the spectrum gave a total integration for the expected seven protons and showed two triplets between δ 7.61 (*J*, 7.4Hz) and 7.66ppm (*J*, 7.4Hz) correponding to the protons at C-2 and C-3, a three proton multiplet between δ 7.90 and 7.97ppm corresponded to the protons at C-1, C-4 and C-5, a doublet at δ 8.60ppm (*J*, 7.8Hz) corresponding to the proton at C-6, and a singlet at δ 8.74ppm corresponding to the proton at C-11. The ^{13}C spectrum showed three signals in the range δ 23-35ppm corresponding to the three saturated carbons

at C-8, and C-10, and thirteen signals in the region 122-167ppm corresponding to the aromatic carbons.

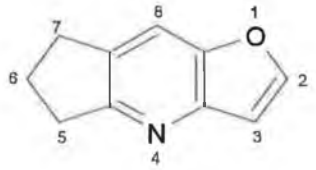
The photochemical cyclisation of the naphthylidenecyclopentanone oxime ether (318) proved to be the most successful preparative photochemical cyclisation of the range of oxime ethers studied, with an isolated yield of (347) of 69%. Naphthalene is known to have less aromatic character than benzene. Quinoline formation on irradiation of any of the oxime ethers studied requires loss of aromaticity to form an intermediate, which then undergoes elimination of methanol to form quinoline. Therefore the increased reactivity of the naphthalene derivative may be due to the decreased aromatic character of the naphthalene ring, allowing more facile formation of the non-aromatic intermediate (348).



2.B.8 The Photochemistry of 2-Furylidenecyclopentanone Oxime O-Methyl Ether (319)

2-Furylidenecyclopentanone oxime O-methyl ether (319) was also found to undergo cyclisation to the corresponding quinoline on irradiation. As with the other oxime ethers studied initial irradiation led to the formation of two new spots on following the photolysis by TLC. However, after further irradiation one of these photoproducts became the major component of the photolysis mixture. Separation and characterisation of this product showed it to be the previously unreported heterocycle 6,7-dihydro-5*H*-furo[3,2-b]cyclopenta[e]pyridine (349)[226]. The ^{1}H NMR spectrum of (349) agreed with the proposed structure. In the region δ 2.15-3.02ppm the spectrum resembles that of the cyclopentaquinolines previously isolated with a quintet at δ 2.15 corresponding to the methylene protons at C-6, and two triplets between δ 2.97 and 3.02ppm corresponding to the methylene groups at C-5 and C-7. In the aromatic region, three one-proton signals appeared. Two doublets appeared at δ 6.84 (*J*, 2.2Hz)and 7.70ppm (*J*, 2.2Hz) from the protons at C-2 and C-3 and a singlet was found at δ 7.51ppm from the proton at C-8.

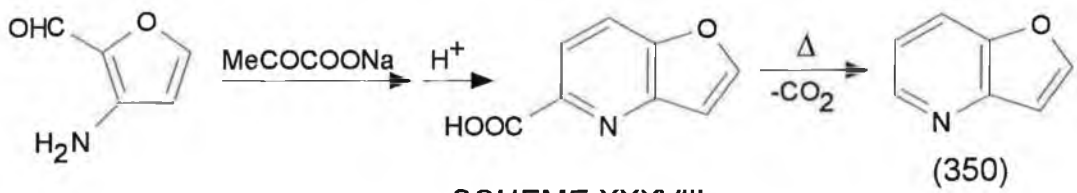
The ^{13}C spectrum agreed with the proposed structure with three signals in the range δ 24-34ppm corresponding to the three methylene carbons at C-5, C-6 and C-7, and seven signals in the range δ 107-162ppm corresponding to the seven aromatic carbons present in (349).



(349)

Although furo[3,2-b]pyridine (350) has previously been prepared[227] by a similar reaction to the Friedländer method (Scheme XXXVIII), the cyclopenta-

derivative (349) has not been reported in the literature.

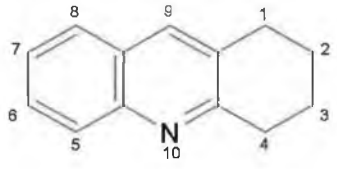


(350)

SCHEME XXXVIII

2.B.9 The Photochemistry of 2-Benzylidenecyclohexanone Oxime O-Methyl Ether (320)

2-Benzylidenecyclohexanone oxime O-methyl ether (320) was found to undergo photochemical cyclisation followed by elimination of methanol as had occurred on irradiation of the cyclopentanone derivative (300). On following the reaction by TLC it was seen that initial irradiation led to the formation of two new spots which were presumed to be due to the other geometrical isomers of (320), although none of these were isolated. Further irradiation led to the formation of a third new spot which gradually increased in size at the expense of the starting material and the other initially formed products until it became the major component of the photolysis mixture. On isolation and characterisation this product was found to be the known heterocycle 1,2,3,4-tetrahydroacridine (289).



(289)

The NMR spectra of (289) agreed with the proposed structure. The ^{1}H-NMR shows two multiplets between δ 1.89 and 1.99ppm from the methylene

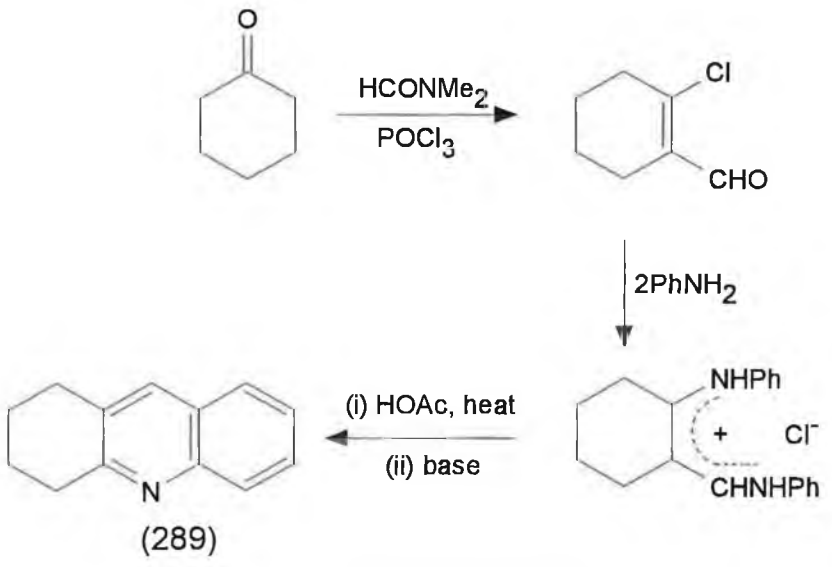
group protons at C-2 and C-3, and two triplets between δ 2.98 and 3.13ppm from the methylene group protons at C-1 and C-4. The aromatic region of the spectra showed the expected five one-proton signals: two triplets at δ 7.43 (*J*, 8.0Hz) and 7.60ppm (*J*, 8.2Hz) from the protons at C-7 and C-6 respectively, two doublets at δ 7.69 (*J*, 7.8Hz) and 7.97ppm (*J*, 8.4Hz) from the protons at C-8 and C-5 respectively, and a singlet at δ 7.80ppm from the proton at C-9. Although the coupling constants $J_{6,7}$, $J_{7,8}$ and $J_{8,9}$ were not identical , the differences between them were small and the signals from the protons at C-5 and C-8 appeared as regular doublets and those from C-6 and C-7 appeared as regular triplets instead of the more complex patterns that would have been expected had the differences in coupling constants been greater. The ^{1}H-NMR spectrum agreed with that previously recorded by Gagan and LLoyd for (289) (presumably at 60MHz)[228].

The carbon-NMR spectrum also agrees with the proposed structure with four signals between δ 22.9 and 33.6ppm from the four methylene group carbons and nine signals in the range δ 125-160ppm from the nine aromatic carbons. The melting point of (289) also agreed with the literature value[229].

Cyclisation of benzylidenecyclohexanone oxime O-methyl ether (320) to 1,2,3,4-tetrahydroacridine (289) occurs more efficiently than does the corresponding cyclisation of the benzylidenecyclopentanone oxime ether (300), with an isolated yield of 43%. This result is similar to that found by Olsen for the corresponding benzylidenecycloalkanone oximes (235) and (289) where the cyclohexane derivative (289) gave a higher yield of cyclised product than the cyclopentane derivative (235)[166].

1,2,3,4-Tetrahydroacridine (289) is not a new heterocycle. An adaptation of the Combes synthesis, for example, gives (289) in 54% overall yield from cyclohexanone (Scheme XXXIX). As with the prepartion of cyclopenta[b]quinoline derivatives the photochemical cyclisation method may

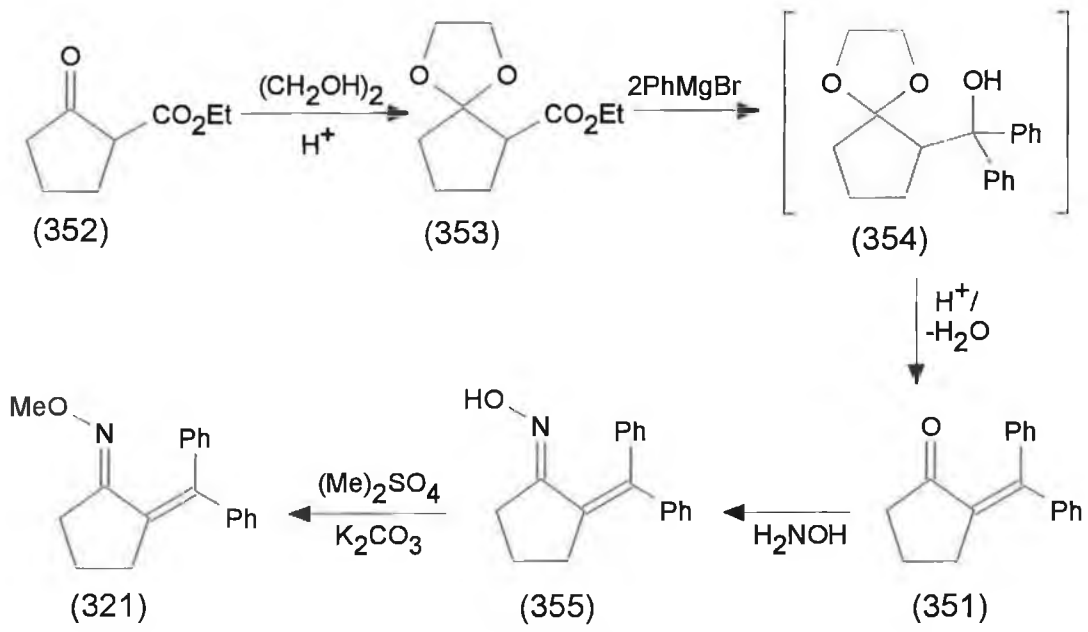
provide a useful route to substituted acridines not readily accessible by classical methods.



SCHEME XXXIX

2.B.10 Preparation of 2-(Diphenylmethylene)cyclopentanone Oxime O-Methyl Ether (321)

2-Diphenylmethylenecyclopentanone (351) was prepared following the procedure of Sharp et al.[230] The cyclopentanone ring carbonyl group of the ethyl ester of 2-cyclopentanone carboxylic acid (352) was initially protected by reaction with ethylene glycol to yield the 2,2-ethylenedioxycyclopentanone-carboxylate (353). Reaction of this with two equivalents of phenyl magnesium bromide yielded the tertiary alcohol (354) which was dehydrated without isolation to the desired 2-(diphenylmethylene)cyclopentanone (351). The reaction is inefficient with only a 24% yield of the desired product (351). Reaction of ketone (351) with hydroxylamine followed by subsequent methylation of oxime (355) with dimethyl sulphate yielded oxime ether (321).



SCHEME XL

The ^{1}H-NMR spectra of the 2-(diphenylmethylene)cyclopentanone (351), its oxime (355) and oxime ether (321) were as anticipated. However the ^{13}C-NMR spectrum of 2-(diphenylmethylene)cyclopentanone (351) and that of its oxime (355) both had one carbon signal missing from the unsaturated region of the spectrum. The spectrum of the oxime ether (321) displayed the required number of signals to agree with the structure proposed. It seems likely that two carbon signals in (351) and in (355) were poorly resolved and appeared as one signal.

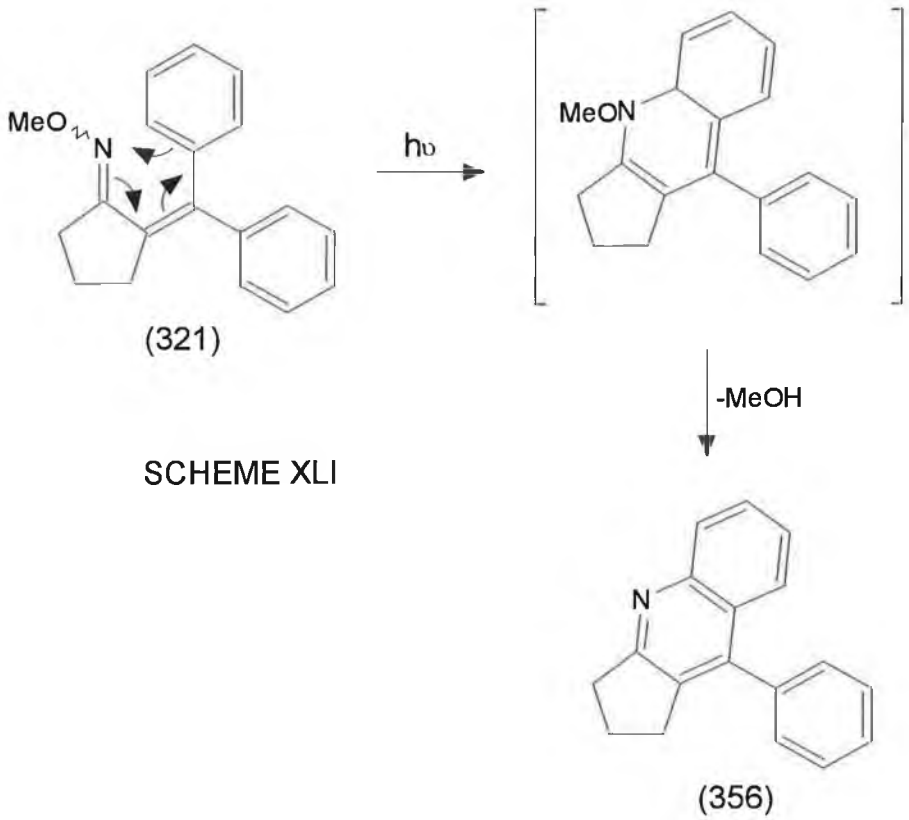
2.B.11 Photochemistry of 2-(Diphenylmethylene)cyclopentanone Oxime O-Methyl Ether (321)

2-Diphenylmethylenecyclopentanone oxime O-methyl ether (321) was irradiated under the normal conditions using methanol as solvent. On following the reaction by TLC two products were seen to be formed on initial irradiation. On further irradiation one of the two photoproducts became the major component of the photolysis mixture at the expense of the starting material

(321) and the other photoproduct. On isolation and characterisation this photoproduct was found to be the known heterocycle[231] 9-phenyl-2,3-dihydro-1*H*-cyclopenta[b]quinoline (356), formed by electrocyclic ring closure of the oxime ether (321) (Scheme XLI).

The NMR specra of (356) agreed with the proposed structure and that previously recorded for (356)[202]. As with the other cyclopenta[b]quinolines isolated three signals appeared in the range δ 2.16-3.24ppm of the ^{1}H-NMR spectrum; a quintet at δ 2.16 corresponding to the central methylene group protons at C-2 and two triplets at δ 2.90 and 3.24ppm corresponding to the other two methylene groups at C-1 and C-3. The aromatic region was more complex than for the other cyclopentaquinolines isolated due to the extra phenyl group present in (356). In the region δ 7.36-8.08ppm three multiplets, with a total integration of eight protons, and a doublet with an integration of one proton appear. The multiplets appeared to be due to the overlapping aromatic signals and it was not possible to assign individual signals. The ^{13}C spectrum shows three signals in the range δ 23-35ppm from the methylene group carbons at C-1, C-2 and C-3, and thirteen signals in the range δ 125-167ppm from the aromatic carbons present in (356).

Photochemical cyclisation of oxime ether (321) to form the quinloline (356) occurred much more rapidly in comparison to the photochemical cyclisations of the other oxime ethers studied. This is understandable since oxime ether (321) always has a phenyl ring correctly orientated towards the oxime ether group for cyclisation to occur, unlike the other oxime ethers studied where carbon-carbon bond isomerisation has to occur prior to achieving the appropriate orientation to permit cyclisation.



SCHEME XLI

2.B.12 Thermolysis of 2-Diphenylmethylenecyclopentanone Oxime O-Methyl Ether (321)

It was possible that electrocyclic ring closure of 2-benzylidenecyclopentanone oxime O-allyl ether (263) and the O-methyl ether (300) and its substituted derivatives (314)-(320) may have been a thermal rather than a photochemical process with the irradiation merely serving to provide an appropriately oriented aromatic ring via excited state E→Z isomerisation around the carbon-carbon double bond of the benzylidene group. Although subsequent thermal and photochemical cyclisation would be expected to follow two different paths for ring closure (conrotatory and disrotatory respectively), the quinoline isolated would be the same from either. 2-(Diphenylmethylene)cyclopentanone oxime O-methyl ether (321), which contains two aromatic groups at the carbon-carbon double bond, does not

require geometrical isomerisation prior to ring closure. Therefore if cyclisation of the oxime ethers to quinolines were a thermal process, cyclisation might be expected to occur on heating of (321). Samples of (321) were heated under reflux in both methanol (the solvent used for the photochemical investigations; b.p. 65°C) and ethylene glycol (b.p. 196-198°C). No reaction of (321) was seen in either of the two solvents on following the reaction by TLC. After the samples had been heated and solvent removed, analysis of the crude residue showed it to contain only starting material (321) with no evidence of formation of the 9-phenyl-2,3-dihydro-1*H*-cyclopenta[b]quinoline (356). It was therefore concluded that cyclisation of the oxime ethers to the corresponding quinoline derivatives is a photochemical process.

