Quinoline synthesis: scope and regiochemistry of photocyclisation of substituted benzylidenecyclopentanone *O*-alkyl and *O*-acetyloximes.

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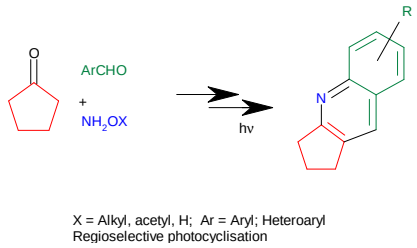
Irradiation of substituted 2-benzylidenecyclopentanone *O*-alkyl and *O*-acetyloximes in methanol provides a convenient synthesis of alkyl, alkoxy, hydroxy, acetoxy, amino, dimethylamino and benzo substituted annulated quinolines. *para*-Substituents yield 6-substituted-2,3-dihydro-1*H*-cyclopenta[*b*]quinolines with 8-substituted products being obtained from *ortho*-substituted starting materials. Reactions of *meta*-substituted precursors are highly regioselective, with alkyl substituents leading to 5-substituted 2,3-dihydro-1*H*-cyclopenta[*b*]quinolines and more strongly electron-donating substituents generally resulting in 7-substituted products. 2-Furylmethylene and 2-thienylmethylene analogues yield annulated furo- and thieno-[2,3*e*]pyridines respectively. Sequential *E*- to *Z*- benzylidene group isomerisation and six π-electron cyclisation steps result in formation of a short-lived dihydroquinoline intermediate which spontaneously aromatises by elimination of an alcohol or acetic acid. For 2-benzylidenecyclopentanone *O*-allyloxime, singlet excited states are involved in both steps.

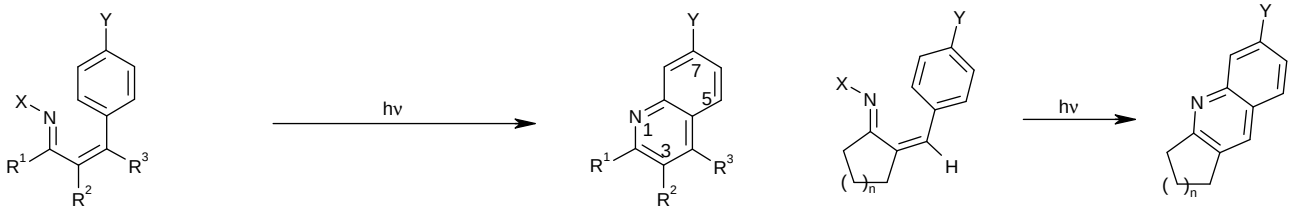


X = Alkyl, acetyl, H; Ar = Aryl; Heteroaryl
Regioselective photocyclisation

Introduction

The quinoline nucleus is widely distributed in nature and is important in the fields of medicinal chemistry and agrochemicals.[1] Consequently, though there are numerous syntheses available for quinoline derivatives,[2] versatile routes to new quinoline intermediates from readily accessible precursors are of interest. Among these have been a limited number of reports of quinoline formation from photocyclisation of β-phenyl-α,β-unsaturated oximino systems (Scheme 1).[3] The open-chain oxime **1a,**[4] *O*-benzoyloximes **1b-e**[5] and *O*-acetyloximes **1f-i**[6] underwent 6π-electron cyclisation, involving both the carbon-nitrogen double bond and the β-aryl group, followed by elimination of water or benzoic acid, to yield the corresponding quinolines **2a-g**, respectively. In contrast, *O*-methyloximes **1j** and **1k** underwent only competing geometrical isomerisation at the carbon-carbon and carbon-nitrogen double bonds on direct and triplet sensitised excitation resulting, in both cases, in a photostationary state comprising the four possible geometrical isomers, but without accompanying cyclisation.[7,8]

Prerequisites for photocyclisation are (a) a *Z*-configuration at the α,β-double bond, achieved by initial geometrical photoisomerisation, and (b) significant contribution from



1a	X = OH; R^1 = Me; R^2 = Ph; R^3 = H; Y = H	**2a**			
1b-e	X = OBz; $R^1 = R^2$ = Ph; R^3 = H; Y = H, Me, OMe, Cl	**2b-e**	**3a-d**	X = OH n = 1, 2, 3, 4 Y = H	**4a-d**
1f,g	X = OAc; R^1 = Me; R^2 = Ph, 2-MeOC_6H_4; R^3 = CONEt_2; Y = H	**2f,g**	**3e**	X = OAc n = 2 Y = H	**4e**
1h,i	X = OAc; R^1 = Ph; R^2 = Ph, 2-MeC_6H_4; R^3 = CONEt_2; Y = H	**2h,i**	**3f**	X = OH n = 2 Y = Me	**4f**
1j,k	X = OMe; R^1 = H, Me; $R^2 = R^3$ = H; Y = H	-			
1l,m	X = OMe; R^1-R^2 = 2,2'-C_6H_4-C_6H_4, 1,8-$C_{10}H_6$; R^3 = CONEt_2; Y = H	**2l,m**			

Scheme 1 Quinolines from photocyclisation of oximino systems.

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† Electronic Supplementary Information (ESI) available: Experimental details and spectral data for the precursors; additional quinoline data. See http://dx.doi.org/10.1039/b000000x/

conformers with an *s*-cis orientation at the R^1C-CR^2 single bond. Systems with this bond within a ring are forced to adopt an *s*-cis conformation. Quinoline formation has been reported where the bond is incorporated within a dihydrophenanthrene or acenaphthene ring,[9] involving formation of **2l** and **2m** from

1l and **1m** respectively, or within a cycloalkane, involving formation of **4a-f** from **3a-f**.[10]

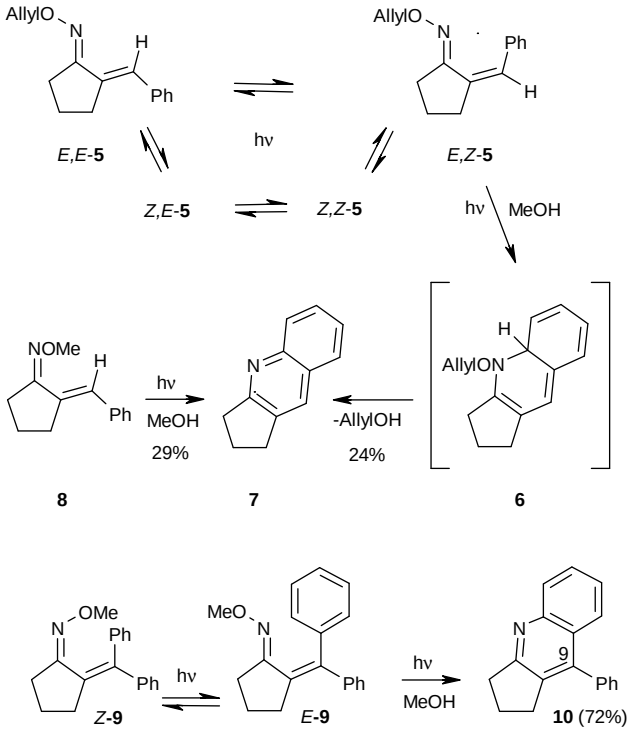
A broad range of potential quinoline precursors is accessible by oximation of readily available α-benzylidene ketones. Aryl ring *ortho*- or *para*-substitution should lead to quinolines substituted at the 5- or 7-ring carbons respectively whereas *meta*-substitution provides the possibility for formation of either 6- or 8-substituted quinolines.

We have used a range of *ortho*- and *para*-substituted benzylidenecyclopentanone *O*-alkyloximes and *O*-acetyloximes (Scheme 3) to examine the scope of the photocyclisation/elimination reaction as a route to annulated quinolines of the 2,3-dihydro-1*H*-cyclopenta[*b*]quinoline family, and the corresponding *meta*-substituted compounds (Scheme 6) to examine regiochemical outcomes. The required compounds were obtained by standard oximation procedures from the appropriate 2-benzylidenecyclopentanones which were in turn readily available from reaction of N-(1-cyclopentenyl)morpholine with the corresponding aromatic aldehydes.

Results

Unsubstituted benzylidenecyclopentanone *O*-alkyloximes

Irradiation of *E*,*E*-*O*-allyloxime **5**[‡] in methanol resulted in initial *E*,*Z*-isomerisation at the carbon-nitrogen and carbon-carbon double bonds (Scheme 2). However isomerisation was accompanied by the slower formation of quinoline **7** as final product, involving photocyclisation of the *E*,*Z*-isomer (and/or the *Z*,*Z*-isomer) to dihydroquinoline **6**, followed by rapid elimination of allyl alcohol. Quinoline **7** was also obtained from the corresponding *O*-methyloxime **8**.



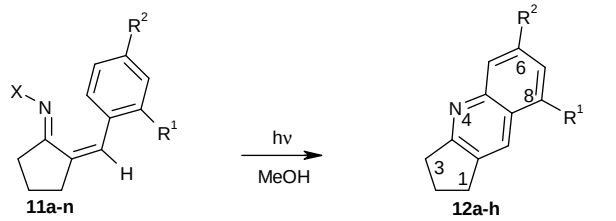
Scheme 2 Cyclisations without aryl substituents.

Unlike **5** and **8**, *E*-2-diphenylmethylenecyclopentanone *O*-methyloxime **9** has an appropriately *Z*-oriented phenyl group and does not require an additional E/Z-photoisomerisation step prior to photocyclisation. On irradiation **9** rapidly formed a mixture of two products, one of which (*Z*-**9**) on further irradiation transformed to the other, final product 9-phenyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline **10.** Taking advantage of the suitably oriented phenyl group in **9**, thermal cyclisation was attempted. However no reaction occurred on prolonged heating of **9** in methanol or in ethylene glycol (bp 198 °C) under reflux.[§]

ortho- and *para*-Substituted benzylidene systems

The *ortho*- and *para*-methyl-, and *ortho*- and *para*-methoxy-benzylidene *O*-methyloximes **11a-d** cyclised to the corresponding 6- and 8-substituted[¶] 2,3-dihydro-1*H*-cyclopenta[*b*]quinolines **12a-d** on irradiation in methanol (Scheme 3). Similarly the *para*-hydroxy-, *para*-acetoxy-, and *para*-*N*,*N*-dimethylamino-benzylidene *O*-acetyloximes **11e-g** and the *para*-amino-benzylidene oxime **11h** cyclised to the quinolines **12e-h** respectively. In each case, TLC analysis showed the initial formation of a number of products, presumed to be the various geometrical isomers and, on further irradiation, these underwent conversion to the corresponding 2,3-dihydro-1*H*-cyclopenta[*b*]quinoline. 2-Benzylidenecyclohexanone *O*-methyloxime similarly yielded tetrahydroacridine **4e**.

In marked contrast *ortho*- and *para*-nitro-, *ortho*- and *para*-chloro- and *para*-cyano-benzylidenecyclopentanone *O*-methyloximes **11i-m**, and 2,4-difluorobenzylidene *O*-acetyloxime **11n** were converted to complex mixtures whose separation was not pursued further.



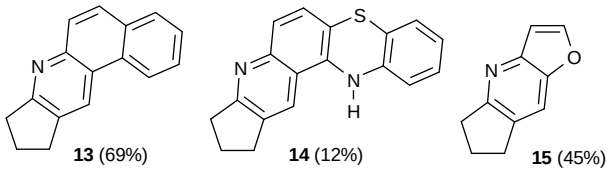
	R^1	R^2	X		Yield (%) [a]
11a	Me	H	OMe	**12a**	35
11b	H	Me	OMe	**12b**	37
11c	OMe	H	OMe	**12c**	48
11d	H	OMe	OMe	**12d**	53
11e	H	OH	OAc	**12e**	36
11f	H	OAc	OAc	**12f**	36
11g	H	NMe_2	OAc	**12g**	26
11h	H	NH_2	OH	**12h**	36
11i	NO_2	H	OMe		-
11j	H	NO_2	OMe		-
11k	Cl	H	OMe		-
11l	H	Cl	OMe		-
11m	H	CN	OMe		-
11n	F	F	OAc		-

[a] Yields are reported for recrystallised products.

Scheme 3 Cyclisations involving *ortho*- and *para*-substituents.

Other participating π-systems

Other π-systems may replace the 2π-electron contribution of the β-phenyl group in these systems (Scheme 4). Thus 2-(1-naphthylmethylene)cyclopentanone *O*-methyloxime yielded fused benzo[*f*]quinoline **13** and 2-(1-phenothiazinylmethylene)cyclopentanone *O*-acetyloxime was converted to the novel pyrido[3,2-*a*]phenothiazine **14**. 2-(2-Furylmethylene)cyclopentanone *O*-methyloxime yielded *N*,*O*-heterocycle **15** and *N*,*S*-heterocycle **16** was similarly obtained from 2-(2-thienylmethylene)cyclopentanone *O*-acetyloxime. Compound **17**, a photoisomer of 2-cinnamylidenecyclopentanone *O*-acetyloxime, also cyclised, yielding pyridine **18** and requiring the adoption of an *s*-cis arrangement for the open-chain dienyl unit in addition to prior *E*,*Z*-isomerisation at the 2-*exo* methylene unit to achieve a viable cyclic transition state for carbon-nitrogen bond formation.



13 (69%) **14** (12%) **15** (45%)

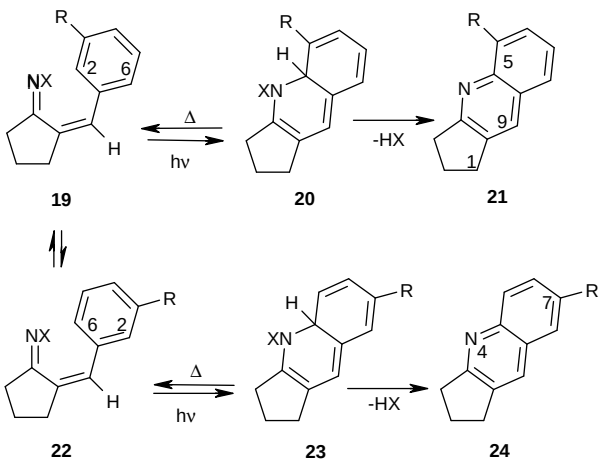
16 (51%) **17** **18** (10%)

Scheme 4 Other cyclisations.

meta-Substituted benzylidene systems

Cyclisation is possible for *meta*-substituted benzylidene derivatives either from rotamer **19**, giving 5-substituted-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline **21**, or from rotamer **22,** giving the 7-substituted isomer **24** (Scheme 5). ‖