3. Experimental

3.1 Introductory remarks

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC-400 instrument operating at 400MHz for ^{1}H-NMR and 100MHz for ^{13}C-NMR. All spectra were recorded using deuteriated chloroform as solvent unless otherwise stated (d=doublet, t=triplet, q=quartet, qn=quintet, m=multiplet).

Infrared spectra (IR) were recorded on either a Perkin Elmer 983G infrared spectrophotometer or a Nicolet 205 FT-IR spectrophotometer.

Ultraviolet spectra (UV) were recorded on a Hewlett Packard 8452A diode array UV-Vis. spectrophotometer. Units for extinction coefficients (ε) are $dm^3\ mol^{-1}\ cm^{-1}$.

Melting ranges were recorded using a Gallenkamp melting point apparatus.

Elemental analyses were carried out by the Microanalytical Laboratory at University College Dublin.

Thin layer chromatography (TLC) was carried out on silica gel TLC plates containing a fluorescent indicator (Riedel-de-Haen, DC-Cards Si F, layer thickness 0.2mm).

Radial centrifugal chromatography (RCC) was carried out using a Harrison Research model 7924T Chromatotron system using rotors coated with silica gel PF_{254} containing 5% calcium sulphate as binder. Light petroleum for mobile phase had b.p. 40-60°C.

High performance liquid chromatography (HPLC) was carried out using a Waters 510 HPLC pump and Waters μbondpack C_{18} RCM cartridges with 15μm packing (RCM 8x10 cartridge for analytical work, and a Waters RCM 25x10 cartridge for preparative work).

Gas chromatography (GC) was carried out using a Carlo Erba Strumentazione 4130 gas chromatograph fitted with a Quadrex Corporation fused silica capillary column (25m, .007 series methyl silicone, 0.32mm ID, 1.0μm film thickness).

Photochemical reactions were carried out using a water-cooled immersion well containing a Photochemical Reactors 400W medium pressure mercury lamp fitted with a Pyrex filter (λ>300nm). All solvents for photochemical reactions were high purity grade. All solutions for photochemistry were deoxygenated by passing a stream of nitrogen through the solution for 30 minutes prior to irradiation and a constant stream of nitrogen was bubbled through solutions during irradiation.

3.2 Preparation of 2-Benzylidenecyclopentanone (266)

Cyclopentanone (9.5cm^3, 0.1mole) and morpholine (8.7cm^3, 0.1mole) were placed in a 250cm^3 round bottom flask containing toluene (100cm^3). The mixture was heated under reflux with continuous azeotropic removal of water using a Dean and Stark apparatus, until a constant volume of water had been collected (1.8cm^3, 1 hour). The reaction mixture was allowed to cool and benzaldehyde (10.2cm^3, 0.1mole) was then added. The mixture was again heated under reflux with removal of water, until a constant volume of water had again been collected, (1.7cm^3, 2 hours). The reaction mixture was allowed to cool and transferred to a 250cm^3 conical flask, a 1:1 mixture of conc. hydrochloric acid / water (50cm^3) was added dropwise with stirring, and the mixture was then stirred for a further hour. The contents of the flask were transfered to a 250cm^3 separating funnel, the acid layer was removed and the organic layer was washed with a 10% aq. sodium carbonate solution (100cm^3) and water (2x100cm^3). The organic layer was dried over anhydrous magnesium sulphate and the toluene was removed by rotary evaporation, yielding a dark coloured oil which solidified on cooling. The product was recrystallised twice from ethanol, yielding 2-benzylidenecyclopentanone (266), (10.8g, 63%), melting range 69-70°C (lit.[192] 71-72°C).

IR (KBr pellet): 3022, 2968, 2955, 2908 (aromatic and aliphatic CH), 1711 (C=O), 1619, 1571, 1489, 1447, 1401, 1321, 1306, 1289, 1276, 1237, 1174, 1078, 1028, 997, 932, 898, 869, 832, 818, 783, 751, 697 and 635cm^{-1}.

^{1}H-NMR: δ 2.03 (qn, 2H, J=7.5Hz, CH_2-C$\underline{H_2}$-CH_2), 2.41 (t, 2H, J=7.9Hz, C$\underline{H_2}$-C=O), 2.98 (t of d, 2H, J_t=7.1Hz, J_d=2.5Hz, C$\underline{H_2}$-C=C), 7.39 (m, 4H, aromatic and vinylic protons) and 7.53ppm (d, 2H, J=7.4Hz, aromatic protons).

^{13}C-NMR: δ 19.71, 28.88, 37.34 (cyclopentanone ring saturated carbons), 128.23, 128.90, 130.06, 131.99, 134.99, 135.58 (aromatic and vinylic carbons) and 208.07ppm (C=O).

3.3 Preparation of 2-Benzylidenecyclopentanone Oxime (235)

A mixture of 2-benzylidenecyclopentanone (235) (5g, 0.029moles) and hydroxylamine hydrochloride (5g, 0.072moles) was heated under reflux in a mixture of ethanol (50cm^3) and pyridine (5cm^3) for 1 hour. The mixture was cooled on an ice bath until the oxime crystallised from solution, and the solid was then removed by suction filtration and recrystallised from methanol, yielding yellow crystals of (235), (3.9g, 71%), melting range 127-129°C (lit.[192] 129°C).

IR (KBr pellet): 3250 (broad, OH), 3099, 3022, 2955, 2927 (aromatic and aliphatic CH), 1607 (C=N), 1570, 1489, 1446, 1433, 1421, 1297, 1287, 1262, 1194, 1154, 1050, 1023, 942, 919, 886, 868, 838, 754, 705 and 691cm^{-1}.

^{1}H-NMR: δ 1.87 (qn, 2H, *J*=7.5Hz, CH_2-CH_2-CH_2), 2.68 (t, 2H, *J*=7.6Hz, CH_2-C=N), 2.80 (t of d, 2H, J_t=7.4Hz, J_d=2.5Hz, CH_2-C=N), 7.21 (t, 1H, *J*=2.5Hz, vinylic proton), 7.26 (m, 1H, aromatic proton), 7.35 (m, 2H, aromatic protons), 7.41 (d, 2H, *J*=7.4Hz, aromatic protons) and 9.55ppm (broad s, 1H, C=NOH).

^{13}C-NMR: δ 22.45, 27.09, 31.45 (cyclopentanone ring saturated carbons), 123.25, 127.35, 128.30, 128.72, 129.28, 130.74, 136.59, 137.02 (aromatic and vinylic protons) and 163.73ppm (C=NOH).

3.4 Allylation of 2-Benzylidenecyclopentanone Oxime (235)

Using Potassium Carbonate as Base

Potassium carbonate (3.75g, 0.027moles) and acetone ($75cm^3$) were placed in a two necked round bottom flask fitted with a reflux condenser and a dropping funnel containing allyl bromide ($2.5cm^3$, 0.029moles) and acetone ($10cm^3$). The allyl bromide solution was added dropwise to the flask with continuous stirring. The reaction mixture was then heated under reflux, the reaction being followed by TLC using a mobile phase of 80:20 light petroleum / ethyl acetate. Slow formation of a new product was noted. After six hours the heating was stopped and the reaction mixture was allowed to cool. Acetone was removed from the reaction mixture by rotary evaporation and hydrochloric acid (0.5M, $50cm^3$) and chloroform ($50cm^3$) were added to the flask and the contents were transferred to a $100cm^3$ separating funnel. The acid layer was removed and the organic layer was extracted with 0.5M hydrochloric acid ($50cm^3$) and water ($2x50cm^3$). The solution was dried over anhydrous magnesium sulphate and the chloroform was removed by rotary evaporation yielding an oil which solidified on standing. The product was recrystallised twice from methanol yielding E,E-2-benzylidene-cyclopentanone oxime O-allyl ether (263), (1.5g, 25%) as colourless crystals, melting range 45-46°C.

IR (KBr pellet): 3083, 3023, 2953, 2873 (aromatic and aliphatic CH), 1646 (C=N), 1590, 1570, 1488, 1446, 1420, 1348, 1319, 1298, 1261, 1221, 1203, 1181, 1157, 1126, 1108, 1079, 1031, 997, 924, 889, 866, 849, 825, 788, 751 and $694cm^{-1}$.

^{1}H-NMR: δ 1.86 (qn, 2H, J=7.5Hz, CH_2-C$\underline{H_2}$-CH_2), 2.63 (t, 2H, J=7.6Hz, C$\underline{H_2}$-C=N), 2.79 (t of d, 2H, J_t=7.3Hz, J_d=2.5Hz, C$\underline{H_2}$-C=C), 4.69 (m, 2H, OC$\underline{H_2}$), 5.25 (d of m, 1H, J_d=11Hz, CH=C$\underline{H_2}$), 5.35 (d of m, 1H, J_d=17Hz, CH=C$\underline{H_2}$),

6.08 (m, 1H, C<u>H</u>=CH_2), 7.26 (m, 2H, aromatic protons), 7.36ppm (m, 2H, aromatic and benzylidene protons).

^{13}C-NMR: δ 22.64, 27.65, 31.38 (cyclopentanone ring saturated carbons), 75.16 (O<u>C</u>H_3), 117.36, 122.89, 127.25, 128.31, 129.27, 134.52, 136.85, 137.24 (aromatic and vinylic carbons) and 162.69ppm (<u>C</u>=N).

UV (methanol): λ_{max}: 302nm (ε=27,090), 222nm (ε=13,170).

Found: C, 79.50; H, 7.57; N, 5.93%. $C_{15}H_{17}NO$ requires: C, 79.26; H, 7.54, N, 6.16%.

<u>Using Sodium Hydroxide as Base</u>

2-Benzylidenecyclopentanone oxime (235) (5g, 0.027moles) and tetrahydrofuran (THF) were placed in a two necked round bottom flask fitted with a reflux condenser and a dropping funnel. Sodium hydroxide solution (15cm^3, 10% aq. soln.) was added to the flask on which the sodium salt of (235) precipitated from solution. Allyl bromide (2.5cm^3, 0.029moles) was then added dropwise to the flask with stirring. The reaction mixture was then heated under reflux, the reaction being followed by TLC using a mobile phase of 80:20 light petroleum / ethyl acetate. Slow formation of (263) was noted. After five hours the reaction was stopped, the contents of the flask were allowed to cool and the THF was removed by rotary evaporation. Chloroform (50cm^3) was added to the reaction mixture which was then transfered to a separating funnel. The chlorofrom solution was then washed with hydrochloric acid (0.5M, 50cm^3) and water (2x100cm^3). The chloroform was dried over magnesium sulphate and the chloroform was then removed by rotary evaporation yielding (263), (1.1g, 18% crude).

3.5 Preparation of N-Allyloxyphthalimide (270)

N-Hydroxyphthalimide (270) (10.0g, 0.06moles) and allyl bromide (7.3g, 0.05moles) were dissolved in acetone (100cm^3) in a 250 cm^3 round bottom flask. Potassium carbonate (6.8g, 0.05moles) was then added and the mixture was refluxed with continuous stirring for 8 hours. The reaction mixture was cooled, the potasium carbonate was removed by suction filtration and the acetone removed by rotary evaporation, yielding a light yellow oil which crystallised on standing. The product was recrystallised from diethyl ether, yielding N-allyloxyphthalimide (269), a white crystalline solid (8.2g, 66%), melting range 61-63°C.

IR (KBr pellet): 3080, 3045, 3025, 2983, 2946 (aromatic and aliphatic CH), 1786, 1733 (C=O), 1608, 1584, 1466, 1446, 1423, 1373, 1353, 1322, 1296, 1287, 1260, 1186, 1159, 1124, 1110, 1082, 1062, 1015, 994, 876, 790, 703 and 639cm^{-1}.

^{1}H-NMR: δ 4.71 (d, 2H, *J*=6.9Hz, OC$\underline{H}_2$), 5.37 (m, 2H, CH=C$\underline{H}_2$), 6.12 (m, 1H, C$\underline{H}$=CH_2), 7.77 (m, 2H, aromatic protons) and 7.84ppm (m, 2H, aromatic protons).

^{13}C-NMR: δ 78.75 (O$\underline{C}H_2$), 122.56, 123.43, 128.66, 131.16, 134.42 (aromatic and vinylic carbons) and 163.63ppm ($\underline{C}$=O).

Found: C, 65.30; H, 4.52; N, 6.86. $C_{11}H_9NO_3$ requires: C, 65.02; H, 4.46; N, 6.89.

3.6 Hydrolysis of N-Allyloxyphthalimide (269)

N-Allyloxyphthalimide (269) (4.5g, 0.02 moles) was heated under reflux in 6M hydrochloric acid (50cm^3) in a 100cm^3 round bottom flask for 2 hours. On cooling, phthalic acid crystallised from solution and was removed by suction filtration. The water was removed by distillation and the product was dried under vacuum over sodium hydroxide, yielding allyloxyamine hydrochloride (1.6g, 80% crude), melting range (crude): 140-145°C (lit.[195], 172-174°C). Attempts to recrystallise the product proved unsuccessful, as did attempts to record an IR spectrum since the product was extremely hygroscopic. The crude product was used for the next stage of the synthesis without further purification.

^{1}H-NMR (D_2O): δ 4.33 (d, 2H, *J*=5.8Hz, O$\underline{CH_2}$), 4.77 (broad s, 3H, -N$\underline{H_3}$Cl), 5.31 (m, 2H, CH=C$\underline{H_2}$) and 5.72ppm (m, 1H, C$\underline{H}$=CH$_2$).

3.7 Preparation of E,E-2-Benzylidenecyclopentanone Oxime O-Allyl Ether (263) from Alloxyamine Hydrochloride (268) and 2-Benzylidene-cyclopentanone (266)

2-Benzylidenecyclopentanone (266) (3.0g, 0.015moles), allyloxyamine hydrochloride (268) (2.7g, 0.015 moles), pyridine (5cm^3) and ethanol (30cm^3) were placed in a 100cm^3 round bottom flask. The mixture was heated under reflux for 30 minutes, cooled and the ethanol was removed by rotary evaporation. Water (30cm^3) was added to the flask and the resulting mixture was cooled on an ice bath, until the oxime ether crystallised from solution. The solid product was filtered, dried and recrystallised from methanol yielding E,E-2-benzylidene-cyclopentanone oxime O-allyl ether (263), (2.9g, 73%).

3.8 Methylation of 2-Benzylidenecyclopentanone oxime (235)

Methyl iodide: 2-Benzylidenecyclopentanone oxime (235) (2g, 0.011 moles) was dissolved in acetone (30cm^3) containing methyl iodide. (3g, 0.021 moles). Potassium carbonate (3g, 0.022 moles) was added and the solution was heated under reflux with continuous stirring, the reaction being followed by TLC using a mobile phase of 90:10 light petroleum / ethyl acetate. Very slow formation of a new product was noted. After 24 hours. the reaction was stopped, the potassium carbonate was removed by suction filtration and the acetone removed by rotary evaporation, yielding an oil. ^{1}H-NMR analysis of the crude product showed it to be predominantly 2-benzylidenecyclopentanone oxime (266), by comparison with that of an original sample of (266).

Dimethyl sulphate: 2-Benzylidenecyclopentanone oxime (266) (2g, 0.011moles) was dissolved in acetone (50cm^3) in a three necked round bottom flask fitted with a reflux condenser and two dropping funnels. A mixture of dimethyl sulphate (6.3g, 0.050moles) and acetone (10cm^3) was placed in one dropping funnel and a 40% aq. sodium hydroxide solution (12cm^3) was placed in the other. The two solutions were slowly added simultaneously with continuous stirring over a period of 30 minutes, and the resulting reaction mixture was then heated under reflux, with stirring, for 1 hour. The acetone was removed by distillation, ice water (200cm^3) was added to the residue and the resulting solid product was separated by suction filtration, dried and recrystallised from light petroleum (B.P. 60-80°C), yielding benzylidenecyclopentanone oxime O-methyl ether (300), (1.5g, 67%), a yellow crystalline solid, melting range 78-79°C.

IR (KBr pellet): 2979, 2955, 2899, 2817 (aromatic and aliphatic CH), 1623 (C=N), 1488, 1447, 1417, 1295, 1266, 1219, 1183, 1157, 1125, 1078, 1045,

924, 889, 848, 823, 789, 759, 701 and 612cm^{-1}.

^{1}H-NMR: δ 1.85 (qn, 2H, J=7.4Hz, $CH_2\underline{CH_2}CH$), 2.58 (t, 2H, J=7.6Hz, $\underline{CH_2}C=C$), 2.78 (t of d, 2H, J_t=7.4Hz, J_d=2.6Hz, $\underline{CH_2}C=C$), 3.97 (s, 3H, $OC\underline{H_3}$), 7.24 (m, 2H, aromatic and benzylidene protons), 7.35 (m, 2H, aromatic protons) and 7.41ppm (m, 2H, aromatic protons).

^{13}C-NMR: δ 22.61, 27.62, 31.35 (cyclopentane ring saturated carbons), 75.12 ($O\underline{C}H_3$), 122.86, 127.22, 128.27, 129.24, 136.81, 137.19 (aromatic and vinylic carbons) and 162.65ppm ($\underline{C}$=N).

UV (methanol): λ_{max} 302nm (ε=24,225); 226nm (ε=11,594).

Found: C, 77.29; H, 7.57; N, 6.66. $C_{13}H_{15}NO$ requires: C, 77.58; H, 7.51; N, 6.96.

3.9 Irradiation of E,E-2-Benzylidenecyclopentanone Oxime O-Allyl Ether (263) in Ethyl Acetate

E,E-2-Benzylidenecyclopentanone oxime O-allyl ether (263) (1.0g, 0.004moles) in ethyl acetate (300cm^3) was irradiated under standard conditions. The reaction was followed by GC using a temperature programmed run (initial temperature: 100°C for 4 minutes; heating rate: 30°C / minute; final temperature: 185°C for 12 minutes; injection volume: 1μl). After 5 minutes of irradiation the formation of a new product (PP1) was noted the concentration of which steadily increased. On further irradiation (30 minutes) the gradual formation of two further photoproducts (PP2) and (PP3) was also noted. The photolysis was continued until a photostationary state had been reached and no new photoproducts were being formed. After 5 hours the irradiation was

stopped, the contents of the immersion well were transferred to a round bottom flask and the ethyl acetate was removed by rotary evaporation.

Separation of photoproducts

Analytical: Attempts to resolve the four components of the photolysis mixture by TLC analysis proved unsuccessful. Only three components could be separated by TLC, two of the photoproducts having the same Rf values (mobile phase: 95:5 light petroleum / ethyl acetate). Attempts to resolve the four components by HPLC analysis also proved unsuccessful with only one of the components being well resolved from the other three (mobile phase 70:30 methanol / water). However, it was found that the two photoproducts that had the same Rf values on TLC gave good separation on HPLC thus allowing separation of the four components of the photolysis mixture via a combination of preparative TLC and HPLC.

Preparative separation: The photolysis mixture was separated using a 4mm Chromatotron plate with a mobile phase of 99:1 light petroleum / ethyl acetate. The first two fractions to be eluted from the plate were each found to contain single compounds by GC analysis ((PP2) and (E,E-263) respectively) . The third fraction eluted was found to contain two compounds by GC analysis (PP1) and (PP3). Solvent was removed from eluted fractions by rotary evaporation, and the first two fractions were purified by short path vacuum distillation onto a cold finger. The two compounds contained in the third fraction were separated using preparative HPLC using a mobile phase of 70:30 methanol/water. The methanol was removed from the eluted HPLC fractions by rotary evaporation and the resulting emulsions were extracted with diethyl ether, the etherel solutions were dried over anhydrous magnesium sulphate and the ether was removed by rotary evaporation, yielding oils which were

purified by short path vacuum distillation onto a cold finger.

The first component eluted from the chromatotron was found to be E,Z-2-benzylidenecyclopentanone oxime O-allyl ether (E,Z-263). GC analysis showed it to be one of the slower formed photoproducts (117mg, 12%) boiling range 45-50°C (0.2mbar).

IR (Thin film): 3070, 3024, 2957, 2918, 2871, 2845 (aromatic and aliphatic CH), 1643 (C=N), 1596, 1497, 1450, 1430, 1364, 1344, 1291, 1264, 1211, 1158, 1098, 1065, 1038, 925, 879, 852, 753 and 700cm^{-1}.

^{1}H-NMR: δ 1.83 (qn, 2H, J=7.4Hz, CH_2-C$\underline{H}_2$-CH_2), 2.70 (m, 4H, CH_2-C=C and C$\underline{H}_2$-C=N), 4.63 (d, 2H, J=5.5Hz, OC$\underline{H}_2$), 5.27 (d of m, 1H, J_d=13Hz, CH=C$\underline{H}_2$), 5.35 (d of m, 1H, J_d=19Hz, CH=C$\underline{H}_2$), 6.08 (m, 1H, C$\underline{H}$=CH_2), 6.62 (t, 1H, J=0.8Hz, benzylidene proton), 7.29 (m, 3H, aromatic protons) and 7.99ppm (d, 2H, J=7.6Hz, aromatic *ortho* protons).

^{13}C-NMR: δ 21.75, 29.61, 37.07 (cyclopentanone ring saturated carbons), 75.08 (O$\underline{C}H_2$), 117.48, 127.33, 127.37, 127.44, 130.06, 134.91, 135.47, 136.26 (aromatic and vinylic carbons) and 160.19ppm ($\underline{C}$=N).

UV (methanol): λ_{max} 304nm (ε=12,205), 224nm (ε=15,540), 204nm (ε=13,669).

Found: C, 79.54; H, 7.56%; N, 6.00%. $C_{15}H_{17}NO$ requires: C, 79.26; H, 7.54; N, 6.16%.

The second component eluted from the chromatotron was found to be recovered starting material, E,E-2-benzylidenecyclopentanone oxime O-allyl

ether (E,E-263). Identified by comparison of its IR and NMR spectra with that of authentic (E,E-263). (176mg, 18% recovery).

The first component eluted from the HPLC was found to be Z,Z-2-benzylidenecyclopentanone oxime O-allyl ether (Z,Z-263). GC analysis showed it to be the other slower formed photoproduct (72mg, 7%), boiling range 49-53°C (0.2 mbar).

IR (Thin film): 3078, 3059, 3023, 2961, 2922, 2848 (aromatic and aliphatic CH), 1642, 1606, 1576, 1497, 1437, 1420, 1368, 1344, 1193, 1163, 1103, 1073, 1043, 1025, 997, 925, 872, 766, 740 and 693cm^{-1}.

^{1}H-NMR: δ 1.89 (qn, 2H, *J*=7.5Hz, CH_2-$C\underline{H}_2$-CH_2), 2.66 (m, 4H, $C\underline{H}_2$-C=N and $C\underline{H}_2$-C=C), 4.25 (d of t, 2H, J_d=4.8Hz, J_t=1.1Hz, $OC\underline{H}_2$), 4.92 (m, 2H, CH=$C\underline{H}_2$), 5.36 (m, 1H, $C\underline{H}CH_2$), 6.72 (t, 1H, *J*=1.9Hz, vinylic proton) and 7.27ppm (m, 5H, aromatic protons).

^{13}C-NMR: δ 21.03, 31.44, 34.32 (cyclopentane ring saturated carbons), 74.69 ($OC\underline{H}_2$), 117.29, 127.09, 127.11, 128.62, 130.66, 131.37, 133.26, 138.43 (aromatic and vinylic carbons) and 157.53ppm ($\underline{C}$=N).

UV (methanol): λ_{max}: 288nm (ε=11,041), 222nm (ε=12,343).

Found: C, 78.98; H, 7.67%; N, 5.96%. $C_{15}H_{17}NO$ requires: C, 79.26; H, 7.54; N, 6.16%.

The second component eluted from the HPLC was found to be Z,E-2-benzylidenecyclopentanone oxime O-allyl ether (Z,E-263). GC analysis

showed it to be the rapidly formed photoproduct (124mg, 12%), boiling range 42-44°C (0.2mbar).

IR (Thin film): 3082, 3023, 2965, 2926, 2871 (aromatic and aliphatic CH), 1648, 1627, 1598 (C=N), 15723, 1491, 1446, 1345, 1294, 1228, 1195, 1111, 1073, 1022, 991, 921, 884, 830, 788, 750 and 696cm^{-1}.

^{1}H-NMR: δ 1.73 (qn, 2H, *J*=7.3Hz, CH_2-C$\underline{H}_2$-CH_2), 2.45 (t, 2H, *J*=7.3Hz, C$\underline{H}_2$-C=N), 2.69 (t of d, 2H, J_t=7.1Hz, J_d=2.4Hz, C$\underline{H}_2$-C=C), 4.60 (d of t, 2H, J_d=5.5Hz, J_t=1.3Hz, OC$\underline{H}_2$), 5.17 (d of m, 1H, J_d=11Hz, CH=C$\underline{H}_2$), 5.30 (m, 1H, J_d=17Hz, CH=C$\underline{H}_2$), 6.00 (m, 1H, C$\underline{H}$=CH_2), 7.18 (m, 1H, aromatic proton), 7.29 (m, 4H, aromatic protons) and 8.11ppm (t, 2H, *J*=2.4Hz, C=C$\underline{H}$Ph).

^{13}C-NMR: δ 23.62, 32.50, 32.95 (cyclopentanone ring saturated carbons), 75.52 (O$\underline{C}H_2$), 117.19, 127.58, 128.15, 129.47, 134.19, 134.44, 134.98, 137.75 (aromatic and vinylic carbons) and 156.65ppm ($\underline{C}$=N).

UV (methanol): λ_{max}: 296nm (ε=13,243), 226nm (ε=5,848), 206nm (ε=6,108).

Found: C, 79.45; H, 7.33%; N, 6.06%. $C_{15}H_{17}NO$ requires: C, 79.26; H, 7.54; N, 6.16%.

3.10 Irradiation of E,E-2-Benzylidenecyclopentanone Oxime O-Allyl Ether (E,E-263) in Methanol

E,E-2-Benzylidenecyclopentanone oxime O-allyl ether (E,E-263) (1.0g, 0.004moles) in methanol (300cm^3) was irradiated under standard conditions, the reaction being followed by GC using the same conditions as for the photolysis of (E,E-263) in ethyl acetate. As with the photolysis of (E,E-263) in

ethyl acetate rapid formation of the Z,E isomer (Z,E-263) was also noted with the slower formation of the other photoproducts, (E,Z-263) and (Z,Z-263), also being seen. However, gradual formation of a new photoproduct (PP4), not seen in the photolysis in ethyl acetate, was also noted. The concentration of this new photoproduct (PP4) increased on continued irradiation, at the expense of the four oxime ether isomers, until it was the major component of the photolysis mixture. The photolysis was stopped after 5 hours of irradiation and the solvent was removed by rotary evaporation. Product (PP4) was separated from the resulting oil using a 4mm Chromatotron plate with a mobile phase of 90:10 light petroleum / ethyl acetate. The solvent was removed from this fraction by rotary evaporation yielding an oil which was distilled under reduced pressure, onto a cold finger to give an off-white solid. Analysis of this product showed it to be 2,3-dihydro-1*H*-cyclopenta[b]quinoline (236) (174mg, 23.4%), melting range 60-61°C (lit.[203] 60-61°C).

IR (KBr pellet): 3033, 2955, 2937, 2849 (aromatic and aliphatic CH), 1614, 1496, 1463, 1405, 1322, 1280, 1265, 1204, 1130, 1093, 1074, 1047, 979, 754, 703cm^{-1}.

^{1}H-NMR: δ 2.18 (qn, 2H, *J*=7.4Hz, CH_2-$C\underline{H}_2$-CH_2), 3.06 (t, 2H, *J*=7.4Hz, $C\underline{H}_2$Ar), 3.14 (t, 2H, *J*=7.4Hz, $C\underline{H}_2$Ar), 7.43 (t, 1H, *J*=7.4Hz, aromatic proton), 7.59 (t, 1H, *J*=7.9Hz, aromatic proton), 7.70 (d, 1H, *J*=7.6Hz, aromatic proton), 7.85 (s, 1H, aromatic proton) and 8.00ppm (d, 1H, *J*=8.0Hz, aromatic proton).

^{13}C-NMR: δ 23.62, 30.50, 34.60 (cyclopentane ring saturated carbons), 125.49, 127.37, 127.43, 128.30, 128.51, 130.29, 135.77, 147.48 and 167.91 (aromatic carbons).

3.11 Photolysis of E,E-2-Benzylidenecyclopentanone Oxime O-Allyl Ether (E,E-263) in Methanol containing 1% w/v Potassium Carbonate

E,E-2-Benzylidenecyclopentanone oxime O-allyl ether (E,E-263) (500mg, 0.002moles) in methanol (300cm^3) containing anhydrous potassium carbonate (3g), was irradiated under standard conditions. After 3 hours the irradiation was ceased, the photolysis mixture was transfered to a round bottom flask, the methanol was removed from the photolysis mixture by rotary evaporation and water (100cm^3) and diethyl ether (100cm^3) were added to the flask. The contents of the flask were transfered to a 250cm^3 separating funnel, the water layer was removed and the etheral layer was washed with water (2x100cm^3) and dried over anhydrous magnesium sulphate. Analysis of the resulting mixture by GC showed it to contain a combination of the four oxime ether isomers of (263) in low concentration with the quinoline derivative (236) again being the major photoproduct formed.

3.12 Irradiation of E,E 2-Benzylidenecyclopentanone Oxime O-Allyl Ether (E,E-263) in Acetonitrile

E,E-2-Benzylidenecyclopentanone oxime O-allyl ether (E,E-263) (500mg, 0.002moles) in acetonitrile was irradiated under standard conditions, the reaction being followed by G.C. Formation of the geometrical isomers of (263) was noted with formation of the Z,E-isomer being the fastest process. On further irradiation very slow formation of 2,3-dihydro-1*H*-cyclopenta[b]quinoline was also noted.

3.13 Irradiation of E,E 2-Benzylidenecyclopentanone Oxime O-Allyl Ether (E,E-263) in Methanol containing Isoprene

A series of solutions of E,E-2-benzylidenecyclopentanone oxime O-allyl ether (E,E-263) (0.0025M) in methanol with varying concentrations of freshly

distilled isoprene (0.0M, 0.001M, 0.01M, 0.1M and 1.0M) were prepared. A 20cm^3 aliquot of each of the solutions was placed in a series of quartz tubes, the solutions were degassed by bubbling argon through each one for 10 minutes and the tubes were stoppered and placed on a carousel apparatus circling an immersion well containing a photolysis lamp fitted with a Pyrex filter. The solutions were irradiated for 15 minutes after which a sample from each tube was analysed by GC. All of the samples were seen to contain each of the four oxime ether isomers of (263) and the cyclopenta[b]quinoline derivative (236) in the same ratios, irrespective of isoprene concentration.

3.14 Irradiation of 2-Benzylidenecyclopentanone Oxime O-Methyl Ether (300)

2-Benzylidenecyclopentanone oxime O-methyl ether (300) (238mg, 0.001moles) in methanol (300cm^3) was irradiated under standard conditions, with the reaction being followed by TLC using a mobile phase of 90:10 light petroleum / ethyl acetate. After 30 minutes of irradiation TLC analysis of the reaction mixture showed two new spots. On further irradiation TLC analysis showed the formation of a third new spot whose concentration steadily increased at the expense of the other components of the photolysis mixture. This product had a retention time on TLC similar to that of the cyclopenta[b]quinoline (236). The irradiation was stopped after 3 hours, the photolysis mixture was transfered to a round bottom flask and the solvent was removed by rotary evaporation. The major photoproduct was purified by separation on a 2mm Chromatotron plate, followed by short path distillation of the resulting oil onto a cold finger to yield off-white solid identified as 2,3-dihydro-1*H*-cyclopenta[b]quinoline (236) (58mg, 29%) by comparison of its IR and NMR spectra with those of (236) obtained from photolysis of the oxime O-allyl ether (E,E-263).

3.15 General Procedure for the Preparation of Arylidenecyclopentanones (322a-i)

Cyclopentanone (9.5cm^3, 0.1mole) and morpholine (8.7cm^3, 0.1mole) were placed in a 250cm^3 round bottom flask containing toluene (100cm^3). The round bottom flask was fitted with a Dean and Stark trap and a reflux condenser and the solution was heated under reflux until a constant volume of water had been collected (1.8cm^3, 1 hour). The solution was allowed to cool and the desired aromatic aldehyde (0.1mole) was then added. The resulting solution was again heated under reflux until a further constant volume of water had been collected. The reaction mixture was allowed to cool, transferred to a 250cm^3 conical flask and a 1:1 mixture of water and hydrochloric acid (50cm^3) was then added dropwise with stirring. The solution was allowed to stir for a further hour and was then transferred to a 250cm^3 separating funnel, washed with a 10% aq. sodium carbonate solution (100cm^3), and dried over anhydrous magnesium sulphate. The toluene was removed by rotary evaporation yielding an oil which solidified on cooling and scratching with a glass rod. The arylidenecyclopentanones (322a-j) were recrystallised from methanol.

3.15.1 Preparation of 2-(o-Nitrobenzylidene)cyclopentanone (322a)

2-(*o*-Nitrobenzylidene)cyclopentanone (322a) was prepared from *o*-nitro-benzaldehyde (15.11g, 0.1 mole), yielding yellow crystals of (322a), (8.6g, 40%), melting range 83-86°C.

IR (KBr pellet): 3060, 2960, 2870 (aromatic and aliphatic CH), 1716 (C=O), 1626, 1603, 1570, 1516 (NO_2), 1474, 1441, 1431, 1403, 1346 (NO_2), 1309, 1292, 1279, 1234, 1215, 1180, 1143, 1081, 1047, 1016, 1002, 959, 916, 902, 857, 830, 788, 739, 675 and 630cm^{-1}.

^{1}H-NMR: δ 1.79 (qn, 2H, *J*=7.5Hz, CH_2-C$\underline{H}_2$-CH_2), 2.20 (t, 2H, *J*=7.6Hz, C$\underline{H}_2$-C=O), 2.57 (t of d, 2H, J_t=7.3Hz, J_d=2.7Hz, C$\underline{H}_2$-C=C), 7.30 (m, 2H, aromatic protons), 7.38 (t, 1H, *J*=2.7Hz, C=C$\underline{H}$Ph), 7.44 (t, 1H, *J*=7.6Hz, aromatic proton) and 7.80ppm (d, 1h, *J*=8.7Hz, aromatic proton).

^{13}C-NMR: δ 20.40, 28.90, 38.11 (cyclopentane ring saturated carbons), 124.97, 127.27, 129.55, 130.72, 131.26, 133.22, 139.68, 148.97 (aromatic and vinylic carbons) and 206.95ppm (C=O).

Found: C, 66.05; H, 5.05; N, 6.25%. $C_{12}H_{11}NO_3$ requires: C, 66.35; H, 5.10; N, 6.45%.

3.15.2 Preparation of 2-(*p*-Nitrobenzylidene)cyclopentanone (322b)

2-(*p*-Nitrobenzylidene)cyclopentanone (322b) was prepared from *p*-nitrobenzaldehyde (15.1g, 0.1 mole), yielding yellow crystals of (322b), (9.7g, 45%), melting range 138-140°C (lit.[232], 145-146°C).

IR (KBr pellet): 3095, 2955 (aromatic and aliphatic CH), 1711 (C=O), 1626, 1595, 1509 (NO_2), 1465, 1434, 1413, 1380, 1339 (NO_2) 1317, 1299, 1289, 1276, 1232, 1220, 1174, 1116, 1107, 1006, 911, 873, 860, 842, 809, 748, 689 and 670cm^{-1}.