A *meta*-methyl substituent results in closure at the aryl 2-position, *ortho* to the methyl group (Scheme 6). 2-(3-Methylbenzylidene)cyclopentanone *O*-methyloxime **25a** yielded a single photoproduct, 5-methyl compound **26a**. Inclusion of an additional ring substituent, a *para*-methyl or *para*-methoxy group, similarly resulted in closure at the 2-position, with 3,4-dimethyl- and 3-methyl-4-methoxy substrates **25b** and **25c** giving 5,6-dimethyl- and 5-methyl-6-methoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinolines **26b** and **26c** respectively. Increasing the steric demand of the *meta*-alkyl substituent again resulted in strong preference for cyclisation/elimination involving the crowded aryl 2-position, with *meta*-*t*-butyl compound **25d** giving 5-*t*-butyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline **26d**.[#]

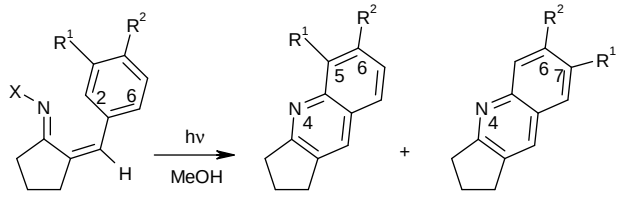


19 **20** **21**

22 **23** **24**

Scheme 5 Alternatives with *meta*-substituents.

In contrast, a *meta*-methoxy group results in closure at the aryl 6-position, *para* to the methoxy substituent. Both 3-methoxybenzylidene *O*-methyloxime **25e** and *O*-acetyloxime **25f** yielded a single photoproduct, 7-methoxy compound **27e**. Incorporation of an additional substituent, methyl or methoxy, in the *para*-position again resulted in closure at the aryl 6-position, with 3,4-dimethoxy and 3-methoxy-4-methyl compounds **25g** and **25h** giving 6,7-dimethoxy- and 6-methyl-7-methoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinolines **27g** and **27h** respectively. 2,5-Dimethoxybenzylidene *O*-acetyloxime **28** (Scheme 7), with the position *para* to the *meta*-methoxy group blocked by the 2-methoxy substituent, cyclised at the vacant *ortho* site to give 5,8-dimethoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline **29**.



25a-p **26a-d, l'** **27e-l**

	R[1]	R[2]	X		Yield (%)[a]		Yield (%)[a]
25a	Me	H	OAc	**26a**	32		
25b	Me	Me	OAc	**26b**	17		
25c	Me	OMe	OAc	**26c**	15		
25d	Bu[t]	H	OAc	**26d**	13		
25e	OMe	H	OMe	-		**27e**	63
25f	OMe	H	OAc	-		**27e**	63
25g	OMe	OMe	OAc	-		**27g**	21
25h	OMe	Me	OAc	-		**27h**	57
25i	OH	H	OAc	-		**27i**	30
25j	NMe_2	H	OAc	-		**27j**	6
25k	NH_2	H	OH	-		**27k**	26
25l	OAc	H	OAc	**26l'** (R^1=OH)	17	**27l**	20
25m	NO_2	H	OAc	-		-	
25n	Cl	H	OAc	-		-	
25o	CN	H	OAc	-		-	
25p	F	H	OAc	-		-	

[a] Yields are reported for recrystallised products.

Scheme 6 Cyclisations with *meta*-substituents.

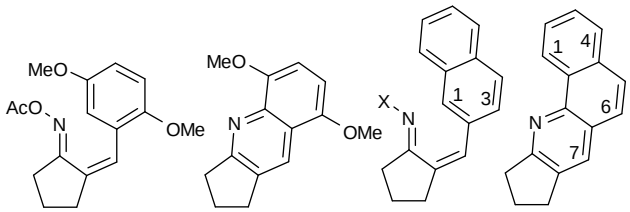
Other electron-donating substituents having a nitrogen or oxygen in the *meta*-position of the benzylidene group similarly resulted in closure at the aryl-6 position (Scheme 6). Thus 3-hydroxy- and 3-*N*,*N*-dimethylaminobenzylidene *O*-

acetyloximes **25i** and **25j**, also the 3-aminobenzylidene oxime **25k**, photocyclised to the corresponding 7-substituted products **27i-k**, respectively.

In contrast to these cyclisations from which a single product was isolated, irradiation of 3-acetoxybenzylidene *O*-acetyloxime **25l** resulted in competitive closure, involving both the aryl-6 and aryl-2 positions, and giving both 7-acetoxy and 5-hydroxy products **27l** and **26l'**. The deacetylation step leading to **26l'** must have occurred subsequent to cyclisation since, if loss of acetyl from **25l** had preceded cyclisation, the resulting initially-formed 3-hydroxybenzylidene *O*-acetyloxime **25i** would have cyclised to 7-hydroxy compound **27i** rather than to 5-hydroxy compound **26l'**. No accompanying photo-Fries rearrangement products were isolated from this reaction.

As observed for the analogous *ortho*- and *para*-substituted benzylidenecyclopentanone derivatives **11j-n**, irradiation of 3-nitro-, 3-chloro-, 3-cyano- and 3-fluoro-benzylidene *O*-acetyloximes **25m-p** proved not to be synthetically useful. Only complex product mixtures were obtained and these were not investigated further.

2-(2-Naphthylmethylene)cyclopentanone *O*-acetyloxime **30a** and *O*-methyloxime **30b** (Scheme 7) cyclised at the naphthyl 1-position to give 9,10-dihydro-8*H*-benzo[*h*]cyclopenta[*b*]quinoline **31,** rather than at the naphthyl 3-position.[13]



28 **29** **30a** X = OAc 74% **30b** X = OMe 72% **31**

Scheme 7.

Discussion

Excited state considerations

The inclusion of various concentrations (up to 1.0 M) of the triplet quencher isoprene in methanol solutions of *E,E*-**5** did not affect the course of product evolution, consistent with both the isomerisation and cyclisation processes arising from singlet excited states on direct irradiation.

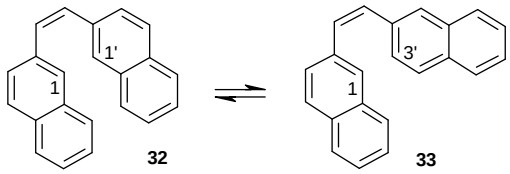
The four geometrical isomers of *O*-allyloxime **5** exhibit strong uv absorption in the 300nm region, probably due to the π,π* band of the conjugated α,β-unsaturated system submerging the much weaker n,π* band. With n,π* transitions in such systems being generally localised at the carbon-nitrogen double bond it is likely that cyclisation of **5** requires a lowest energy π,π* excited state. In ethyl acetate cyclisation of **5** does not occur,[‡] suggesting a lowest energy n,π* transition in this solvent. Methanol may assist the formation of quinoline **7** from **5** by hydrogen bonding to the nitrogen lone pair of the *O*-allyloxime thereby ensuring a lowest energy π,π* excited state and methanol may also facilitate elimination of allyl alcohol from dihydroaromatic intermediate **6**. In acetonitrile formation of **7** from **5** is approximately 25 times less rapid, consistent with hydrogen-bonding playing a role in facilitating the photocyclisation/elimination process. The rate of quinoline formation was approximately doubled for both *meta*- and *para*-*N,N*-dimethylaminobenzylidene *O*-acetyloximes, **25j** and **11g** respectively, by inclusion of a small amount of trifluoroacetic acid but, whereas the yield of quinoline **27j** from *meta*-dimethylaminobenzylidene oxime acetate **25j** improved (from 6% to 35%) in the presence of the acid, no improvement in cyclisation yield (26%) was observed for *para*-dimethylaminobenzylidene oxime acetate **11g**. Methanol with added mineral acid has been used as the medium for quinoline formation from oximes **3a-d,f**.[10]

Analogy with stilbene cyclisation

The photocyclisation/elimination process for quinoline synthesis is analogous to the well-established conrotatory photocyclisation process for 1,3,5-hexatrienes, the most studied being the oxidative photoconversion of stilbenes to phenanthrenes[14,15,16] *via* dihydrophenanthrene intermediates which aromatise either in the presence of oxygen or, more commonly, in the presence of an added oxidant such as iodine. Though chloro, fluoro and cyano substituents are compatible with stilbene photoconversion to phenanthrenes,[14c,15,17] also with quinoline formation from *p*-chlorophenyl *O*-benzoyloxime **1e**,[5] this is not the case for quinoline formation from benzylidenecyclopentanone oxime ethers or acetates **11k-n** and **25n-p**. Possibilities for this difference in behaviour include (a) enhanced intersystem crossing for these particular β-aryl-α,β-unsaturated oxime derivatives, with alternative reaction pathways being available to the triplet excited state,[††] (b) the nature of their lowest excited singlet states, with n,π* states being generally less amenable to 6π-electron cyclisation and (c) the intervention of other reaction pathways, possibly involving radicals and leading to alternative reaction outcomes. The lack of photocyclisation when electron-withdrawing groups are present on the β-aryl ring may imply the necessity for a polarised transition state in which electron density is transferred through the π-system from the aryl ring to the oximino nitrogen, facilitating aryl-nitrogen bond formation and detachment of the leaving group.

Regioselectivity

In general 2-naphthyl homologues of stilbene (Scheme 8) have been found[15] to undergo oxidative photocyclisation at the 1-naphthyl position, though more recent studies have shown that reaction may also occur at the naphthyl 3-position.



32 **33**

Scheme 8 Alternative cyclisation options from ground state rotamers.

Thus the ground state rotamers **32** and **33** of *Z*-di(2-naphthyl)ethene undergo competitive 1,1'- and 1,3'-cyclisation respectively to give the corresponding dihydrophenanthrenes on excitation[19,20,‡‡] and oxidative conditions can be adjusted to yield predominantly dibenzo[*c,g*]phenanthrene or dibenzo[*b,g*]phenanthrene respectively.[19,21] Prediction of the preferred cyclisation route for diarylethenes has been assisted by the use of calculated free valence numbers or electronic overlap populations[22] as measures of reactivity for electrocyclic processes, with most success being for polycyclic aromatic substituents.

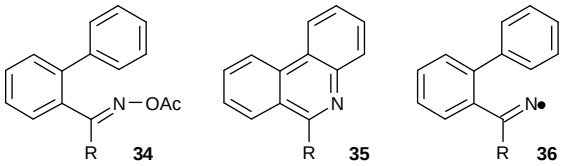
Though more favourable substituent-dependent frontier orbital overlap in the transition state for cyclisation of one of the rotamers of a *meta*-substituted stilbene may play a contributing part in determining regioselectivity, it would not seem to be a determining one since, for many *meta*-substituted stilbenes, approximately equal amounts of the corresponding 2- and 4-substituted phenanthrenes are found.[14c,23] Recent consideration of the photocyclisations of styrylpyridines and 2-aminostyrylpyridines[24] has pointed to the role of rotamers and led to the suggestion that the regiochemical outcome for a *meta*-substituted stilbene analogue is determined by the relative rates of oxidation and ring-opening of the intermediate dihydrophenanthrenes. Similar substituent-related competition between ring-opening and elimination steps for the non-aromatic intermediates from *meta*-substituted benzylidenecyclopentanone oxime derivatives, **20** and **23** from rotamers **19** and **22** respectively (Scheme 5), probably also determines whether 5-substituted or 7-substituted products, **21** or **24** respectively, are obtained. The nature and interactions of these substituent effects has yet to be determined.

Other observations

The nature of the group eliminated does not affect the cyclisation outcome. Both *O*-allyloxime **5** and *O*-acetyloxime **8** yielded 2,3-dihydro-1*H*-cyclopenta[*b*]quinoline **7** (24% and 29%, respectively). Similarly *O*-acetyloxime **30a** and *O*-methyloxime **30b** yielded 9,10-dihydro-*8H*-benzo[*f*]cyclopenta[*b*]quinoline **31** and 7-methoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline **27e** was obtained from both *O*-methyloxime **25e** and *O*-acetyloxime **25f**. Initial studies were undertaken with *O*-methyloximes but, when it became apparent that the cyclisation outcome was independent of the nature of the leaving group, the more readily prepared *O*-acetyloximes were subsequently used.

Photocyclisation of the O-acetyloximes **34** of 2-phenylbenzaldehyde, 2-phenylacetophenone and 2-phenylbenzophenone to the corresponding phenanthridines **35** (Scheme 9) has recently been reported.[25] The 2-vinyl analogues are similarly converted to the corresponding isoquinolines. These outcomes may also be rationalised by a six π-electron cyclisation process. However iminyl radicals **36** have been proposed as intermediates in the formation of **35**, generated by nitrogen-oxygen bond photocleavage. Such homolysis, yielding acyloxy and aryliminyl radicals, occurs in the photochemistry of *O*-acyloxime derivatives of simple aromatic carbonyl compounds such as benzaldehyde, acetophenone, benzophenone and 9-fluorenone and has been used as a convenient source of carbon-centred radicals for synthetic investigations[26, 27] and as a photochemical source of amines for polymer cross-linking, the amines resulting from hydrolysis of the imines formed following nitrogen-oxygen bond cleavage.[28]

Whether the phenanthridines **35** are formed by a six π-electron photocyclisation process in competition with radical formation, or are formed through the intermediacy of photogenerated iminyl radicals **36**, is unclear. Iminyl radicals may be readily generated by a variety of non-photochemical routes,[29] and there is precedence for radicals analogous to **36** undergoing closure to phenanthridines and quinolines[30] though five-membered ring formation has been reported to accompany quinoline formation in favourable cases.[31]



R = H, Me, Ph

Scheme 9.

Benzaldehyde *O-alkyl*oximes undergo very inefficient carbon-nitrogen bond photocleavage on direct or triplet sensitised excitation,[32] though the efficiency of radical formation from benzaldehyde *O-acyl*oximes can be increased by the use of triplet photosensitisers.[33] However, given that the compounds which comprise the present study lack the phenone *O*-acyl or *O*-alkyloxime functionality which seems to be essential for such cleavage on direct excitation, it can be concluded that these cyclisations proceed by the proposed six π-electron photocyclisation.[§§] This conclusion is supported by the absence of reports of nitrogen-oxygen bond homolysis on direct or triplet sensitised excitation of a wide range of other *O*-alkyl and *O*-acyloximes such as acetophenone *O*-methyloxime,[35] acetonaphthone *O*-methyloxime,[36] β-phenyl-α,β-unsaturated oximino systems **1a-m**,[4-10] β-ionone *O*-ethyloxime,[37] β,γ-unsaturated oxime acetates[38] and cholestanone *O*-acetyloximes.[39]

Conclusions

This photocyclisation/elimination process provides a convenient route to a wide variety of substituted 2,3-dihydro-1*H*-cyclopenta[*b*]quinolines from readily accessible precursors and has the potential for extension to the synthesis of numerous novel fused pyridines/quinolines of biomolecular interest derived, for example, from terpenoid or steroidal ketones.