^{1}H-NMR: δ 2.02 (qn, 2H, *J*=7.5Hz, CH_2-C$\underline{H}_2$-CH_2), 2.39 (t, 2H, *J*=7.9Hz, C$\underline{H}_2$-C=O), 2.94 (t of d, 2H, J_t=7.2Hz, J_d=2.7Hz, C$\underline{H}_2$-C=C), 7.60 (d, 2H, *J*=8.8Hz, aromatic protons) and 8.19ppm (2H, *J*=8.8Hz, aromatic protons).

^{13}C-NMR: δ 20.18, 29.53, 37.80 (cyclopentane ring saturated carbons), 123.98, 129.39, 130.91, 140.00, 142.02, 147.78 (aromatic and vinylic carbons) and 207.53ppm (C=O).

Found: C, 66.05; H, 5.05; N, 6.31%. $C_{12}H_{11}NO_3$ requires: C, 66.35; H, 5.10; N, 6.25%.

3.15.3 Preparation of 2-(*o*-Chlorobenzylidene)cyclopentanone (322c)

2-(*o*-Chlorobenzylidene)cyclopentanone (322c) was prepared from *o*-chlorobenzaldehyde (11.3cm^3, 0.1 mole), yielding yellow crystals of (322c), (14.2g, 69%), melting range 55-57°C.

IR (KBr pellet): 3050, 2955 (aromatic and aliphatic CH), 1712 (C=O), 1620, 1586, 1561, 1465, 1436, 1409, 1367, 1308, 1288, 1277, 1232, 1216, 1179, 1126, 1049, 1038, 1017, 1004, 989, 948, 924, 908, 872, 857, 837, 818, 777, 758, 693 and 638cm^{-1}.

^{1}H-NMR: δ 1.87 (qn, 2H, *J*=7.5Hz, CH_2-C$\underline{H}_2$-CH_2), 2.28 (t, 2H, *J*=7.8Hz, C$\underline{H}_2$-C=O), 2.75 (t of d, 2H, J_t=7.1Hz, J_d=2.7Hz, C$\underline{H}_2$-C=C), 7.15 (m, 2H, aromatic protons), 7.29 (m, 1H, aromatic proton), 7.36 (m, 1H, aromatic protons) and 7.56ppm (t, 1H, *J*=2.7Hz, C=C$\underline{H}$Ph).

^{13}C-NMR: δ 20.51, 29.41, 38.05 (cyclopentane ring saturated carbons), 126.74, 128.26, 130.09, 130.27, 130.40, 133.81, 136.02, 138.46 (aromatic and vinylic carbons), and 207.66ppm (C=O).

Found: C, 69.64; H, 5.24%. $C_{12}H_{11}ClO$ requires: C, 69.74; H, 5.36%.

3.15.4 Preparation of 2-(*p*-Chlorobenzylidene)cyclopentanone (322d)

2-(*p*-Chlorobenzylidene)cyclopentanone (322d) was prepared from *p*-chlorobenzaldehyde (14.06g, 0.1 mole), yielding off-white crystals of (322d), (12.5g, 61%), melting range 77-79°C (lit.[233], 78-80°C).

IR (KBr pellet): 3000, 2920 (aromatic and aliphatic CH), 1712 (C=O), 1622, 1584, 1561, 1488, 1460, 1429, 1403, 1300, 1275, 1232, 1172, 1105, 1089, 1005, 905, 871, 835, 816 and 687cm^{-1}.

^{1}H-NMR: δ 1.98 (qn, 2H, *J*=7.6Hz, CH_2-$C\underline{H}_2$-CH_2), 2.35 (t, 2H, *J*=7.9Hz, $C\underline{H}_2$-C=O), 2.88 (t of d, 2H, J_t=7.2Hz, J_d=2.6Hz, $C\underline{H}_2$-C=C), 7.26 (t, 1H, *J*=2.6Hz, C=C<u>H</u>Ph), 7.31 (d, 2H, *J*=8.5Hz, aromatic protons) and 7.4ppm (d, 2H, *J*=8.5Hz, aromatic protons).

^{13}C-NMR: δ 20.24, 29.40, 37.85 (cyclopentane ring saturated carbons), 129.08, 131.02, 131.72, 134.11, 135.36, 136.6 (aromatic and vinylic carbons) and 207.99ppm (<u>C</u>=O).

3.15.5 Preparation of 2-(*o*-Methoxybenzylidene)cyclopentanone (322e)

2-(*o*-Methoxybenzylidene)cyclopentanone (322e) was prepared from o-anisaldehyde (12.8cm^3, 0.1mole), yielding off white crystals of (322e), (14.64g, 72.4%), melting range 90-92°C.

IR (KBr pellet): 3005, 2960 (aromatic and aliphatic CH), 1709 (C=O), 1621, 1595, 1573, 1486, 1461, 1439, 1402, 1357, 1310, 1297, 1278, 1251, 1234, 1210, 1181, 1166, 1109, 1054, 1020, 1007, 973, 925, 877, 850, 837, 820, 753 and 633cm^{-1}.

^{1}H-NMR: δ 2.00 (qn, 2H, *J*=7.5Hz, CH_2-$C\underline{H}_2$-CH_2), 2.40, (t, 2H, *J*=7.9Hz, $C\underline{H}_2$-C=O), 2.92, (t of d, 2H, J_t=7.1Hz, J_d=2.4Hz, $C\underline{H}_2$-C=C), 3.86 (s, 3H, OMe), 6.91 (d, 1H, *J*=7.9Hz, aromatic proton), 6.98 (t, 1H, *J*=7.9Hz, aromatic proton), 7.34 (t, 1H, *J*=7.9Hz, aromatic proton), 7.47, (d, 1H, *J*=7.9Hz, aromatic proton) and 7.81ppm (t, 1H, *J*=2.4Hz, C=C<u>H</u>Ph).

^{13}C-NMR: δ 20.52, 29.61, 38.06 (cyclopentane ring saturated carbons), 110.83, 120.32, 124.70, 127.07, 129.77, 130.89, 136.17, 159.00 (aromatic and vinylic carbons) and 208.17ppm (C=O).

Found: C, 76.94; H, 6.91%. $C_{13}H_{14}O_2$ requires: C, 77.20; H, 6.98%.

3.15.6 Preparation of 2-(*p*-Methoxybenzylidene)cyclopentanone (322f)

2-(*p*-Methoxybenzylidene)cyclopentanone (322f) was prepared from *p*-anisaldehyde (12.2cm^3, 0.1mole), yielding yellow crystals of (322f), (14.4g, 71%), melting range 68-69°C (lit.[234], 68-69°C).

IR (KBr pellet): 2960, 2825 (aromatic and aliphatic CH), 1701, 1619, 1599, 1567, 1511, 1463, 1421, 1407, 1309, 1257, 1175, 1116, 1023, 909, 825 and 754cm^{-1}.

^{1}H-NMR: δ 1.83 (qn, 2H, *J*=7.6Hz, CH_2-CH_2-CH_2), 2.20 (t, 2H, *J*=7.9Hz, CH_2-C=O) 2.75 (t of d, 2H, J_t=7.2Hz, J_d=2.5Hz, CH_2-C=C), 3.65 (s, 3H, Me), 6.75 (d, 2H, *J*=8.8Hz, aromatic protons), 7.16 (t, 1H, *J*=2.5Hz, C=CHPh) and 7.31ppm (d, 2H, *J*=8.8Hz, aromatic protons).

^{13}C-NMR: δ 20.16, 29.28, 37.77 (cyclopentane ring saturated carbons), 55.37 (MeO), 114.28, 128.24, 132.22, 132.32, 133.69, 160.52 (aromatic and vinylic carbons) and 208.8ppm (C=O).

3.15.7 Preparation of 2-(*o*-Methylbenzylidene)cyclopentanone (322g)

2-(*o*-Methylbenzylidene)cyclopentanone (322g) was prepared from *o*-tolualdehyde (11.8cm^3, 0.1 mole), yielding off white crystals of (322g), (11.2g, 60%), melting range 68-70°C.

IR (KBr pellet): 2980, 2940 (aromatic and aliphatic CH), 1704 (C=O), 1626, 1598, 1572, 1536, 1483, 1461, 1451, 1435, 1399, 1381, 1286, 1276, 1249, 1202, 1180, 1174, 1131, 1104, 1048, 1345, 1019, 1004, 922, 903, 873, 819, 791, 767, 758, 718 and 638cm^{-1}.

^{1}H-NMR: δ 1.81 (qn, 2H, *J*=7.5Hz, CH_2-C$\underline{H}_2$-CH_2), 2.23 (s, 3H, Me), 2.54 (t, 2H, *J*=7.8Hz, C$\underline{H}_2$-C=O), 2.72 (t of d, 2H, J_t=7.1Hz, J_d=2.4Hz, C$\underline{H}_2$-C=C), 7.07, (m, 3H, aromatic protons), 7.25 (d, 1H, *J*=7.3Hz, aromatic proton) and 7.43ppm (t, 1H, *J*=2.4Hz, C=C$\underline{H}$Ph).

^{13}C-NMR: δ 20.01, 20.51, 29.42, 38.07 (Me and cyclopentane ring saturated carbons), 126.80, 128.64, 129.17, 129.81, 130.54, 134.31, 136.84, 138.90 (aromatic and vinylic carbons) and 208.00ppm ($\underline{C}$=O).

Found: C, 83.54; H, 7.51%. $C_{13}H_{14}O$ requires: C, 83.83; H, 7.51%.

3.15.8 Preparation of 2-(*p*-Methylbenzylidene)cyclopentanone (322h)

2-(*p*-Methylbenzylidene)cyclopentanone (322h) was prepared from *p*-tolualdehyde (11.6cm^3, 0.1mole), yielding yellow crystals of (322h), (10.96g, 58.8%), melting range 64-65°C (lit.[235], 62-63°C).

IR (KBr pellet): 3025, 2960 (aromatic and aliphatic CH), 1706 (C=O), 1620, 1601, 1562, 1511, 1461, 1434, 1409, 1318, 1305, 1291, 1275, 1234, 1213, 1191, 1174, 1126, 1044, 1016, 1006, 969, 956, 915, 873, 842, 815, 760, 712, 649 and 638cm^{-1}.

^{1}H-NMR: δ 1.93 (qn, 2H, *J*=7.6Hz, CH_2-C<u>H</u>$_2$-CH_2), 2.30 (m, 5H, Me and C<u>H</u>$_2$C=O), 2.87 (t of d, 2H, J_t=7.2Hz, J_d=2.5Hz, C<u>H</u>$_2$-C=C), 7.14 (d, 2H, *J*=8.0Hz, aromatic protons), 7.29 (t, *J*=2.5Hz, 1H, C=C<u>H</u>Ph) and 7.35ppm (d, 2H, *J*=8.0Hz, aromatic protons).

^{13}C-NMR: δ 20.39, 21.65, 29.52, 37.94 (Me and cyclopentane ring saturated carbons), 129.63, 130.76, 132.51, 132.89, 135.25, 139.87 (aromatic and vinylic carbons) and 208.33ppm (C=O).

3.15.9 Preparation of 2-(1-Naphthylidene)cyclopentanone (322i)

2-(1-Naphthylidene)cyclopentanone (322i) was prepared from 1-napthaldehyde (15.6g, 0.1mole), yielding yellow crystals of (322i), (16.1g, 72%), melting range 67-70°C.

IR (KBr pellet): 3060, 2955 (aromatic and aliphatic CH), 1707 (C=O), 1625, 1574, 1506, 1460, 1432, 1403, 1376, 1335, 1301, 1286, 1266, 1225, 1212, 1189, 1170, 1121, 1086, 1027, 1018, 1000, 919, 895, 857, 827, 809, 794, 786, 767, 732 and 634cm^{-1}.

^{1}H-NMR: δ 1.87 (qn, 2H, *J*=7.5Hz, CH_2-C<u>H</u>$_2$-CH_2), 2.35 (t, 2H, *J*=7.8Hz, C<u>H</u>$_2$-C=O), 2.60 (t of d, 2H, J_t=7.1Hz, J_d=2.6Hz, C<u>H</u>$_2$-C=C), 7.42 (m, 4H, aromatic protons), 7.75 (m, 2H, aromatic protons) and 8.05ppm (m, 2H, aromatic proton C=C<u>H</u>Ar).

^{13}C-NMR: δ 20.54, 29.65, 38.22 (cyclopentane ring saturated carbons), 123.93, 125.07, 126.18, 126.64, 127.01, 128.68, 128.80, 129.70, 132.25, 132.27, 133.53, 138.31 (aromatic and vinylic carbons) and 207.71ppm (<u>C</u>=O).

Found: C, 86.07; H, 6.38%. $C_{16}H_{14}O$ requires: C, 86.45; H, 6.35%.

3.15.10 Preparation of 2-Furylidenecyclopentanone (322j)

2-Furylidenecyclopentanone (322j) was prepared from 2-furaldehyde (8.3cm^3, 0.1mole), yielding off-white crystals of (322j), (5.9g, 37%), melting range 58-59°C (lit.[236], 60.5°C).

IR (KBr pellet): 3120, 2960 (aromatic and aliphatic CH), 1700 (C=O), 1617, 1472, 1430, 1401, 1390, 1351, 1287, 1234, 1163, 1135, 1083, 1025, 937, 909, 883, 870, 811, 767 and 626cm^{-1}.

^{1}H-NMR: δ 2.03 (qn, 2H, *J*=7.6Hz, CH_2-C$\underline{H}_2$-CH_2), 2.40 (t, 2H, *J*=7.9Hz, C$\underline{H}_2$-C=O), 2.98 (t of d, 2H, J_t=7.4Hz, J_d=2.6Hz, C$\underline{H}_2$-C=C), 6.51 (d of d, 1H, J_d=3.4Hz, J_d=2.0Hz, furyl H-4), 6.66 (d, 1H, *J*=3.4Hz, furyl H-3), 7.16 (t, 1H, *J*=2.6Hz, C=C$\underline{H}$-furyl) and 7.56ppm (d, 1H, *J*=2.0Hz, furyl H-5).

^{13}C-NMR: δ 19.78, 29.05, 38.06 (cyclopentane ring saturated carbons), 112.54, 115.96, 118.79, 133.66, 144.94, 152.28 (vinylic and furyl carbons) and 207.88ppm (C=O).

3.15.11 Preparation of 2-Benzylidenecyclohexanone (322k)

2-Benzylidenecyclohexanone (322k) was prepared following the procedure used for arylidenecyclopentanones. with the exception that the cyclohexanone enamine was prepared instead of the cyclopentanone enamine, using 10.4cm^3 (0.1 mole) of cyclohexanone. Preparation of the enamine required refluxing of the reaction mixture for 12hrs. Work up of product in the previously described manner yields off white crystals of (322k), (10.9g, 59%), melting range 52-54°C (lit.[192], 54°C).

IR (KBr pellet): 2924, 2870 (aromatic and aliphatic CH), 1673 (C=O), 1597, 1569, 1514, 1490, 1444, 1410, 1317, 1293, 1256, 1237, 1205, 1141, 1067, 1028, 974, 939, 921, 873, 820, 765, 720, 699 and 653cm^{-1}.

^{1}H-NMR: δ 1.74 (m, 2H, C$\underline{H_2}$), 1.91 (m, 2H, C$\underline{H_2}$), 2.52 (t, 2H, J=6.7Hz, C$\underline{H_2}$-C=O), 2.82 (t of d, 2H, J_t=6.4Hz, J_d=2.1Hz, C$\underline{H_2}$-C=C), 7.34 (m, 5H, aromatic protons) and 7.50ppm (t, 1H, J=2.1Hz, C=C$\underline{H}$Ph).

^{13}C-NMR: δ 23.36, 23.85, 28.93, 40.32 (cyclohexane ring saturated carbons), 128.52, 130.29, 135.53, 136.63(aromatic and vinylic carbons) and 201.7ppm (C=O).

3.16 General Procedure for the Preparation of Arylidenecycloalkanone Oximes (283) and (323a-j)

The desired arylidenecyloalkanone (5.0g) was added to a solution containing pyridine (5cm^3) and hydroxylamine hydrochloride (5.0g) in ethanol (50cm^3) in a 250cm^3 round bottom flask. The reaction mixture was then heated under reflux for 30 minutes and allowed to cool. The ethanol was removed by rotary evaporation, chloroform (75cm^3) was added to the flask and its contents transferred to a 250cm^3 separating funnel. The mixture was washed with 1M hydrochloric acid (2x100cm^3) and water (2x100cm^3) and dried over anhydrous magnesium sulphate. The chloroform was removed by rotary evaporation yielding product. The oximes were recrystallised from methanol.

3.16.1 Preparation of 2-(*o*-Nitrobenzylidene)cyclopentanone Oxime (324a)

2-(*o*-Nitrobenzylidene)cyclopentanone oxime (324a) was prepared from 2-(*o*-nitrobenzylidene)cyclopentanone (322a), yielding dark brown crystals of (324a), (4.2g. 78%), melting range 146-148°C (decomp.).

IR (KBr pellet): 3247 (broad, OH), 3045, 2980, 2925 (aromatic and aliphatic CH), 1605 (C=N), 1568, 1525, 1457, 1440, 1423, 1339, 1307, 1294, 1278, 1258, 1199, 1133, 1076, 1052, 1042, 1029, 935, 892, 854, 789, 747, 704, 670 and 608cm^{-1}.

^{1}H-NMR: δ 1.85 (qn, 2H, J=7.4Hz, CH_2-C$\underline{H}_2$-CH_2), 2.63 (t of d, 2H, J_t=7.4Hz, J_d=2.5Hz, C$\underline{H}_2$-C=C), 2.68 (t, 2H, J=7.6Hz, C$\underline{H}_2$-C=N), 7.42 (m, 2H, C=C$\underline{H}$Ph and aromatic proton), 7.49 (m, 1H, aromatic proton), 7.59 (m, 1H, aromatic proton), 8.00 (m, 1H, aromatic proton) and 8.66ppm (broad s, 1H, O$\underline{H}$).