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Experimental Section

NMR spectra were recorded on a Bruker AC-400 instrument operating at 400MHz for ^{1}H and 100MHz for ^{13}C. Unless otherwise stated, spectra were recorded using $CDCl_3$ as solvent, with Me_4Si as internal standard. TLC was on silica gel plates containing a fluorescent indicator (Riedel-de-Haen, DC-Cards SiF, layer thickness 0.2 mm). Light petroleum for recrystallisation had bp 80-100 °C, unless stated otherwise. Yields were not optimised. Melting points are uncorrected. Satisfactory elemental analyses were obtained for all new compounds.

Photochemical reactions were carried out using a water-cooled immersion well containing a Photochemical Reactors 400W medium pressure mercury vapour lamp fitted with a Pyrex filter (λ>300nm). Solutions for photochemistry used high purity grade solvents which were deoxygenated by passing a stream of nitrogen or argon through the solution for 30 minutes prior to irradiation and the inert gas atmosphere was maintained over the solutions during irradiation.

Preparative details and nmr spectra are reported here for the annulated quinolines. Other analytical data for the quinolines, also experimental and spectral data for the other compounds included in this work, are reported in the Electronic Supplementary Information accompanying this paper.[†]

Preparation of 2-benzylidenecyclopentanones

Preparations involved reaction of the morpholine enamine of cyclopentanone with the appropriate aromatic aldehyde.[40]

Preparation of 2-benzylidenecyclopentanone oximes

Preparations involved reaction of the ketones with hydroxylamine hydrochloride in pyridine.

Preparation of benzylidenecyclopentanone *O*-methyloximes

Preparations involved reaction of the required oxime with excess dimethyl sulphate in the presence of sodium hydroxide.

Preparation of benzylidenecyclopentanone *O*-acetyloximes

Preparations involved reaction of the required oxime with acetyl chloride in pyridine.

General procedure for synthesis of 2,3-dihydro-1*H*-cyclopenta[*b*]quinolines

A methanol solution (250-350 cm^3) of the appropriate *O*-methyloxime, *O*-acetyloxime or oxime (2.5-10.0x10^{-3} M) was irradiated under the standard conditions. Reaction progress was monitored by TLC using light petroleum/ethyl acetate [ethanol in the cases of **12g, 14** and **27j**]. In general a number of products appeared soon after irradiation began and on continued irradiation one of these became the sole/predominant product, at which time irradiation was discontinued. Removal of the methanol yielded the crude 2,3-dihydro-1*H*-cyclopenta[*b*]quinoline. Purification was by recrystallisation or by chromatography on silica, with light petroleum/ethyl acetate as eluent, prior to recrystallisation. Unless otherwise stated, recrystallisation was from light petroleum/ethyl acetate.

2,3-Dihydro-1*H*-cyclopenta[*b*]quinoline 7 (24% from **5**; 29% from **8**), mp 60-61 °C (lit.,[41] 60-61 °C); δ_H 2.18 (2H, qn, *J* 7.4, $CH_2CH_2CH_2$), 3.06 (2H, t, *J* 7.4, CH_2Ar), 3.14 (2H, t, *J* 7.4, CH_2Ar), 7.43 (1H, t, *J* 7.7) and 7.59 (1H, t, *J* 7.9) (arH-7 and arH-6), 7.70 (1H, d, *J* 7.7, arH-8), 7.85 (1H, br s, arH-9) and 8.00 (1H, d, *J* 7.9, arH-5); δ_C 23.62, 30.50, 34.60 (3 x CH_2), 125.49, 127.43, 128.30 and 128.51(benzenoid-*C*H), 130.29 (pyridyl-*C*H), 127.37, 135.77, 147.48 and 167.91 (quaternary *C*s).

9-Phenyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 10 (72%), mp 132-134 °C (methanol) (lit.,[42] 134-135 °C); δ_H 2.16 (2H, qn, *J* 7.5, $CH_2CH_2CH_2$), 2.90 (2H, t, *J* 7.5, CH_2Ar), 3.24 (2H, t, *J* 7.5, CH_2Ar), 7.36 (3H, m), 7.49 (3H, m) and 7.62 (2H, m) (8 x arH), 8.08 (1H, d, *J* 8.4, arH-5); δ_C 23.42, 30.22, 35.08 (3 x CH_2), 125.39, 125.54, 126.09, 127.88, 128.13, 128.39, 128.68, 129.18, 133.55, 136.62, 142.59, 147.81 and 167.31 (13 x arC).

8-Methyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 12a (35%), mp 64-65 °C (light petroleum); δ_H 2.21 (2H, qn, *J* 7.4, $CH_2CH_2CH_2$), 2.65 (3H, s, Me), 3.11 (2H, t, *J* 7.4, CH_2Ar), 3.16 (2H, t, *J* 7.4, CH_2Ar), 7.28 (1H, d, *J* 8.4, arH-7), 7.50 (1H, t, *J* 8.4, arH-6), 7.87 (1H, d, *J* 8.4, arH-5) and 8.07 (1H, s, arH-9); δ_C 18.83 (Me), 23.65, 30.72 and 34.50 (3 x CH_2), 126.12, 126.53, 126.75, 126.89, 127.94, 133.98, 135.22, 147.68 and 167.23 (9 x arC).

6-Methyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 12b (37%), mp 86-88 °C (light petroleum); δ_H 2.20 (2H, qn, *J* 7.5, $CH_2CH_2CH_2$), 2.54 (3H, s, Me), 3.07 (2H, t, *J* 7.5, CH_2Ar), 3.15 (2H, t, *J* 7.5, CH_2Ar), 7.30 (1H, d, *J* 8.2, arH-7), 7.63 (1H, d, *J* 8.2, arH-8), 7.79 (1H, s, arH-5) and 7.85 (1H, s, arH-9); δ_C 21.82 (Me), 23.66, 30.48 and 34.63 (3 x CH_2), 125.37, 127.07, 127.70, 128.98, 130.15, 131.93, 134.73, 138.49 and 167.80 (9 x arC).

8-Methoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 12c (48%), mp 76-77 °C (light petroleum); δ_H 2.21 (2H, qn, *J* 7.6, $CH_2CH_2CH_2$), 3.09 (2H, t, *J* 7.6, CH_2Ar), 3.15 (2H, t, *J* 7.6, CH_2Ar), 3.99 (3H, s, MeO), 6.81 (1H, d, *J* 8.1, arH-7), 7.51 (1H, t, *J* 8.1, arH-6), 7.61 (1H, d, *J* 8.1, arH-5) and 8.33 (1H, s, arH-9); δ_C 23.61, 30.64, 34.62 (3 x CH_2), 55.68 (OMe), 103.62, 119.56, 120.89, 125.06, 128.17, 134.76, 148.34, 155.07 and 168.05 (9 x arC).

6-Methoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 12d (53%), mp 58-60 °C (light petroleum); δ_H 2.20 (2H, qn, *J* 7.5, $CH_2CH_2CH_2$), 3.06 (2H, t, *J* 7.5, CH_2Ar), 3.15 (2H, t, *J* 7.5, CH_2Ar), 3.93 (3H, s, OMe), 7.12 (1H, dd, *J* 8.8, 2.2, arH-7), 7.37 (1H, d, *J* 2.2, arH-5), 7.62 (1H, d, *J* 8.8, arH-8) and 7.82 (1H, s, arH-9); δ_C 23.58, 30.32, 34.59 (3 x CH_2), 55.35 (OMe), 106.95, 118.20, 122.34, 128.30, 130.23, 133.31, 148.98, 159.86 and 167.98 (9 x arC).

6-Hydroxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 12e. (36%), mp 168-169 °C; δ_H $(CD_3)_2SO$ 2.09 (2H, qn, *J* 7.5, $CH_2CH_2CH_2$), 2.93-3.01 (4H, m, 2 x CH_2Ar), 7.00 (1H, dd, *J* 8.8, 2.2, arH-7), 7.24 (1H, d, *J* 2.2, arH-5), 7.50 (1H, d, *J* 8.8, arH-8), 7.73 (1H, s, arH-9) and 9.65 (1H, br s, OH); δ_C $(CD_3)_2SO$ 22.64, 29.27, 33.59 (3 x CH_2), 109.30, 117.16, 120.73, 127.36, 129.43, 131.50, 148.06, 157.06 and 166.67 (9 x arC).

6-Acetoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 12f (36%), mp 96-97 °C; δ_H 2.21 (2H, qn, *J* 7.6, $CH_2CH_2CH_2$), 2.36 (3H, s, MeCO), 3.08 (2H, td, J_t 7.6, J_d 1.0, CH_2Ar), 3.08 (2H, t, *J* 7.6, CH_2Ar), 7.24 (1H, dd, *J* 8.8, 2.4, arH-7), 7.71-7.74 (2H, m, arH-5/8) and 7.88 (1H, br s, arH-9); δ_C 21.19

(Me), 23.58, 30.42, 34.57 (3 x CH_2), 119.64, 120.80, 125.40, 128.34, 130.15, 135.62, 147.91, 150.46, 168.57 and 169.41(9 x arC + C=O).

6-*N*,*N*-Dimethylamino-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 12g (26%), mp 104-106 °C; δ_H 2.16 (2H, qn, *J* 7.5, $CH_2CH_2CH_2$), 3.01 (2H, td, J_t 7.5, J_d 1.0, CH_2Ar), 3.06 (6H, s, NMe_2), 3.09 (2H, t, *J* 7.5, CH_2Ar), 7.13 (1H, dd, *J* 8.8, 2.6, arH-7), 7.14 (1H, d, *J* 2.6, arH-5), 7.55 (1H, d, *J* 8.8, arH-8) and 7.72 (1H, s, arH-9); δ_C 23.60, 30.33, 34.70 (3 x CH_2), 40.60 (NMe_2), 107.11, 115.15, 119.93, 127.86, 130.08, 131.41, 149.20, 150.67 and 167.77 (9 x arC).

A similar yield (24%) of 6-*N*,*N*-dimethylamino-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline **12g** was obtained following similar irradiation in the presence of added trifluoroacetic acid (1 equiv., 3.6mM). Isolation, by diethyl ether extraction and chromatography, followed initial adjustment of the irradiated solution to pH~8 by addition of 10% aq. sodium carbonate solution.

6-Amino-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 12h (36%), mp 94-96 °C; δ_H 2.15 (2H, qn, *J* 7.6, $CH_2CH_2CH_2$), 3.02 (2H, td, J_t 7.6, J_d 1.0, CH_2Ar), 3.26 (2H, t, *J* 7.6, CH_2Ar), 4.22 (2H, br, NH_2), 6.89 (1H, dd, *J* 8.5, 2.3, arH-7), 7.36 (1H, s, arH-9), 7.50 (1H, d, *J* 8.5, arH-8) and 7.80 (1H, d, *J* 2.3, arH-5); δ_C 22.73, 30.31, 31.17 (3 x CH_2), 99.83, 118.84, 121.96, 123.55, 129.47, 133.34, 141.82, 148.14 and 152.25 (9 x arC).

9,10-Dihydro-*8H*-benzo[*f*]cyclopenta[*b*]quinoline 13 (69%), mp 126-128 °C (light petroleum); δ_H 2.27 (2H, qn, *J* 7.4, $CH_2CH_2CH_2$), 3.19 (2H, t, *J* 7.4, $ArCH_2$), 3.22 (2H, *J* 7.4, $ArCH_2$), 7.61 (1H, t, *J* 7.4) and 7.66 (1H, t, *J* 7.4) (arH-2/3), 7.92 (3H, m; arH-1/4/5), 8.60 (1H, d, *J* 7.8, arH-6) and 8.74 (1H, s, arH-11); δ_C 23.66, 30.92, 34.47 (3 x CH_2), 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 166.86 (13 x arC).

1,2,3,12-Tetrahydrocyclopenta[5,6]pyrido[3,2-*a*]phenothiazine 14 (12%), mp 67-68 °C; δ_H 2.14 (2H, qn, *J* 7.2, $CH_2CH_2CH_2$), 2.44 (2H, t, *J* 7.2) and 3.29 (2H, t, *J* 7.2) (2 x CH_2Ar), 6.38 (1H, s, NH), 6.68 (1H, dd, *J* 7.2, 0.8), 6.95 (2H, m), 7.10 (3H, m) and 7.32 (1H, dd, *J* 8.8, 1.0) (7 x arH); δ_C 16.69, 24.56, 29.78 (3 x CH_2), 107.64, 116.34, 116.46, 116.74, 117.19, 119.18, 123.02, 123.77, 124.74, 126.52, 127.56, 128.25, 136.08, 136.18 and 137.56 (15 x arC).

6,7-Dihydro-5*H*-cyclopenta[*b*]furo[2,3-*e*]pyridine 15 (45%), mp 64-65 °C (light petroleum); δ_H 2.15 (2H, qn, *J* 7.4, $CH_2CH_2CH_2$), 2.97 (2H, t, *J* 7.4, CH_2Ar), 3.02 (2H, t, *J* 7.4, CH_2Ar), 6.84 (1H, d *J* 2.5, furoH-3), 7.51 (1H, s, pyridylH-8) and 7.70 (1H, d, *J* 2.5, furoH-2); δ_C 24.14, 30.70, 33.65 (3 x CH_2), 107.68, 114.64, 133.36, 145.67, 147.31, 147.74 and 162.15 (furopyridine).

6,7-Dihydro-5*H*-cyclopenta[*b*]thieno[2,3-*e*]pyridine 16 (51%), mp 84-85 °C; δ_H 2.21 (2H, qn, *J* 7.4, $CH_2CH_2CH_2$), 3.03 (2H, t, *J* 7.4, CH_2Ar), 3.11 (2H, t, *J* 7.4, CH_2Ar), 7.47 (1H, d, *J* 5.9) and 7.52 (1H, d, *J* 5.9) (thienoH-2/3), 7.95 (1H, s, pyridylH-8); δ_C 23.83, 30.45, 33.87 (3 x CH_2), 124.43, 125.70, 128.66, 131.24, 133.10, 154.64 and 164.39 (7 x arC).

2-Phenyl-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine 18 (10%), mp 79-80 °C (lit.,[43] 81-82 °C); δ_H 2.04 (2H, qn, *J* 7.6, $CH_2CH_2CH_2$), 2.84 (2H, t, *J* 7.6, CH_2Ar), 2.96 (2H, t, *J* 7.6, CH_2Ar), 7.24 (1H, tt, *J* 7.6, 1.2), 7.32 (3H, m), 7.42 (1H, d, *J* 7.6) and 7.81 (2H, m) (7 x arH); δ_C 23.23, 30.48, 34.41 (3 x CH_2), 118.25, 126.89, 128.32, 128.64, 132.56, 135.41, 140.00, 155.87 and 165.83 (9 x arC).