^{13}C-NMR: δ 22.35, 27.16, 31.17 (cyclopentane ring saturated carbons), 118.24, 124.68, 128.00, 130.99, 132.39, 132.65, 140.24, 146.67 (aromatic and vinylic carbons) and 162.51ppm ($\underline{C}$=N).

Found: C, 61.79; H, 5.28; N, 11.77. $C_{12}H_{12}N_2O_3$ requires: C, 62.06; H, 5.21; N, 12.06%.

3.16.2 Preparation of 2-(*p*-Nitrobenzylidene)cyclopentanone Oxime (324b)

2-(*p*-Nitrobenzylidene)cyclopentanone oxime (324b) was prepared from 2-(*p*-nitrobenzylidene)cyclopentanone (322b), yielding dark brown crystals of (324b), (3.9g. 74%), melting range 146-148°C (decomp.).

IR (KBr pellet): 3460 (broad, OH), 3090, 2950 (aromatic and aliphatic CH), 1592 (C=N), 1509, 1421, 1407, 1336, 1199, 1110, 1044, 1023, 937, 922, 908, 883, 857, 840, 812, 778, 747, 706 and 686cm^{-1}.

^{1}H-NMR: δ 1.95 (qn, 2H, *J*=7.5Hz, CH_2-C$\underline{H}_2$-CH_2), 2.71 (t, 2H, *J*=7.9Hz, C$\underline{H}_2$-C=N), 2.84 (t of d, 2H, J_t=7.4Hz, J_d=2.4Hz, C$\underline{H}_2$-C=C), 7.22 (t, 1H, *J*=2.4Hz, C=C$\underline{H}$Ph), 7.53 (d, 2H, *J*=8.4Hz, aromatic protons), 8.22ppm (d, 2H, *J*=8.4Hz, aromatic protons) and 8.99ppm (broad s, 1H, O$\underline{H}$).

^{13}C-NMR: δ 22.45, 27.01, 31.76 (cyclopentane ring saturated carbons), 121.00, 123.76, 129.66, 141.34, 143.55, 147.45 (aromatic and vinylic carbons) and 163.30ppm ($\underline{C}$=N).

Found: C, 62.07; H, 5.43; N, 11.94. $C_{12}H_{12}N_2O_3$ requires: C, 62.06; H, 5.21; N, 12.06%.

3.16.3 Preparation of 2-(*o*-Chlorobenzylidene)cyclopentanone Oxime (324c)

2-(*o*-Chlorobenzylidene)cyclopentanone oxime (324c) was prepared from 2-(*o*-chlorobenzylidene)cyclopentanone (322c) yielding red-brown crystals of (324c), (3.8g, 70%), melting range 176-178°C (decomp.).

IR (KBr pellet): 3200 (broad, OH), 3050, 2880 (aromatic and aliphatic CH), 1613 (C=N), 1589, 1564, 1465, 1435, 1419, 1305, 1292, 1280, 1257, 1221, 1200, 1131, 1047, 1034, 937, 856, 845, 826, 784, 754, 732 and 684cm^{-1}.

^{1}H-NMR: δ 1.86 (qn, 2H, *J*=7.5Hz, CH_2-$C\underline{H}_2$-CH_2), 2.70 (m, 4H, $C\underline{H}_2$-C=N and $C\underline{H}_2$-C=C), 7.23 (m, 2H, aromatic protons), 7.41 (m, 3H, C=C<u>H</u>Ph and aromatic protons), and 8.35ppm (broad s, 1H, O<u>H</u>).

^{13}C-NMR: δ 22.49, 27.09, 31.36 (cyclopentanone ring saturated carbons), 119.54, 126.33, 128.55, 129.58, 129.87, 134.15, 135.16, 138.92 (aromatic and vinylic carbons) and 163.21ppm (<u>C</u>=N).

Found: C, 65.28; H, 5.43; N, 6.05%. $C_{12}H_{12}NOCl$ requires: C, 65.02; H, 5.46; N, 6.32%.

3.16.4 Preparation of 2-(*p*-Chlorobenzylidene)cyclopentanone Oxime (324d)

2-(*p*-Chlorobenzylidene)cyclopentanone oxime (324d) was prepared from 2-(*p*-chlorobenzylidene)cyclopentanone (322d), yielding off-white crystals of (324d), (3.4g, 63%), melting range 117-120°C (decomp.).

IR (KBr pellet): 3350 (broad, OH), 3090, 2980 (aromatic and aliphatic CH), 1653 (C=N), 1587, 1489, 1422, 1405, 1305, 1278, 1259, 1090, 1052, 1010, 944, 929, 894, 873, 817 and 674cm^{-1}.

^{1}H-NMR: δ 1.89 (qn, 2H, *J*=7.5Hz, CH_2-$C\underline{H}_2$-CH_2), 2.68 (t, 2H, *J*=7.6Hz, $C\underline{H}_2$-C=N), 2.77 (t of d, 2H, J_t=7.4Hz, J_d=2.7Hz, $C\underline{H}_2$-C=C), 7.13 (t, 1H, *J*=2.7Hz, C=C<u>H</u>Ph), 7.32 (s, 4H, aromatic protons) and 9.45ppm (broad s, 1H, O<u>H</u>).

^{13}C-NMR: δ 22.45, 27.10, 31.45 (cyclopentane ring saturated carbons), 122.05, 128.55, 130.46, 130.76, 133.10, 135.49, 137.21 (aromatic and vinylic carbons) and 163.62ppm (<u>C</u>=N).

Found: C, 64.93; H, 5.49; N, 6.08%. $C_{12}H_{12}NOCl$ requires: C, 65.02; H, 5.46; N, 6.32%.

3.16.5 Preparation of 2-(o-Methoxybenzylidene)cyclopentanone Oxime (324e)

2-(*o*-Methoxybenzylidene)cyclopentanone oxime (324e) was prepared from 2-(*o*-methoxybenzylidene)cyclopentanone (322e), yielding light brown crystals of (324e), (3.8g, 70%), melting range 130-132°C (decomp.).

IR (KBr pellet): 3200 (broad, OH), 3000, 2950 (aromatic and aliphatic CH), 1597 (C=N), 1487, 1463, 1434, 1421, 1355, 1297, 1288, 1263, 1246, 1221, 1198, 1164, 1136, 1111, 1046, 1027, 933, 888, 869, 851, 841, 832, 779, 750 and 698cm^{-1}.

^{1}H-NMR: δ 1.83 (qn, 2H, *J*=7.5Hz, CH_2-C$\underline{H}_2$-CH_2), 2.66 (t, 2H, *J*=7.6Hz, C$\underline{H}_2$-C=N), 2.72, (t of d, 2H, J_t=7.1Hz, J_d=2.4Hz, C$\underline{H}_2$-C=C), 6.87 (d, 1H, *J*=8.4Hz, aromatic proton), 6.94 (t, 1H, *J*=7.9Hz, aromatic proton), 7.25, (t, 1H, *J*=7.9Hz, aromatic proton), 7.35 (d, 1H, *J*=7.4Hz, aromatic proton), 7.44 (t, 1H, *J*=2.4Hz, C=C$\underline{H}$Ph) and 9.15ppm (broad s, 1H, O$\underline{H}$).

^{13}C-NMR: δ 22.49, 27.15, 31.52 (cyclopentane ring saturated carbons), 55.43 (MeO), 110.32, 118.00, 120.03, 126.13, 128.85, 129.48, 136.72, 157.59 (aromatic and vinylic carbons) and 163.51ppm (C=N).

Found: C, 72.13; H, 7.09; N, 6.28%. $C_{13}H_{15}NO$ requires: C, 71.87; H, 6.96; N, 6.45%.

3.16.6 Preparation of 2-(*p*-Methoxybenzylidene)cyclopentanone Oxime (324f)

2-(*p*-Methoxybenzylidene)cyclopentanone oxime (324f) was prepared from 2-(*p*-methoxybenzylidene)cyclopentanone (322f), yielding light brown crystals of (324f), (3.8g, 71%), melting range 154-156°C.

IR (KBr pellet): 3238 (broad, OH), 3025, 2979 , 2953, 2922 (aromatic and aliphatic CH), 1598 (C=N), 1509, 1461, 1423, 1298, 1251, 1199, 1171, 1112, 1030, 934, 884, 870, 823, 764, 750, 721, 697 and 634cm^{-1}.

^{1}H-NMR: δ 1.88 (qn, 2H, *J*=7.5Hz, CH_2-C$\underline{H}_2$-CH_2), 2.67 (t, 2H, *J*=7.6Hz, C$\underline{H}_2$-C=N), 2.78 (t of d, 2H, J_t=7.4 Hz, J_d=2.6Hz, C$\underline{H}_2$-C=C), 3.82 (s, 3H, OMe), 6.89 (d, 2H, *J*=7.9Hz, aromatic protons), 7.14 (t, 1H, *J*=2.6, C=C$\underline{H}$Ph), 7.36 (d, 2H, *J*=7.9Hz, aromatic protons) and 8.45ppm (broad s, 1H, O$\underline{H}$).

^{13}C-NMR: δ 22.04, 26.60, 30.91 (cyclopentane ring saturated carbons), 54.82 (MeO), 113.38, 122.35, 129.44, 130.25, 133.92, 158.47 (aromatic and vinylic carbons) and 163.51ppm (C=N).

Found: C, 72.03; H, 6.96; N, 6.54%. $C_{13}H_{15}NO$ requires: C, 71.87; H, 6.96; N, 6.45%.

3.16.7 Preparation of 2-(*o*-Methylbenzylidene)cyclopentanone Oxime (324g)

2-(*o*-Methylbenzylidene)cyclopentanone oxime (324g) was prepared from 2-(*o*-methylbenzylidene)cyclopentanone (322g), yielding light brown crystals of (324g) (3.6g, 67%), melting range 74-76°C.

IR (KBr pellet): 3200 (broad, OH), 3025, 2940 (aromatic and aliphatic CH), 1614 (C=N), 1598, 1481, 1459, 1434, 1420, 1392, 1377, 1353, 1287, 1261, 1217, 1045, 1030, 935, 888, 848, 788, 749, 721 and 692cm^{-1}

^{1}H-NMR: δ 1.77 (qn, 2H, *J*=7.4Hz, CH_2-$C\underline{H}_2$-CH_2), 2.30 (s, 3H, Me), 2.63 (m, 4H, $C\underline{H}_2$-C=N and $C\underline{H}_2$-C=C), 7.13 (m, 3H, C=C<u>H</u>Ph and aromatic protons), 7.27 (m, 2H, aromatic protons) and 9.41ppm (broad s, 1H, C=NO<u>H</u>).

^{13}C-NMR: δ 19.54, 22.06, 26.92, 30.97 (Me and cyclopentanone ring saturated carbons), 120.93, 125.05, 127.07, 128.11, 129.62, 135.54, 136.63, 136.89 (aromatic and vinylic carbons) and 163.19ppm (<u>C</u>=N).

Found: C, 77.46; H, 7.54; N, 6.88%. $C_{13}H_{15}NO$ requires: C, 77.58; H, 7.51; N, 6.96%.

3.16.8 Preparation of 2-(*p*-Methylbenzylidene)cyclopentanone Oxime (324h)

2-(*p*-Methylbenzylidene)cyclopentanone oxime (324h) was prepared from 2-(*p*-methylbenzylidene)cyclopentanone (322h), yielding yellow crystals of (324h), (3.6g, 67%), melting range 132-134°C (decomp.) (lit.[235], 139-140°C).

IR (KBr pellet): 3250 (broad, OH), 3090, 2960 (aromatic and aliphatic CH), 1601 (C=N), 1563, 1453, 1428, 1381, 1359, 1311, 1288, 1262, 1178, 1050, 1021, 936, 891, 846, 805, 747 and 713cm^{-1}.

^{1}H-NMR: δ 1.87 (qn, 2H, *J*=7.5Hz, CH_2-C$\underline{H}_2$-CH_2), 2.35 (s, 3H, Me), 2.67 (t, 2H, *J*=7.6Hz, C$\underline{H}_2$-C=N), 2.79 (t of d, 2H, J_t=7.1Hz, J_d=2.6Hz, C$\underline{H}_2$-C=C), 7.12 (m, 3H, C=C$\underline{H}$Ph and aromatic) 7.31 (d, 2H, J=8.4Hz, aromatic protons) and 9.14ppm (broad s, 1H, O$\underline{H}$).

^{13}C-NMR: δ 20.83, 22.05, 26.64, 31.02 (Me and cyclopentanone ring saturated carbons), 122.75, 128.64, 128.84, 133.84, 135.21, 136.92 (aromatic and vinylic carbons) and 163.42ppm (C=N).

Found: C, 77.87; H, 7.63; N, 6.66%. $C_{13}H_{15}NO$ requires: C, 77.58; H, 7.51; N, 6.96%.

3.16.9 Preparation of 2-(1-Naphthylidene)cyclopentanone Oxime (324i)

2-(1-Naphthylidene)cyclopentanone oxime (324i) was prepared from 2-(1-naphthylidene)cyclopentanone (322i), yielding off-white crystals of (324i), (4.3g, 80%), melting range 134-136°C (decomp.).

IR (KBr pellet): 3240 (broad, OH), 3050, 2925 (aromatic and aliphatic CH), 1609 (C=N), 1509, 1420, 1395, 1333, 1291, 1275, 1249, 1237, 1047, 936, 884, 860, 797, 770, 722 and 618cm^{-1}.

^{1}H-NMR: δ 1.81 (qn, 2H, *J*=7.4Hz, CH_2-C$\underline{H}_2$-CH_2), 2.70 (t of d, 2H, J_t=7.4Hz, J_d=2.5Hz, C$\underline{H}_2$-C=C), 2.74 (t, 2H, *J*=7.4Hz, C$\underline{H}_2$-C=N), 7.47 (m, 4H, aromatic protons), 7.77 (m, 1H, aromatic proton), 7.84 (m, 1H, aromatic proton), 7.85 (t, 1H, *J*=2.4Hz, C=C$\underline{H}$Ph), 8.13 (m, 1H, aromatic proton) and 9.70ppm (broad s, 1H, O$\underline{H}$).

^{13}C-NMR: δ 22.46, 25.58, 31.69 (cyclopentane ring saturated carbons), 120.52, 124.52, 124.13, 125.85, 126.11, 126.49, 128.01, 128.43, 131.97, 133.48, 134.03, 138.19 (aromatic and vinylic carbons) and 163.44ppm (C=N).

Found: C, 80.94; H, 6.40; N, 5.79%. $C_{16}H_{15}NO$ requires: C, 80.98; H, 6.37; N, 5.90%.

3.16.10 Preparation of 2-Furylidenecyclopentanone Oxime (324j)

2-Furylidenecyclopentanone oxime (324j) was prepared following the general procedure described, with the exception that only 3.0g of furylidene-cyclopentanone (322j) were used, yielding yellow crystals of (324j), (2.5g, 75.1%), melting range 116-117°C (lit.[236], 116-117°C).

IR (KBr pellet): 3220 (broad, OH), 3066, 3033, 2951, 2931 (aromatic and aliphatic CH), 1661, 1609, 1549, 1482, 1462, 1421, 1390, 1292, 1271, 1256, 1241, 1205, 1053, 1043, 1019, 949, 938, 927, 883, 875, 867, 812, 735 and 694cm^{-1}.

^{1}H-NMR: δ 1.90 (qn, 2H, *J*=7.6Hz, CH_2-CH_2-CH_2), 2.68 (t, 2H, *J*=7.6Hz, CH_2-C=N), 2.84 (t of d, 2H, J_t=7.4Hz, J_d=2.5Hz, CH_2-C=C), 6.38 (d, 1H, *J*=3.4Hz, furyl H-3), 6.44 (d of d, 1H, *J*(d)=3.4Hz, *J*(d)=1.5Hz, furyl H-4), 7.02 (t, 2H, J=2.5Hz, C=CH-furyl), 7.44 (d, 1H, *J*=1.5Hz, furyl H-5), 9.75 (broad s, 1H, OH).

^{13}C-NMR: δ 21.85 (cyclopentane ring saturated carbons), 110.80, 111.10, 111.63, 134.03, 142.51, 153.03 (aromatic and vinylic carbons) and 163.26ppm (C=N).

3.16.11 Preparation of 2-Benzylidenecyclohexanone Oxime (283)

2-Benzylidenecyclohexanone oxime (283) was prepared from 2-benzylidenecyclohexanone (322k), following the same procedure as that for arylidenecyclopentanone oximes, yielding off white crystals of (283), (3.50g, 64.8%), melting range 126-127°C (lit.[192], 126°C).

IR (KBr pellet): 3220 (broad, OH), 3075, 2940 (aromatic and aliphatic CH), 1598 (C=N), 1488, 1445, 1332, 1319, 1297, 1241, 1155, 1090, 982, 967, 957, 920, 909, 890, 865, 820, 765, 736, 697 and 675cm^{-1}.

^{1}H-NMR: δ 1.63 (m, 2H, CH_2-C$\underline{H}_2$-CH_2), 1.72 (m, 2H, CH_2-C$\underline{H}_2$-CH_2), 2.65 (m, 4H, C$\underline{H}_2$-C=N and C$\underline{H}_2$-C=C), 6.89 (s, 1H, aromatic proton), 7.29 (m, 5H, aromatic and vinylic protons) and 9.70ppm (broad s, 1H, O$\underline{H}$).

^{13}C-NMR: δ 23.34, 24.96, 25.02, 29.00 (saturated carbons), 127.11, 127.36, 128.08, 129.68, 135.00, 136.82 (aromatic and vinylic carbons) and 160.30ppm ($\underline{C}$=N).