5-Methyl-2,3-dihydro-[1*H*]-cyclopenta[*b*]quinoline 26a (32%), mp 92-94°C (light petroleum); δ_H 2.19 (2H, qn, *J* 7.4, $CH_2CH_2CH_2$), 2.80 (3H, s, Me), 3.05 (2H, t, *J* 7.4, CH_2), 3.16 (2H, t, *J* 7.4, CH_2), 7.32 (1H, t, J 8.3, arH-7), 7.44 (1H, d, *J* 8.3, arH-8 or -6), 7.55 (1H, d, *J* 8.3, arH-6 or -8) and 7.81 (1H, s, arH-9); δ_C 18.32 (Me), 23.72, 30.43, 34.87 (3 x CH_2), 125.04, 125.52, 127.22, 128.54, 130.46, 135.08, 136.20, 146.63 and 166.88 (arC).

5,6-Dimethyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 26b (17%), mp 90-91 °C; δ_H 2.10 (2H, qn, *J* 7.5, $CH_2CH_2CH_2$), 2.40 (3H, s, Me), 2.67 (3H, s, Me), 2.98 (2H, t, *J* 7.5, CH_2), 3.09 (2H, t, *J* 7.5, CH_2), 7.19 (1H, d, *J* 8.2) and 7.40 (1H, d, *J* 8.2) (arH-7 and arH-8), 7.71 (1H, s, arH-9); δ_C 13.48, 20.64 (2 x Me), 23.75, 30.33, 34.88 (3 x CH_2), 124.45, 125.55, 128.17, 130.46, 133.49, 133.97, 135.91, 146.53 and 166.75 (9 x arC).

5-Methyl-6-Methoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 26c (15%), mp 89-91 °C; δ_H 2.12 (2H, qn, *J* 7.5, $CH_2CH_2CH_2$), 2.62 (3H, s, Me), 2.98 (2H, t, *J* 7.5, CH_2), 3.10 (2H, t, *J* 7.5, CH_2), 3.90 (3H, s, OMe), 7.15 (1H, d, *J* 9.0, arH-7), 7.50 (1H, d, *J* 9.0, arH-8) and 7.73 (1H, s, arH-9); δ_C 9.94 (Me), 23.78, 30.30, 35.00 (3 x CH_2), 56.41 (OMe), 112.25, 121.54, 122.47, 125.56, 130.47, 132.81, 147.15, 156.68 and 167.65 (9 x arC).

5-*t*-Butyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline[#] 26d (13%), mp 62-64 °C (light petroleum); δ_H 1.70 (9H, s, CMe_3), 2.20 (2H, qn, *J* 7.6, $CH_2CH_2CH_2$), 3.07 (2H, t, *J* 7.6, $ArCH_2$), 3.14 (2H, t, J 7.6, $Ar'CH_2$), 7.36 (1H, t, *J* 7.6, arH-7), 7.58 (2H, coincident doublets, *J* 7.6, arH-6 and arH-8) and 7.83 (1H, s, arH-9); δ_C 22.61, 28.68, 29.39, 30.03, 33.82 (3 x CH_2, CMe_3 and CMe_3), 123.73, 123.78, 125.35, 127.04, 129.50, 132.94, 145.59, 146.31 and 163.70 (9 x arC).

7-Methoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 27e (63% from both **25e** and **25f**), mp 96-97°C (light petroleum) (lit.[44] 99-100 °C); δ_H 2.72 (2H, qn, *J* 7.9, $CH_2CH_2CH_2$), 3.58 (2H, t, *J* 7.9, $ArCH_2$), 3.65 (2H, t, *J* 7.9, $ArCH_2$), 4.42 (3H, s, OMe), 7.53 (1H, d, *J* 2.5, arH-8), 7.81 (1H, dd, *J* 8.9, 2.5, arH-6), 8.32 (1H, s, arH-9), and 8.45 (1H, d, *J* 8.9, arH-5); δ_C 23.28, 30.18, 33.93 (3 x CH_2), 55.06 (OMe), 105.16, 120.07, 127.87, 128.93, 129.46, 135.52, 143.05, 156.70 and 164.98 (9 x arC)

6,7-Dimethoxy-2,3-dihydro-1H-cyclopenta[b]quinoline 27g (21%), mp 99-100 °C (lit.,[45] 112-113 °C; lit.,[46] 120-121 °C); δ_H 2.12 (2H, qn, *J* 7.6, $CH_2CH_2CH_2$), 2.98 (2H, t, *J* 7.6, CH_2), 3.04 (2H, t, *J* 7.6, CH_2), 3.92 (3H, s, OMe), 3.94 (3H, s, OMe), 6.92 (1H, s, arH-8), 7.31 (1H, s, arH-5) and 7.68 (1H, s, arH-9); δ_C 23.59, 30.46, 34.34 (3 x CH_2), 55.90, 55.94 (both OMe), 105.21, 107.53, 122.44, 129.10, 133.69, 143.99, 148.82, 151.34 and 165.24 (9 x arC).

6-Methyl-7-methoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 27h (57%), mp 129-130 °C; δ_H 2.10 (2H, qn, *J* 7.6, $CH_2CH_2CH_2$), 2.31 (3H, s, Me), 2.96 (2H, t, *J* 7.4, CH_2), 3.03 (2H, t, *J* 7.6, CH_2), 3.84 (3H, s, Me), 6.85 (1H, s, arH-8) and 7.68 (2H, coincident singlets, arH-5/9); δ_H $(CD_3)_2SO$ 2.01 (2H, qn, *J* 7.6, $CH_2CH_2CH_2$), 2.21 (3H, s, Me), 2.88 (4H, m, $CH_2C{=}C$ and $CH_2C{=}N$), 3.80 (3H, s, OMe), 7.03 (1H, s, arH-8), 7.55 (1H, s) and 7.74 (1H, s) (arH-5/9); δ_C

17.01 (Me), 23.62, 29.49, 34.24 (3 x CH_2), 55.34 (OMe), 103.72, 126.75, 129.05, 129.20, 130.93, 134.54, 143.07, 156.21 and 164.83 (9 x arC).

7-Hydroxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 27i (30%), mp 142-143 °C; δ_H $(CD_3)_2SO$ 2.08 (2H, qn, *J* 7.6 $CH_2CH_2CH_2$), 2.96 (4H, m, $ArCH_2$ and Ar'CH_2), 6.96 (1H, d, *J* 2.4, arH-8), 7.13 (1H, dd, *J* 8.9, 2.4, arH-6), 7.63 (1H, s, arH-9), 7.70 (1H, d, *J* 8.9, arH-5) and 9.35 (1H, s, OH); δ_C $(CD_3)_2SO$ 23.19, 30.00, 33.68 (3 x CH_2), 108.45, 120.09, 128.14, 128.48, 128.91, 135.22, 141.99, 154.44 and 164.02 (9 x arC).

7-*N*,*N*-Dimethylamino-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 27j (6%), mp 122-123 °C; δ_H 2.10 (2H, qn, *J* 7.5, $CH_2CH_2CH_2$), 2.96 (2H, t, *J* 7.5, $ArCH_2$), 2.98 (6H, s, NMe_2), 3.03 (2H, t, *J* 7.5, $ArCH_2$), 6.71 (1H, d, *J* 2.6, arH-8), 7.21 (1H, dd, *J* 9.2, 2.6, arH-6), 7.65 (1H, s, arH-9) and 7.80 (1H, d, *J* 9.2, arH-5); δ_C 23.48, 30.57, 34.14 (3 x CH_2), 40.88 (NMe_2), 105.75, 118.27, 128.70, 128.83, 128.87, 135.75, 141.29, 148.18 and 163.56 (9 x arC).