3.17 General Procedure for the Preparation of Arylidenecycloalkanone Oxime-O-Methyl Ethers (310)-(320)

The desired benzylidenecycloalkanone oxime (2g) was dissolved in acetone ($50cm^3$), in a $250cm^3$ three necked round bottom flask fitted with a reflux condenser and two $25cm^3$ dropping funnels. A solution containing dimethyl sulphate ($5cm^3$) and acetone ($20cm^3$) was placed in one dropping funnel and 40% w/v aqueus sodium hydroxide ($12cm^3$) solution was placed in the other. The two solutions were then added simultaneously, slowly, dropwise with stirring to the oxime solution and the resulting solution was then heated under reflux. The reaction was followed by TLC using a mobile phase of light petroleum / ethyl acetate (90:10) until all the oxime had been used up (approx. one hour). A further $10cm^3$ of the 40% sodium hydroxide solution were then added to the reaction mixture to remove any unreacted dimethyl sulphate, and the acetone was removed by rotary evaporation. Diethyl ether ($50cm^3$) was added to the reaction mixture and this was then transferred to a $100cm^3$ separating funnel and the aqueus layer was run off. The etheral layer was then washed with dil. hydrochloric acid ($2x50cm^3$) and water ($2x50cm^3$), dried over anhydrous magnesium sulphate and the ether was removed by rotary evaporation. A 90:10 mixture of light petroleum / ethyl acetate ($100cm^3$) was added to the resulting oil, this solution was passed through a sintered glass crucible covered with a small layer of silica gel to remove impurities and the light petroleum / ethyl acetate was removed by rotary evaporation, yielding an oil which solidified on cooling. The oxime ethers prepared were recystalised from methanol.

3.17.1 Preparartion of 2-(o-Nitrobenzylidene)cyclopentanone Oxime O-Methyl Ether (310)

2-(*o*-Nitrobenzylidene)cyclopentanone oxime O-methyl ether (310) was prepared from 2-(*o*-nitrobenzylidene)cyclopentanone oxime (324a), yielding white crystals of (310), (1.3g, 62%) melting range 82-84°C.

IR (KBr pellet): 3260, 3220, 2975, 2905, 2840 (aromatic and aliphatic CH), 1645 (C=N), 1595, 1575, 1485, 1462, 1434, 1359, 1301, 1267, 1243, 1186, 1174, 1161, 1112, 1049, 1031, 937, 923, 886, 844, 778, 750 and 700cm^{-1}.

^{1}H-NMR: δ 1.82 (t, 2H, *J*=7.3Hz, CH_2-C$\underline{H}_2$-CH_2), 2.59 (m, 4H, C$\underline{H}_2$-C=N and C$\underline{H}_2$-C=C), 3.98 (s, 3H, C=NOC$\underline{H}_3$), 7.43 (m, 3H, C=C$\underline{H}$Ph and aromatic protons), 7.58 (m, 1H, aromatic proton) and 7.97ppm (m, 2H, aromatic proton).

^{13}C-NMR: δ 22.56, 27.60, 31.22 (cyclopenatane ring saturated carbons), 62.29 (C=NO$\underline{C}$H$_3$), 117.93, 124.69, 127.98, 131.05, 132.50, 132.67, 140.51, 148.51 (aromatic and vinylic protons) and 161.06ppm ($\underline{C}$=N).

UV (methanol): λ_{max} 272nm (ε=13,727), 220nm (ε=5,874).

Found: C, 63.13; H, 5.72; N, 11.08%. $C_{13}H_{14}N_2O_3$ requires: C, 63.40; H, 5.73; N, 11.38%.

3.17.2 Preparartion of 2-(*p*-Nitrobenzylidene)cyclopentanone Oxime O-Methyl Ether (311)

2-(*p*-Nitrobenzylidene)cyclopentanone oxime O-methyl ether (311) was prepared from 2g of 2-(*p*-nitrobenzylidene)cyclopentanone oxime (324b), yielding yellow crystals of (311), (1.2g, 58%) melting range 122-124°C.

IR (KBr pellet), 3190, 2980, 2925 (aromatic and aliphatic CH), 1594 (C=N), 1582, 1513, 1460, 1436, 1422, 1337, 1303, 1269, 1224, 1181, 1118, 1109, 1039, 902, 889, 871, 847, 831, 815, 751, 711, 687 and 662cm^{-1}.

^{1}H-NMR: δ 1.90 (qn, 2H, *J*=7.3Hz, CH_2-C$\underline{H}_2$-CH_2), 2.59 (t, 2H, *J*=7.7Hz, C$\underline{H}_2$-C=N), 2.80 (t of d, 2H, *J*(t)=7.2Hz, *J*(d)=2.5Hz, C$\underline{H}_2$-C=C), 3.99 (s, 3H, C=NOC$\underline{H}_3$), 7.26, (t, 1H, *J*=2.5Hz, C=C$\underline{H}$Ph), 7.53 (d, 2H, *J*=8.4Hz, aromatic protons) and 8.19ppm (d, 2H, *J*=8.4Hz, aromatic protons).

^{13}C-NMR: δ 22.45, 27.21, 31.51 (cyclopentane ring saturated carbons), 62.19 (C=NOC$\underline{H}_3$), 120.39, 123.59, 129.43, 141.42, 143.66, 146.11 (aromatic and vinylic carbons) and 161.55ppm (C=N).

UV (methanol): λ_{max} 346nm (ε=20,182), 268nm (ε=8,801), 206nm (ε=12,013).

Found: C, 63.16; H, 5.71; N, 11.10%. $C_{13}H_{14}N_2O_3$ requires: C, 63.40; H, 5.73; N, 11.38%.

3.17.3 Preparation of 2(*o*-Chlorobenzylidene)cyclopentanone Oxime O-Methyl Ether (312)

2-(*o*-Chlorobenzylidene)cyclopentanone oxime O-methyl ether (312) was prepared from 2-(*o*-chlorobenzylidene)cyclopentanone oxime (324c), yielding (312), a colourless oil, (0.8g, 36%) boiling range 75-79 °C (1mmHg).

IR (thin film): 2970, 2940, 2885 (aromatic and aliphatic CH), 1632 (C=N), 1591, 1468, 1437, 1400, 1351,1298, 1183, 1052, 891, 852, 754, 734 and 686cm^{-1}.

^{1}H-NMR: δ 1.82 (qn, 2H, *J*=7.6Hz, CH_2-$C\underline{H}_2$-CH_2), 2.58 (t, 2H, *J*=7.6Hz, $C\underline{H}_2$-C=N), 2.67 (t of d, 2H, J_t=7.5Hz, J_d=2.5Hz, $C\underline{H}_2$-C=C), 3.95 (s, 3H, C=NO$C\underline{H}_3$), 7.21 (m, 2H, aromatic protons) and 7.40ppm (m, 3H, C=C$\underline{H}$Ph and aromatic protons).

^{13}C-NMR: δ 22.58, 27.47, 31.29 (cyclopentane ring sat. carbons), 62.17 (C=NO$\underline{C}H_3$), 119.34, 126.29, 128.44, 129.54, 129.94, 134.38, 135.32, 139.12 (aromatic and vinylic carbons) and 161.73ppm ($\underline{C}$=N).

UV (methanol): λ_{max} 298nm (ε=16,108), 230nm (ε=9,690), 208m (ε=12,689).

Found: C, 66.09; H, 5.95; N, 5.77%. $C_{13}H_{14}ClNO$ requires: C, 66.24; H, 5.99; N, 5.94%.

3.17.4 Preparation of 2-(*p*-Chlorobenzylidene)cyclopentanone Oxime O-Methyl Ether (313)

2-(*p*-Chlorobenzylidene)cyclopentanone oxime O-methyl ether (313) was prepared from 2-(*p*-chlorobenzylidene)cyclopentanone oxime (324d), yielding white crystals of (313), (1.2g, 55%) melting range 50-51°C.

IR (KBr pellet): 3020, 2980, 2965, 2815 (aromatic and aliphatic CH), 1643 (C=N), 1590, 1489, 1461, 1433, 1417, 1404, 1304, 1290, 1276, 1265, 1219, 1181, 1125, 1104, 1091, 1047, 1009, 968, 962, 950, 924, 897, 867, 848, 825, 721, and 678cm^{-1}.

^{1}H-NMR: δ 1.85 (qn, 2H, *J*=7.3Hz, CH_2-C$\underline{H}_2$-CH_2), 2.57 (t, 2H, *J*=7.6Hz, C$\underline{H}_2$-C=N), 2.73 (t of d, 2H, *J*(t)=7.3Hz, *J*(d)=2.4Hz, C$\underline{H}_2$-C=C), 3.97 (s, 3H, C=NOC$\underline{H}_3$), 7.16 (t, 2H, *J*=2.4Hz, C=C$\underline{H}$Ph) and 7.31ppm (m, 4H, aromatic protons).

^{13}C-NMR: δ 22.64, 26.94, 27.44 (cyclopentane ring saturated carbons), 62.14 (C=NO$\underline{C}H_3$), 121.56, 128.57, 130.44, 132.98, 135.70, 137.47 (aromatic and vinylic carbons) and 162.27ppm ($\underline{C}$=N).

UV (methanol): λ_{max} 306nm (ε=28,070), 228nm (ε=9,607).

Found: C, 66.17; H, 6.03; N, 5.83%. $C_{13}H_{14}ClNO$ requires: C, 66.24; H, 5.99; N, 5.94%.

3.17.5 Preparation of 2-(*o*-Methoxybenzylidene)cyclopentanone Oxime O-Methyl Ether (314)

2-(*o*-Methoxybenzylidene)cyclopentanone oxime O-methyl ether (314) was prepared from 2-(*o*-methoxybenzylidene)cyclopentanone oxime (324e), yielding white crystals of (314), (1.4g, 65%) melting range 62-64°C.

IR (KBr pellet): 3050, 2950, 2900, 2825 (aromatic and aliphatic CH), 1645 (C=N), 1592, 1575, 1486, 1461, 1435, 1423, 1354, 1300, 1290, 1240, 1186, 1166, 1128, 1111, 1048, 1027, 942, 925, 886, 851, 829, 779, 766, 737, 696 and 609cm^{-1}.

^{1}H-NMR: δ 1.63 (qn, 2H, *J*=7.3Hz, CH_2-C$\underline{H}_2$-CH_2), 2.40 (t, 2H, *J*=7.6Hz, C$\underline{H}_2$-C=N), 2.54 (t of d, 2H, J_t=7.3Hz, J_d=2.4Hz, C$\underline{H}_2$-C=N), 3.98, (s, 3H, ArOC$\underline{H}_3$), 4.10 (s, 3H, C=NOC$\underline{H}_3$), 6.71 (d, 1H, *J*=8.1Hz, aromatic proton), 6.77 (t, 1H, *J*=7.4Hz, aromatic proton), 7.08 (m, 1H, aromatic proton), 7.18 (m, 1H, aromatic proton) and 7.31ppm (t, 1H, *J*=2.4Hz, C=C$\underline{H}$Ph).

^{13}C-NMR: δ 22.72, 27.60, 31.52 (cyclopentane ring saturated carbons), 55.49 (PhO$\underline{C}H_3$), 62.08 (C=NO$\underline{C}H_3$), 110.37, 117.73, 120.11, 126.32, 128.82, 129.55, 136.99, 157.67 (aromatic and vinylic carbons) and 162.43ppm ($\underline{C}$=N).

UV (methanol): λ_{max} 318nm (ε=17,000), 230nm (ε12,276), 206nm (ε=17,710).

Found: C, 72.41; H, 7.39; N, 5.84%. $C_{14}H_{17}NO$ requires: C, 72.70; H, 7.41; N, 6.06.

3.17.6 Preparation of 2-(*p*-Methoxybenzylidene)cyclopentanone Oxime O-Methyl Ether (315)

2-(*p*-Methoxybenzylidene)cyclopentanone oxime O-methyl ether (315) was prepared from 2-(*p*-methoxybenzylidene)cyclopentanone oxime (324f), yielding white crystals of (315), (1.3g, 59%) melting range 93-94°C.

IR (KBr): 3000, 2960, 2905, 2840 (aromatic and aliphatic CH), 1648 (C=N), 1605, 1569, 1511, 1463, 1437, 1417, 1300, 1254, 1176, 1114, 1046, 1028, 958, 945, 925, 900, 889, 850, 828, 755, 723 and 705cm^{-1}.

^{1}H-NMR: δ 1.85 (qn, 2H, *J*=7.5Hz, CH_2-$C\underline{H}_2$-CH_2), 2.57 (t, 2H, *J*=7.5Hz, $C\underline{H}_2$-C=N), 2.75 (t of d, 2H, J_t=7.2Hz, J_d=2.0Hz, $C\underline{H}_2$-C=C), 3.84 (s, 3H, ArO$C\underline{H}_3$), 3.99 (s, 3H, C=NO$C\underline{H}_3$), 6.90 (d, 2H, *J*=8.5Hz, aromatic protons), 7.19 (t, 1H, *J*=2.0Hz, C=C$\underline{H}$Ph) and 7.38ppm (d, 2H, *J*=8.5Hz, aromatic protons).

^{13}C-NMR: δ 22.68, 27.50, 31.30 (cyclopentane ring saturated carbons), 55.31 (PhO$\underline{C}H_3$), 62.00 (C=NO$\underline{C}H_3$), 113.86, 122.49, 130.06, 130.71, 134.52, 158.89 (aromatic and vinylic carbons) and 162.82ppm ($\underline{C}$=N).

UV (methanol): λ_{max} 314nm (ε=27,014), 224nm (ε=11,006), 202nm (ε=23,084).

Found: C, 72.42; H, 7.42; N, 5.87%. $C_{14}H_{17}NO$ requires: C, 72.70;H, 7.41; N, 6.06%.

3.17.7 Preparation of 2-(o-Methylbenzylidene)cyclopentanone Oxime O-Methyl Ether (316)

2-(o-Methylbenzylidene)cyclopentanone oxime O-methyl ether (316) was prepared from 2-(*o*-methylbenzylidene)cyclopentanone oxime (324g) yielding white crystals of (316), (1.4g, 67%) melting range 45-47°C.

IR (KBr pellet): 3040, 2950, 2900 (aromatic and aliphatic CH), 1646 (C=N), 1482, 1460, 1437, 1424, 1382, 1297, 1289, 1266, 1220, 1176, 1044, 1010, 990, 952, 921, 891, 865, 850, 831, 792, 752, 745, 724 and 692cm^{-1}.

^{1}H-NMR: δ 1.81 (qn, 2H, *J*=7.6Hz, CH_2-$C\underline{H}_2$-CH_2), 2.41, (s, 3H, Me), 2.61 (t, 2H, *J*=7.6Hz, $C\underline{H}_2$-C=N), 2.69 (t of d, 2H, J_t=7.3Hz, J_d=2.3Hz, $C\underline{H}_2$-C=N), 4.02 (s, 3H, OMe), 7.21 (m, 3H, aromatic protons) and 7.35ppm (m, 2H, C=C$\underline{H}$Ph and aromatic proton).

^{13}C-NMR: δ 19.94, 22.48, 27.47, 31.17 (Ph<u>C</u>H$_3$ and cyclopentane ring sat. carbons), 61.85 (C=NO<u>C</u>H$_3$), 120.89, 125.31, 127.26, 128.21, 129.86, 135.96, 137.06, 137.18 (aromatic and vinylic carbons) and 162.02ppm (<u>C</u>=N).

UV (methanol): λ_{max} 299nm (ε=18,300), 226nm, (ε=8,446).

Found: C, 77.75; H, 7.90; N, 6.17%. $C_{14}H_{17}NO$ requires: C, 78.10;H, 7.96; N, 6.51%.

3.17.8 Preparation of 2-(*p*-Methylbenzylidene)cyclopentanone Oxime O-Methyl Ether (317)

2-(*p*-Methylbenzylidene)cyclopentanone oxime O-methyl ether (317) was prepared from 2-(*p*-methylbenzylidene)cyclopentanone oxime (324h) yielding white crystals of (317), (1.34g, 63%) melting range 63-65°C.

IR (KBr pellet): 3060, 2940, 2825 (aromatic and aliphatic CH), 1645 (C=N), 1608, 1512, 1467, 1436, 1424, 1316, 1292, 1268, 1220, 1181, 1127, 1053, 952, 927, 904, 884, 847, 813, 759, 718 and 704cm^{-1}.

^{1}H-NMR: δ 1.86 (qn, 2H, *J*=7.2Hz, CH_2-<u>C</u>H$_2$-CH_2), 2.37 (s, 3H, PhC<u>H</u>$_3$), 2.59 (t, 2H, *J*=7.5Hz, C<u>H</u>$_2$C=N), 2.79 (t of d, 2H, J_t=7.2Hz, J_d=2.6Hz, C<u>H</u>$_2$-C=C), 4.00 (s, 3H, C=NOC<u>H</u>$_3$), 7.19 (d, 2H, *J*=7.8Hz, aromatic protons), 7.23 (t, 1H, *J*=2.6Hz, C=C<u>H</u>Ph) and 7.33ppm (d, 2H, *J*=7.8Hz, aromatic proton).

^{13}C-NMR: δ 21.38, 22.73, 27.55, 31.46 (Ph<u>C</u>H$_3$ and cyclopentane ring saturated carbons), 62.09 (C=NO<u>C</u>H$_3$), 122.88, 129.18, 129.34, 134.48, 135.88, 137.36 (aromatic and vinylic carbons) and 162.74ppm (<u>C</u>=N).

UV (methanol): λ_{max} 306nm (ε=24,851), 230nm (ε=5,116).

Found: C, 77.93; H, 7.96; N, 6.29%. $C_{14}H_{17}NO$ requires: C, 78.10;H, 7.90; N, 6.17%.

3.17.9 Preparation of 2-(1-Naphthylidene)cyclopentanone Oxime O-Methyl Ether (318)

2-(1-Naphthylidene)cyclopentanone oxime O-methyl ether (318) was prepared from 2-(1-naphthylidene)cyclopentanone oxime (324i). Recrystallisation from methanol yielded yellow crystals of (318), (1.46g, 69%), melting range 109-111°C.

IR (KBr pellet): 3040, 2955, 2940, 2875, 2800 (aromatic and aliphatic CH), 1648 (C=N), 1588, 1507, 1459, 1433, 1421, 1396, 1334, 1293, 1276, 1217, 1186, 1167, 1046, 1012, 922, 915, 892, 863, 852, 801, 777, 751, 731 and 623cm^{-1}.

^{1}H-NMR: δ 1.77 (qn, 2H, *J*=7.4Hz, CH_2-C$\underline{H}_2$-CH_2), 2.64 (m, 4H, C$\underline{H}_2$-C=N, and C$\underline{H}_2$-C=C), 4.02 (s, 3H, C=NOC$\underline{H}_3$), 7.48 (m, 4H, C=C$\underline{H}$Ph and aromatic protons), 7.77 (m, 1H, aromatic proton), 7.84 (m, 2H, aromatic protons) and 8,12ppm (m, 1H, aromatic proton).

^{13}C-NMR: δ 22.57, 27.75, 31.54 (cyclopentane ring saturated carbons), 62.06 (C=NOC$\underline{H}_3$), 119.82, 124.52, 125.14, 125.81, 126.00, 126.49, 127.88, 128.44, 131.93, 133.47, 134.16, 138.89 (aromatic and vinylic carbons) and 161.91ppm (C=N).

UV (methanol): λ_{max} 326nm (ε=16,613), 230nm (ε=26,372), 272nm (ε=28,108).

Found: C, 81.52; H, 6.87; N, 5.14%. $C_{17}H_{17}NO$ requires: C, 81.24; H, 6.82; N, 5.57%.

3.17.10 Preparation of 2-Furylidenecyclopentanone Oxime O-Methyl Ether (319)

2-furylidene cyclopentanone oxime O-methyl ether (319) was prepared from 2g of 2-furylidenecyclopentanone oxime (324j), yielding an oil which was purified by short path distallation under reduced pressure into a sample collection tube to give (319) a yellow oil (0.9g, 42%), boiling range 62-66°C (0.5 mm Hg).

IR (Thin film) 3095, 2955, 2940, 2895, 2810 (aromatic and aliphatic CH), 1650 (C=N), 1556, 1485, 1465, 1437, 1424, 1299, 1271, 1257, 1183, 1151, 1141, 1087, 1051, 1016, 940, 927, 884, 857, 796, 736 and 696cm^{-1}.

^{1}H-NMR: δ 1.84 (qn, 2H, *J*=7.5Hz, CH_2-C$\underline{H}_2$-CH_2), 2.55 (t, 2H, *J*=7.6Hz ,C$\underline{H}_2$-C=N), 2.79 (t of d, 2H, J_t=7.4Hz, J_d=2.8Hz, C$\underline{H}_2$-C=C), 3.88 (s, 3H, C=NOC$\underline{H}_3$), 6.36 (m, 1H, aromatic proton), 6.41 (m, 1H, aromatic proton), 7.02 (t, 1H, *J*=2.5Hz, C=C$\underline{H}$Ph) and 7.42ppm (m, 1H, aromatic proton).

^{13}C-NMR: δ 22.07, 27.62, 31.02 (cyclopentane ring saturated carbons), 61.86 (C=NOC$\underline{H}_3$), 110.28, 110.86, 111.63, 134.29, 142.46, 153.24 (aromatic and vinylic carbons) and 161.82ppm (C=N).

UV (methanol): λ_{max} 320nm (ε=30,601), 224nm (ε=5,545).

Found: C, 69.23; H, 6.79; N, 7.33%. $C_{11}H_{13}NO_2$ requires: C, 69.09; H, 6.85; N, 7.32%.

3.17.11 Preparation of 2-Benzylidenecyclohexanone Oxime O-Methyl Ether (320)

2-Benzylidenecyclohexanone oxime O-methyl ether (320) was prepared from 2-benzylidenecyclohexanone oxime (283), yielding an oil which was purified by short path distallation under reduced pressure into a sample collection tube. On cooling the distilled oil solidified to give (320), an off white, waxy solid (1.0g, 46%), melting range 23.5-25.5°C.

IR (KBr pellet): 3030, 3000, 2940, 2860, 2805 (aromatic and aliphatic CH), 1684 (C=N), 1598, 1491, 1462, 1447, 1438, 1420, 1330, 1303, 1183, 1158, 1071, 1048, 982, 942, 922, 883, 872, 820, 806, 767 and 698cm^{-1}.

^{1}H-NMR: δ 1.63 (m, 2H, cyclohexane ring protons), 1.69 (m, 2H, cyclohexane ring protons), 2.59 (t, 2H, J=6.6Hz, cyclohexane ring protons), 2.66 (t, 2H, J=6.2Hz, cyclohexane ring protons), 3.94 (s, 3H, C=NOC$\underline{H}_3$), 6.92 (s, 1H, C=C$\underline{H}$Ph), 7.24 (m, 1H, aromatic proton) and 7.32ppm (m, 4H, aromatic protons).

^{13}C-NMR: δ 23.39, 24.91, 25.62, 28.96 (cyclopentane ring saturated carbons), 61.63 (C=NO$\underline{C}H_3$), 126.99, 127.43, 127.99, 129.69, 134.80, 136.86 (aromatic and vinylic carbons) and 159.77 ($\underline{C}$=N).

UV (methanol): λ_{max} 276nm (ε=15,940), λ 206nm (ε=12,151).

Found: C, 78.28; H, 7.88; N, 6.75%. $C_{14}H_{17}NO$ requires: C, 78.10; H, 7.96; N, 6.51%.

3.18 Irradiation of 2-(*o*-Nitrobenzylidene)cyclopentanone Oxime O-Methyl ether (310)

2-(*o*-Nitrobenzylidene)cyclopentanone oxime O-methyl ether (310) (217mg, 8.8×10^{-4}moles) in methanol ($300cm^3$) was irradiated under standard conditions, with the reaction being followed by TLC using a mobile phase of 85:15 light petroleum/ethyl acetate. During irradiation a steadily increasing number of products were formed, in low concentrations with no large amount of any one product being noted. After 75 minutes irradiation the photolysis mixture contained a complex mixture of products. At this stage the irradiation was stopped and no attempt was made to isolate any of the products.

3.19 Irradiation of 2-(*p*-Nitrobenzylidene)cyclopentanone Oxime O-Methyl Ether (311)

2-(*p*-Nitorobenzylidene)cyclopentanone oxime O-methyl ether (311) (196mg, 8.0×10^{-4}moles) in methanol ($300cm^3$) was irradiated under standard conditions, with the reaction being followed by TLC using a mobile phase of 85:15 light petroleum/ethyl acetate. As had been seen with the *o*-nitro derivative (310), irradiation led to the formation of a steadily increasing number of products in the photolysis mixture with no appreciable amounts of any one component being formed. The photolysis was ceased after 60 minutes and no attempt was made to separate the components of the complex mixture.

3.20 Irradiation of 2-(*o*-Chlorobenzylidene)cyclopentanone Oxime O-Methyl Ether (312)

2-(*o*-Chlorobenzylidene)cyclopentanone oxime O-methyl ether (312) (183mg, 7.8×10^{-4}moles) in methanol ($300cm^3$) was irradiated under standard conditions, the photolysis being followed by TLC using a mobile phase of 85:15 light petroleum/ethyl acetate. Irradiation led to a steadily increasing number of

products, with no appreciable amounts of any one photoproduct being noted. The irradiation was ceased after 1 hour and due to the complex nature of the photolysis mixture, no attempt was made to separate the products.

3.21 Irradiation of 2-(*p*-Chlorobenzylidene)cyclopentanone Oxime O-Methyl Ether (313)

2-(*p*-Chlorobenzylidene)cyclopentanone oxime O-methyl ether (313) (209mg, 8.7×10^{-4}moles) in $300cm^3$ of methanol was irradiated under standard conditions, with the reaction being followed by TLC using a mobile phase of 85:15 light petroleum/ethyl acetate. As for the *o*-chloro derivative, irradiation led to the formation of a complex mixture of products and no attempt was made to separate the large number of components of the photolysis mixture.

3.22 Irradiation of 2-(*o*-Methoxybenzylidene)cyclopentanone Oxime O-Methyl Ether (314)

2-(*o*-Methoxybenzylidene)cyclopentanone oxime O-methyl ether (314) (239mg, 1×10^{-3}moles) in methanol ($300cm^3$) was irradiated under standard conditions, the photolysis being followed by TLC using a mobile phase of 90:10 light petroleum ether/ethyl acetate. After a short irradiation time (30 minutes) three new spots were detected on TLC analysis, whilst after 1 hour of irradiation only one of these spots remained, formed at the expense of the starting material and the other initially formed products. The irradiation was ceased at this stage, the contents of the photolysis cell were transfered to a $500cm^3$ round bottom flask and the methanol was removed by rotary evaporation yielding a dark coloured oil. The major photoproduct was separated from residual amounts of other products formed using a 1mm chromatotron plate with a mobile phase of 90:10 light petroleum/ethyl acetate followed by recrystallisation from light petroleum b.p. 80-100°C, yielding, as a

light brown solid, 8-methoxy-2,3-dihydro-1*H*-cyclopenta[b]quinoline (340) (98mg, 48%), melting range 76-77°C.

IR (KBr pellet): 3070, 2952, 2927, 2836 (aromatic and aliphatic CH), 1613, 1573, 1473, 1433, 1399, 1367, 1311, 1259, 1219, 1193, 1119, 1065, 958, 911, 878, 811 and 759cm^{-1}.

^{1}H-NMR: δ 2.21 (qn, 2H, *J*=7.6Hz, CH_2-C$\underline{H_2}$-CH_2), 3.09 (t, 2H, *J*=7.4Hz, C$\underline{H_2}$), 3.15 (t, 2H, *J*=7.6Hz, C$\underline{H_2}$), 3.99 (s, 3H, MeO), 6.81 (d, 1H, *J*=7.9Hz, aromatic proton), 7.51 (t, 1H, *J*=8.1Hz, aromatic proton), 7.61 (d, 1H, *J*=8.4Hz, aromatic proton) and 8.33ppm (s, 1H, aromatic proton).

^{13}C-NMR: δ 23.61, 30.64, 34.62 (ring saturated carbons), 55.68 (OMe), 103.62, 119.56, 120.89, 125.06, 128.17, 134.76, 148.34, 155.07 and 168.05ppm (aromatic carbons).

UV (methanol): λ_{max} 308nm (ε=2,616), 248nm (ε=21,937), 208nm (ε=12,689).

Found: C, 78.29; H, 6.62; N, 6.85%. $C_{13}H_{13}NO$ requires: C, 78.36; H, 6.58; N, 7.03%.

3.23 Irradiation of 2-(*p*-Methoxybenzylidene)cyclopentanone Oxime O-Methyl Ether (315)

2-(*p*-Methoxybenzylidene)cyclopentanone oxime O-methyl ether (315) (222mg, 9.6x10^{-1}moles) in methanol (300cm^3) was irradiated under standard conditions, the photolysis being followed by TLC using a mobile phase of 90:10 light petroleum/ethyl acetate. During the first 30 minutes of irradiation, three new spots were seen to be formed on TLC, at the expense of the starting

material, whilst over the next 30 minutes one of these spots became the major component of the photolysis mixture at the expense of the starting material and other initially formed products. The irradiation was ceased at this stage, the contents of the photolysis cell were transfered to a 500cm^3 round bottom flask and the methanol was removed by rotary evaporation yielding a dark coloured oil. The major photoproduct was separated from the other minor components, using a 1mm chromatotron plate with a mobile phase of 90:10 light petroleum/ethyl acetate followed by recrystallisation from light petroleum b.p. 80-100°C, yielding, as a brown solid, 6-methoxy-2,3-dihydro-1*H*-cyclopenta[b]quinoline (341) (110mg, 53%), melting range 58-60°C.

IR (KBr pellet): 3014, 2952, 2831 (aromatic and aliphatic CH), 1620, 1569, 1499, 1467, 1450, 1411, 1379, 1369, 1301, 1278, 1262, 1227, 1201, 1168, 1150, 1132, 1087, 1028, 961, 914, 876, 845, 814, 767 and 659cm^{-1}.

^{1}H-NMR: δ 2.20 (qn, 2H, *J*=7.5Hz, $CH_2C\underline{H}_2CH_2$), 3.06 (t, 2H, *J*=7.4Hz, $C\underline{H}_2$), 3.15 (t, 2H, *J*=7.6Hz, $C\underline{H}_2$), 3.93 (s, 3H, OMe), 7.12 (d of d, 1H, *J*(d)=8.8Hz, *J*(d)=2.2Hz, aromatic proton), 7.37 (d, 1H, *J*=2.2Hz, aromatic proton), 7.62 (d, 1H, *J*=8.8Hz, aromatic proton) and 7.82ppm (s, 1H, aromatic proton).

^{13}C-NMR: δ 23.58, 30.32, 34.59 (ring saturated carbons), 55.35 (OMe), 106.95, 118.20, 122.34, 128.30, 130.23, 133.31, 148.98, 159.86 and 167.98ppm (aromatic carbons).

UV (methanol): λ_{max} 336nm (ε=1,191), 236nm (ε=8,433), 212nm (ε=24,349).

Found: C, 78.27; H, 6.49; N, 7.13%. $C_{13}H_{13}NO$ requires: C, 78.36; H, 6.58; N, 7.03%.

3.24 Irradiation of 2-(*o*-Methylbenzylidene)cyclopentanone Oxime O-Methyl Ether (316)

2-(*o*-Methylbenzylidene)cyclopentanone oxime O-methyl ether (316) (195mg, 9.1×10^{-4}moles) in methanol ($300cm^3$) was irradiated under standard conditions, the photolysis being followed by TLC using a mobile phase of 90:10 pet ether/ethyl acetate. Two new spots were noted on TLC after a short period, whilst further irradiation led to the formation of a new spot which gradually became the major component of the photolysis mixture. After 3 hours the irradiation was ceased, the contents of the photolysis cell were transfered to a $500cm^3$ round bottom flask and the methanol was removed by rotary evaporation yielding a dark coloured oil. The major photoproduct was purified by separation using a 1mm chromatotron plate with a mobile phase of 90:10 light petroleum/ethyl acetate followed by recrystallisation from petroleum b.p. 80-100°C, yielding, as a light yellow solid, 8-methyl-2,3-dihydro-1*H*-cyclopenta[b]quinoline (345) (58mg, 35%), melting range 64-65°C.

IR (KBr pellet): 3058, 2957, 2895, 2861, 2837 (aromatic and aliphatic CH), 1609, 1572, 1494, 1455, 1424, 1399, 1374, 1364, 1311, 1229, 1203, 1152, 1114, 1039, 970, 909, 892, 873, 810, 756, 695, 649 and $627cm^{-1}$.

^{1}H-NMR: δ 2.21 (qn, 2H, *J*=7.5Hz, CH_2-$C\underline{H}_2$-CH_2), 2.65 (s, 3H, Me), 3.11 (t, 2H, *J*=7.4Hz, $C\underline{H}_2$), 3.16 (t, 2H, *J*=7.4Hz, $C\underline{H}_2$), 7.28 (d, 1H, *J*=7.4Hz, aromatic proton), 7.50 (t, 1H, *J*=7.9Hz, aromatic proton), 7.87 (d, 1H, *J*=8.4Hz, aromatic proton) and 8.07ppm (s, 1H, aromatic proton).

^{13}C-NMR: δ 18.83, 23.65, 30.72, 34.50 (saturated carbons), 126.12, 126.53, 126.75, 126.89, 127.94, 133.98, 135.22, 147.68 and 167.23ppm (aromatic carbons).

UV (methanol): λ_{max} 322nm (ε=4,752), 240nm (ε=29,793), 206nm (ε=30,436).

Found: C, 85.35; H, 7.06; N, 7.38%. $C_{13}H_{13}N$ requires: C, 85.21; H, 7.15; N, 7.64%.

3.25 Irradiation of 2-(*p*-Methylbenzylidene)cyclopentanone Oxime O-Methyl Ether (317)

2-(*p*-Methylbenzylidene)cyclopentanone oxime O-methyl ether (317) (212mg, $9.8x10^{-4}$moles) in methanol ($300cm^3$) was irradiated under standard conditions, the photolysis being followed by TLC using a mobile phase of 90:10 pet ether/ethyl acetate. Two new spots were noted on TLC after a short irradiation time (30 minutes). After further irradiation (1 hour), the formation of a third new spot was noted, with the gradual disappearance of the starting material and those products formed initially. Prolonged irradiation (3 hours) led to the almost complete disappearance of the starting material and products initially formed with the final product formed being the major component of the photolysis mixture. The irradiation was ceased at this stage, the contents of the photolysis cell were transfered to a $500cm^3$ round bottom flask and the methanol was removed by rotary evaporation yielding a dark coloured oil. The major photoproduct was purified by separation using a 1mm chromatotron plate with a mobile phase of 90:10 light petroleum/ethyl acetate followed by recrystallisation from petroleum b.p. 80-100°C, yielding a light yellow solid, 6-methyl-2,3-dihydro-1*H*-cyclopenta[b]quinoline (346) (62mg, 37%), melting range 86-88°C.

IR (KBr pellet): 3032, 2948, 2924 (aromatic and aliphatic CH), 1626, 1566, 1498, 1455, 1438, 1427, 1411, 1360, 1305, 1277, 1223, 1152, 1090, 1035, 1009, 923, 881 and $808cm^{-1}$.

^{1}H-NMR: δ 2.20 (qn, 2H, *J*=7.5Hz, CH_2-$C\underline{H_2}$-CH_2), 2.54 (s, 3H, Me), 3.07 (t, 2H, *J*=7.1Hz, $C\underline{H_2}$), 3.15 (t, 2H, *J*=7.6Hz, $C\underline{H_2}$), 7.30 (d, 1H, *J*=8.2Hz, aromatic proton), 7.63 (d, 1H, *J*=8.2Hz, aromatic proton), 7.79 (s, 1H, aromatic proton) and 7.85ppm (s, 1H, aromatic proton).