A higher yield (35%) of 7-*N*,*N*-dimethylamino-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline **27j** was obtained following similar irradiation in the presence of added trifluoroacetic acid (1 equiv., 2.4mM). Isolation, by diethyl ether extraction and chromatography, followed initial adjustment of the irradiated solution to pH~8 by addition of 10% aq. sodium carbonate solution.

7-Amino-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 27k (26%), mp 121-122 °C; δ_H 2.00 (2H, qn, *J* 7.6, $CH_2CH_2CH_2$), 2.85 (2H, t, *J* 7.6, $ArCH_2$), 2.94 (2H, t, *J* 7.6, $ArCH_2$), 3.80 (2H, s, NH_2), 6.67 (1H, d, *J* 2.4, arH-8), 6.89 (1H, dd, *J* 8.8, 2.4, arH-6), 7.47 (1H, s, arH-9) and 7.68 (1H, d, *J* 8.8, arH-5); δ_C 23.51, 30.37, 33.93 (3 x CH_2), 107.91, 120.13, 128.39, 128.59, 128.46, 135.75, 142.14, 143.81 and 163.90 (9 x arC).

7-Acetoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 27l and 5-hydroxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 26l': The two products which remained following irradiation of 2-(3-acetoxybenzylidene)cyclopentanone *O*-acetyloxime were separated on a silica column with mobile phase 10:90 light petroleum/ethyl acetate to give:

(i) 7-acetoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 27l (20%), mp 118-119 °C; δ_H 2.13 (2H, qn, *J* 7.5, $CH_2CH_2CH_2$), 2.27 (3H, s, MeCO), 2.99 (2H, td, J_t 7.5, J_d 1.2, $ArCH_2$), 3.07 (2H, t, *J* 7.5, Ar'CH_2), 7.27 (1H, dd, *J* 8.9, 2.5, arH-6), 7.39 (1H, d, *J* 2.5, arH-8), 7.76 (1H, s, arH-9) and 7.95 (1H, d, *J* 8.9, arH-5); δ_C 20.17 (Me), 22.59, 29.49, 33.45 (3 x CH_2), 117.21, 122.27, 126.62, 128.84, 129.05, 135.35, 144.38, 146.81, 166.94 (9 x arC) and 168.53 (C=O);

(ii) 5-hydroxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 26l' (17%), mp 74-75 °C; δ_H $(CD_3)_2SO$ 2.14 (2H, qn, *J* 7.5, $CH_2CH_2CH_2$), 3.05 (4H, m, 2 x $ArCH_2$), 6.98 (1H, dd, *J* 8.0, 1.6, arH-6) and 7.28 (1H, dd, *J* 8.0, 1.6, arH-8), 7.32 (1H, t, *J* 8.0, arH-7), 8.03 (1H, s, arH-9) and 8.29 (1H, s, OH); δ_C 23.65, 30.47, 34.11 (3 x CH_2), 109.15, 117.65, 126.39, 127.53, 130.35, 136.60, 137.35, 151.49 and 165.70 (9 x arC).

5,8-Dimethoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline 29 (8%), mp 104-105 °C (lit.,[47] 98-100 °C); δ_H 2.11 (2H, qn, *J* 7.5, $CH_2CH_2CH_2$), 3.00 (2H, td, J_t 7.5, J_d 1.0, CH_2Ar), 3.13 (2H, t, *J* 7.5, CH_2Ar), 3.86 (3H, s, OMe), 3.94 (3H, s, OMe), 6.61 (1H, d, *J* 8.8) and 6.77 (1H, d, *J* 8.8) (arH-6/7), 8.22 (1H, s, arH-9); δ_C 22.62, 29.64, 33.86 (3 x CH_2), 54.76, 54.89 (OMe), 101.89, 104.76, 119.58, 124.20, 134.44, 138.64, 147.73, 148.24 and 166.25 (9 x arC).

9,10-Dihydro-8*H*-benzo[*h*]cyclopenta[*b*]quinoline 31 (74% from **30a**; 72% from **30b**), mp 115-116 °C; δ_H 2.23 (2H, qn, *J* 7.9, $CH_2CH_2CH_2$), 3.07 (2H, t, *J* 7.9, $ArCH_2$), 3.26 (2H, t, *J* 7.9, $ArCH_2$), 7.59 (1H, d, *J* 8.5), 7.70 (3H, m), 7.84 (1H, s, arH-7), 7.89 (1H, dd, *J* 7.9, 0.9Hz) and 9.35 (1H, d, *J* 8.5); δ_C 23.57, 30.49, 34.70 (3 x CH_2), 124.12, 124.90, 125.52, 126.30, 126.48, 127.34, 127.55, 130.60, 131.42, 133.20, 135.85, 145.32 and 166.14 (13 x arC).

Notes and references

‡ Compound **5** was obtained as a single isomer on reaction of 2-benzylidenecyclopentanone with *O*-allylhydroxylamine. In ethyl acetate **5** underwent only *E*,*Z*-photoisomerisation to a photostationary state comprising the *E*,*E*- (19%), *Z*,*E*- (48%), *E*,*Z*- (23%) and *Z*,*Z*- (10%) isomers. These were separated chromatographically and their stereochemistries assigned.

§ The analogous open-chain *O*-acetyloxime of 4,4-diphenylbut-3-en-2-one (Ph_2C=CHCMe=NOAc) undergoes conversion to 2-methyl-4-phenylquinoline at 187 °C. Semi-empirical calculations have been used in support of a pericyclic mechanism involving disrotatory closure to an intermediate analogous to **6**, followed by subsequent intramolecular elimination of acetic acid *via* a cyclic transition state.[11] O-Methyloxime **1l** undergoes closure/elimination above 120 °C to yield **2l**.[9] The low activation barrier was ascribed to aromatic stabilisation of the cyclised intermediate due to generation of a phenanthrene unit prior to methanol elimination. In the case of **9** however no such stabilisation is possible.

¶ Nomenclature convention results in different numbering of the aromatic ring positions for quinolines and 2,3-dihydro-1*H*-cyclopenta[*b*]quinolines. Benzenoid ring positions 5, 6, 7 and 8 in the former correspond to positions 8, 7, 6 and 5 respectively in the latter.

‖ Possible in principle for *ortho*-substituted benzylidene analogues, cyclisation with elimination of a 2-substituent (R) has not been observed, presumably because of the difficulty of eliminating a species such as MeOR or AcOR. Replacement of 2-substituents has been observed for 2-substituted stilbene oxidative cyclisations, involving elimination of HR.[12]

Prior to recrystallisation, the ^{1}H-NMR spectrum of the chromatographed product showed it to be 5-*t*-butyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (92%) together with a small amount of another *t*-butyl-containing component (8%), possibly the other regioisomer.

†† For the currently included substituents this seems likely only for the nitro group. There do not appear to have been any reports of oxidative photocyclisations of nitrostilbenes.

‡‡ The principle of non-equilibration of excited rotamers (NEER) implies that the ground state populations of **32** and **33** determine the excited state populations.[18]

§§ In the presence of excited 1,5-dimethoxynaphthalene (DMN) as a single electron transfer agent, γ,δ-unsaturated ketone *O*-acyl and *O*-methyloximes are converted to radical anions which cyclise by an iminyl radical mechanism to 3,4-dihydro-2*H*-pyrroles. Alternatively triplet energy transfer from excited DMN may result in the iminyl radical formation and cyclisation.[34] Such reaqction conditions were absent from the present study.

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