^{13}C-NMR: δ 21.82, 23.66, 30.48, 34.63 (saturated carbons), 125.37, 127.07, 127.70, 128.98, 130.15, 131.93, 134.73, 138.49 and 167.80ppm (aromatic carbons).

UV (methanol): λ_{max} 326nm (ε=3,605), 236nm (ε=11,894), 210nm (ε=18,998).

Found: C, 85.17; H, 7.09; N, 7.79%. $C_{13}H_{13}N$ requires: C, 85.21; H, 7.15; N, 7.64%.

3.26 Irradiation of 2-(1-Naphthylidene)cyclopentanone Oxime O-Methyl Ether (318)

2-(1-Naphthylidene)cyclopentanone oxime O-methyl ether (318) (309mg $1.2x10^{-3}$moles) in methanol (300cm^3) was irradiated under standard conditions, the photolysis being followed by TLC using a mobile phase of 90:10 light petroleum/ethyl acetate. After irradiation for 15 minutes, three new spots had been formed on TLC at the expense of the starting material, whilst after a further 30 minutes of irradiation the starting material and all but one of the initially formed spots were only present in small quantities, the other photoproduct being the major component of the photolysis mixture. The photolysis was ceased at this stage, the contents of the photolysis cell were transfered to a 500cm^3 round bottom flask and the methanol was removed by rotary evaporation yielding a dark coloured oil. The major photoproduct was separated using a 1mm chromatotron plate with a mobile phase of 90:10 light

petroleum/ethyl acetate and recrystallised from petroleum b.p. 80-100°C, yielding brown solid, 9,10-dihydro-*8H*-cyclopenta[b]benzo[f]quinoline (347) by analysis (185mg, 68.8%), melting range 126-128°C.

IR (KBr pellet): 3058, 3038, 2955, 2929 (aromatic and aliphatic CH), 1612, 1567, 1485, 1444, 1426, 1406, 1380, 1354, 1279, 1231, 1191, 1163, 1122, 1029, 1006, 983, 946, 902, 877, 867, 838, 754, 746 and 699cm^{-1}.

^{1}H-NMR: δ 2.27 (qn, 2H, *J*=7.5Hz, CH_2-C$\underline{H_2}$-CH_2), 3.22 (m, 4H, ring protons), 7.61 (t, 1H, *J*=7.4Hz, aromatic proton), 7.66 (t, 1H, *J*=7.4Hz, aromatic proton), 7.92 (m, 3H, aromatic protons), 8.60 (d, 1H, *J*=7.8Hz, aromatic proton) and 8.74ppm (s, 1H, aromatic proton).

^{13}C-NMR: δ 23.66, 30.92, 34.47 (saturated carbons), 122.36, 123.99, 125.75, 126.60, 126.69, 127.91, 128.61, 129.63, 129.82, 131.48, 135.82, 147.08 and 147.08ppm (aromatic carbons).

UV (methanol): λ_{max} 350nm (ε=6,880), 334nm (ε=5,780), 280nm (ε=17,190), 236nm (ε=35,831).

Found: C, 87.84; H, 6.07; N, 6.12%. $C_{16}H_{13}N$ requires: C, 87.64; H, 5.98; N, 6.39%.

3.27 Irradiation of 2-Furylidenecyclopentanone Oxime O-Methyl Ether (319)

2-Furylidenecyclopentanone oxime O-methyl ether (319) (214mg, 1.1x10^{-3}moles) in methanol (300cm^3) was irradiated under standard conditions, the photolysis being followed by TLC using a mobile phase of 90:10 light

petroleum/ethyl acetate. Three new spots were noted on TLC after a short period of irradiation (30 minutes), whilst further irradiation led to one of these products becoming the major component of the photolysis mixture. After 1.5 hours the irradiation was ceased, the contents of the photolysis cell were transfered to a 500cm^3 round bottom flask and the methanol was removed by rotary evaporation yielding a dark coloured oil. The major photoproduct was purified by separation using a 1mm chromatotron plate with a mobile phase of 90:10 light petroleum/ethyl acetate followed by recrystallisation from petroleum b.p. 80-100°C, yielding an off white solid, 6,7-dihydro-5*H*-furo[3,2-b]cyclopenta[e]pyridine (349) (58mg, 45%), melting range 64-65°C.

IR (KBr pellet): 3118, 2898, 2847 (aromatic and aliphatic CH), 1575, 1531, 1434, 1395, 1334, 1266, 1209, 1154, 1121, 1066, 1019, 913, 887, 872, 784 and 743cm^{-1}.

^{1}H-NMR: δ 2.15 (qn, 2H, *J*=7.4Hz, CH_2-C$\underline{H}_2$-CH_2), 2.97 (t, 2H, *J*=7.4Hz, C$\underline{H}_2$), 3.02 (t, 2H, *J*=7.4Hz, C$\underline{H}_2$), 6.84 (d, 1H, *J*=2.2Hz, aromatic proton), 7.51 (s, 1H, aromatic proton) and 7.70ppm (d, 1H, *J*=2.2Hz, aromatic proton).

^{13}C-NMR: δ 24.14, 30.70, 33.65 (saturated carbons), 107.68, 114.64, 133.36, 145.67, 147.31, 147.74 and 162.15ppm (aromatic carbons).

UV (methanol): λ_{max} 298nm (ε=4,847), 238nm (ε=1,678), 206nm (ε=5,045).

Found: C, 75.59; H, 5.65; N, 8.57%. $C_{10}H_9NO$ requires: C, 75.45; H, 5.70; N, 8.80%.

3.28 Irradiation of 2-Benzylidenecyclohexanone Oxime O-Methyl Ether (320)

2-Benzylidenecyclohexanone Oxime O-methyl ether (320) (194mg $9.0x10^{-4}$moles) in methanol ($300cm^3$) were photolysed under standard conditions, the reaction being followed by TLC using a mobile phase of 95:5 light petroleum/ethyl acetate. After 15 minutes of irradiation three new spots had appeared on TLC analysis. On further irradiation one of these components became the major component of the photolysis mixture at the expense of the starting material and the other photoproducts initially formed. The photolysis was ceased after 45 minutes, the contents of the photolysis cell were transfered to a $500cm^3$ round bottom flask and the methanol was removed by rotary evaporation yielding a dark coloured oil. The major photoproduct was separated from the other minor components of the photolysis mixture using a 1mm chromatotron plate with a mobile phase of 90:10 light petroleum/ethyl acetate. Recrystallisation from petroleum b.p. 80-100°C, yielded, as an off white solid, 1,2,3,4-tetrahydroacridine (289) (95mg, 57.6%), melting range 52-53°C (lit.[229], 54.5°C).

IR (KBr pellet), 3055, 2940, 2875 (aromatic and aliphatic CH), 1623, 1600, 1562, 1492, 1438, 1414, 1242, 1151, 1010, 966, 913, 846, 805, 778, 748 and $614.4cm^{-1}$.

^{1}H-NMR: δ 1.89 (m, 2H, C$\underline{H_2}$), 1.99 (m, 2H, C$\underline{H_2}$), 2.98 (t, 2H, *J*=6.1Hz, C$\underline{H_2}$), 3.13 (t 2H, *J*=6.4Hz, C$\underline{H_2}$), 7.43 (t, 1H, *J*=8.0Hz, aromatic proton), 7.60 (t, 1H, *J*=8.2Hz, aromatic proton), 7.69 (d, 1H, *J*=7.8Hz, aromatic proton), 7.80 (s, 1H, aromatic proton) and 7.97ppm (d, 1H, *J*=8.4Hz, aromatic proton).

^{13}C-NMR: δ 22.90, 23.23, 29.26, 33.56 (saturated carbons), 125.54, 126.89, 127.19, 128.23, 128.51, 130.98, 135.02, 146.56 and 159.32ppm (aromatic carbons).

3.29 Preparation of 2-Diphenylmethylenecyclopentanone (351)

Bromobenzene (21cm^3, 0.2moles) in dry diethyl ether (80cm^3) was added dropwise with stirring to magnesium turnings (5.1g, 0.2moles) and diethyl ether (20cm^3) in a 250cm^3 round bottom flask. After addition was complete the mixture was heated under reflux for 20 minutes and then 2,2-ethylenedioxycyclopentanonecarboxylate (353) (19.6g, 0.1moles, prepared by condensation of 2-cyclopentanonecarboxylate (352) with ethylene glycol) in dry diethyl ether (45cm^3) was slowly added, with stirring, and the resulting mixture was heated under reflux for a further 30 minutes. The reaction mixture was cooled and saturated aqueus ammonium chloride solution (120cm^3) was added. The contents of the flask were then transferred to a separating funnel, the etheral layer was separated and the aqueus layer was washed with diethyl ether (2x50cm^3). The etheral solutions were combined and the ether removed by rotary evaporation to yield a yellow oil. The oil was added to a mixture of methanol (50cm^3), water (35cm^3) and conc. hydrochloric acid (2.5cm^3), and this mixture was then heated under reflux with vigorous stirring for 5 hours. The reaction mixture was allowed to cool. The yellow solid which crystallised from solution was filtered off and then recrystallised from methanol yielding yellow crystals of 2-diphenylmethylenecyclopentanone (351) (5.9g, 24%), melting range 115-116°C (lit., 115-116°C).

IR (KBr pellet): 3049, 3025, 2945, 2900 (aromatic and aliphatic CH), 1701 (C=O), 1587, 1568, 1490, 1459, 1442, 1407, 1323, 1296, 1276, 1197, 1171, 1074, 1056, 1031, 1007, 932, 838, 822, 771, 755, 701 and 608cm^{-1}.

^{1}H-NMR: δ 1.91 (qn, 2H, *J*=7.2Hz, CH_2-C$\underline{H}_2$-CH_2), 2.36 (t, 2H, *J*=7.5Hz, C$\underline{H}_2$), 2.81 (t, 2H, *J*=7.0Hz, C$\underline{H}_2$), 7.12 (m, 2H, aromatic protons), 7.28 (m, 2H, aromatic protons) and 7.31ppm (m, 6H, aromatic protons).

^{13}C-NMR: δ 20.50, 32.94, 39.78 (saturated carbons), 127.80, 127.96, 128.36, 129.42, 129.60, 134.31, 140.12, 141.78, 148.27 (aromatic and olefinic carbons) and 206.56ppm (C=O).

3.30 Preparation of 2-Diphenylmethylenecyclopentanone Oxime (355)

2-Diphenylmethylenecyclopentanone (351) (5.0g, 0.02moles) was dissolved in ethanol (50cm^3) containing pyridine (5cm^3) and hydroxylamine hydrochloride (5.0g, 0.07moles) in a 100cm^3 round bottom flask. The mixture was heated under reflux for 1 hour, cooled and the ethanol was removed by rotary evaporation. Water (50cm^3) was added to the flask and the mixture was allowed to stand. The oxime precipitated from solution and was removed by suction filtration. The product was washed with water, dried and recrystallised from methanol, yielding off white crystals of (355), (3.9g, 74%), melting range 178-180°C.

IR (KBr pellet): 3200 (broad, OH), 3080, 2966, 2884 (aromatic and aliphatic CH), 1649 (C=N), 1598, 1575, 1488, 1442, 1421, 1317, 1296, 1239, 1215, 1188, 1127, 946, 931, 897, 871, 846, 827, 769, 729, 701, 651 and 615cm^{-1}.

^{1}H-NMR: δ 1.72 (qn, 2H, *J*=7.3Hz, CH_2-C$\underline{H}_2$-CH_2), 2.54 (m, 4H, C$\underline{H}_2$-C=N and C$\underline{H}_2$-C=C), 7.12 (m, 4H, aromatic protons), 7.24 (m, 6H, aromatic protons) and 7.85ppm (broad s, 1H, C=NO$\underline{H}$).

^{13}C-NMR: δ 21.92, 27.77, 34.40 (saturated carbons), 126.84, 127.17, 127.75, 128.14, 129.55, 133.97, 139.42, 142.15, 143.10 (aromatic and olefinic carbons) and 162.08ppm (C=N).

Found: C, 81.97; H, 6.61; N, 5.12%. $C_{18}H_{17}NO$ requires: C, 82.10; H, 6.51; N, 5.32%.

3.31 Preparation of 2-Diphenylmethylenecyclopentanone Oxime O-Methyl Ether (321)

2-Diphenylmethylenecyclopentanone oxime (355) (3.0g, 0.011moles) was dissolved in acetone (50cm^3) in a 250cm^3 round bottom flask fitted with a reflux condenser and two dropping funnels. 40% Aqueus sodium hydroxide solution (10cm^3) was placed in one dropping funnel and dimethyl sulphate (4.5g, 0.036moles) in acetone (10cm^3) were placed in the other. The two solutions were simultaneously added, slowly, with stirring, to the oxime solution and after addition was completed the reaction mixture was heated under reflux with continous stirring for 1 hour. The reaction mixture was cooled, the acetone was removed by rotary evaporation and water (50cm^3) and diethyl ether (50cm^3) were added to the flask. The contents of the flask were then transferred to a 250cm^3 separating funnel and the etheral layer was removed. The aqueus layer was washed with ether (2x30cm^3), the ether extracts were combined, dried over anhydrous magnesium sulphate and the ether was removed by rotary evaporation yielding a dark yellow oil. The oil was distilled using a micro distillation apparatus to yield 2-diphenylmethylenecyclopentanone oxime O-methyl ether (321) (1.2g, 38%) a yellow oil, boiling point 55-60°C (1.0mbar).

IR (Thin Film): 3095, 3065, 3040, 2965, 2940, 2895, 2845, 2810 (aromatic and aliphatic CH), 1632, 1599, 1492, 1464, 1443, 1423, 1256, 1221, 1179, 1076, 1046, 885, 853, 763, 740, 698 and 650cm^{-1}.

^{1}H-NMR: δ 1.66 (qn, 2H, *J*=7.4Hz, CH_2-C$\underline{H}_2$-CH_2), 2.47 (t, 2H, *J*=7.1Hz, C$\underline{H}_2$), 2.52 (t, 2H, *J*=7.3Hz, C$\underline{H}_2$), 3.43 (s, 3H, C=NOC$\underline{H}_3$), and 7.09-7.23ppm (m, 10H, aromatic protons).

^{13}C-NMR: δ 22.10, 27.77, 33.91 (saturated carbons), 61.45 (C$\underline{H}_3$), 126.41, 126.99, 127.55, 127.60, 129.40, 129.50, 134.04, 139.31, 142.37, 142.79 (aromatic and olefinic carbons) and 160.65ppm (C=N).

UV (methanol): λ_{max} 298nm (ε=7,229), 2345nm (ε=8,530), 206nm (ε=12,621).

Found: C, 82.14; H, 6.95; N, 5.23%. $C_{19}H_{19}NO$ requires: C, 82.28; H, 6.90; N, 5.05%.

3.32 Irradiation of 2-Diphenylmethylenecyclopentanone Oxime O-Methyl Ether (321)

2-Diphenylmethylenecyclopentanone oxime O-methyl ether (321) (250mg, 9.0x10^{-4}moles) in methanol (300cm^3) was irradiated under standard conditions, with the reaction being followed by TLC using a mobile phase of 95:5 light petroleum/ethyl acetate. After 5 minutes formation of a new product was noted and after 10 minutes all of the oxime ether had been used up with only one photoproduct being formed. Prolonged irradiation led to a large number of photoproducts. A second 250mg sample of the oxime ether was irradiated under the same conditions, with the reaction being stopped after 10

minutes. The methanol was removed by rotary evaporation and the photoproduct was recrystallised from methanol to yielding 9-phenyl-2,3-dihydro-1*H*-cyclopenta[b]quinoline (356), an off white solid (160mg, 72%), melting range 132-134°C (lit.[231], 134-135°C).

IR (KBr pellet): 3058, 2965, 2917 (aromatic and aliphatic CH), 1608, 1589, 1571, 1486, 1436, 1425, 1385, 1342, 1311, 1274, 1210, 1179, 1142, 1078, 1026, 766, 724, 704, 668 and 612cm^{-1}.

^{1}H-NMR: δ 2.16 (qn, 2H, J=7.5Hz, CH_2-C$\underline{H_2}$-CH_2), 2.90 (t, 2H, J=7.5Hz, ring C$\underline{H_2}$), 3.24 (t, 2H, J=7.5Hz, ring C$\underline{H_2}$), 7.36 (m, 3H, aromatic protons), 7.49 (m, 3H, aromatic protons), 7.62 (m, 2H, aromatic protons) and 8.08ppm (d, 1H, J=8.4Hz, aromatic proton).

^{13}C-NMR: δ 23.42, 30.22, 35.08 (saturated carbons), 125.39, 125.54, 126.09, 127.88, 128.13, 128.39, 128.68, 129.18, 133.55, 136.62, 142.59, 147.81 (aromatic carbons) and 167.31 (aromatic $\underline{C}$=N).

3.33 Thermolysis of 2-Diphenylmethylenecyclopentanone Oxime O-Methyl Ether (321)

Methanol: 2-Diphenylmethylenecyclopentanone oxime O-methyl ether (321) (50mg, 1.8x10^{-4}moles) was dissolved in methanol (50cm^3) and placed in a 100cm^3 round bottom flask. The solution was heated under reflux for 10 hours and TLC analysis was performed on the solution at hourly intervals. No formation of products was noted by TLC. After 10 hours the solution was cooled and the methanol was removed by rotary evaporation, yielding a solid An IR spectrum of the solid was recorded, which showed it to be recovered starting material by comparison of the IR to that of the oxime ether (321).

Ethylene glycol: 2-Diphenylmethylenecyclopentanone oxime O-methyl ether (321) (50mg, $1.8x10^{-4}$moles) was dissolved in ethylene glycol ($50cm^3$) and placed in a $100cm^3$ round bottom flask. The solution was heated under reflux for 10 hours and TLC analysis of the solution was taken at hourly intervals. No formation of products was noted by TLC. After 10 hours the solution was cooled and the etylene glycol was removed by vacuum distillation, yielding solid. An IR spectrum of the solid was recorded, which showed the solid to be recovered starting material by comparison of the spectrum with that of the oxime ether (321).

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