Novel photochemical behaviour of the oximes and hydrazones of β,γ-unsaturated carbonyl compounds

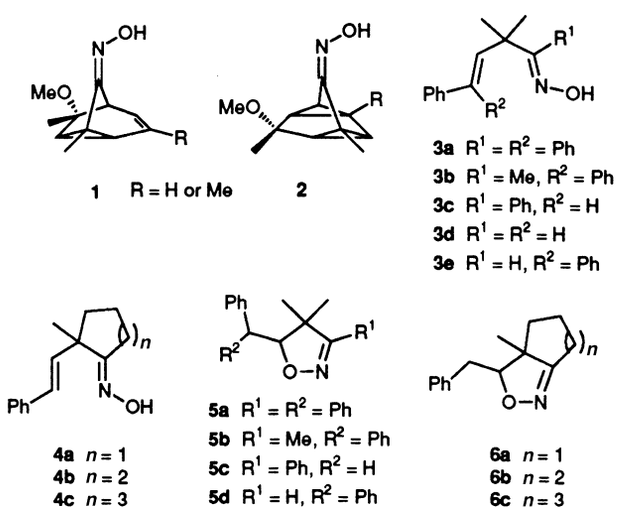
Diego Armesto,* Ana Ramos, Maria J. Ortiz, William M. Horspool,† Maria J. Mancheño, Olga Caballero and Elena P. Mayoral

Departamento de Quimica Organica, Facultad de Ciencias Quimicas, Universidad Complutense, 28040-Madrid, Spain

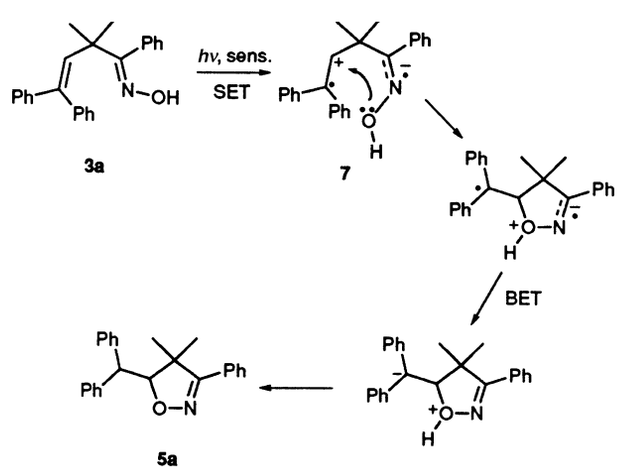
A study of the photochemical reactivity of a series of β,γ-unsaturated oximes and hydrazone derivatives under triplet sensitized conditions has been carried out. The oximes 3c, 4a and 4c cyclize to the corresponding dihydroisoxazoles 5c, 6a and 6c while the tosyl hydrazone 8a affords the dihydropyrazole 9a. An intramolecular single electron-transfer mechanism from the alkene moiety to the oximino group, in the case of the oximes 3c, 4a and 4c, and to the tosyl group for the tosyl hydrazone 8a, is proposed to account for these results. Oximes and hydrazine derivatives from aldehydes behave differently. Thus, the oxime 3d yields the cyclopropyl oxime 10 by an aza di-π-methane (ADPM) rearrangement while the aldoxime 3e gives a mixture of the corresponding dihydroisoxazole 5d and cyclopropane 11a resulting from an ADPM process. Irradiation of the hydrazine derivatives 8b, 8c and 8d gives a mixture of the corresponding dihydropyrazoles 9b, 9c and 9d and the cyclopropanes 11b, 11c and 11d, respectively. However, under the same experimental conditions, dihydronaphthalene derivatives such as the oxime 12a and the tosyl hydrazone 12b undergo ADPM rearrangements exclusively, affording the cyclopropanes 13a and 13b, respectively. Sensitized irradiation of the tosyl hydrazone 12c yields the cyclopropane 13c, as the major product. In this instance a small amount of the hexahydrophenanthroline 14, resulting from an *endo* cyclization is also formed. The influence of substitution on the outcome of the reaction is discussed.

Introduction

For many years acyclic β,γ-unsaturated oximes and oxime ethers were thought to be photochemically unreactive.[1,2] Until very recently the only reported reactivity of this type of compounds was *E,Z*-isomerization around the C–N double bond in acyclic systems[2] and the aza-di-π-methane (ADPM) reactivity of the β,γ-unsaturated oximes **1** where irradiation brings about the formation of the tetracyclic compounds **2**.[3] Contrary to the



supposed inertness of the acyclic derivatives we have demonstrated recently that some β,γ-unsaturated oximes are reactive by the ADPM mode.[4] This rearrangement occurs in molecules where the reaction proceeds *via* 'stable' biradical intermediates. Alternatively we have reported examples where irradiation of ketoximes such as **3a**, **3b** and **4b** results in the formation of the new dihydroisoxazoles **5a**, **5b** and **6b**, respectively.[5] This cyclization was considered to be controlled by an SET process from the alkene moiety to the oximino group as shown in Scheme 1



Scheme 1

for the oxime **3a**. Cyclization within the zwitterionic biradical **7** followed by back electron transfer and hydrogen migration affords the final product.

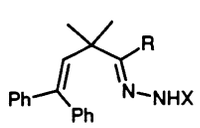
In our previous report[5] of the photochemical formation of dihydroisoxazoles from the oximes **3a**, **3b** and **4b**, the cyclization was most effective with a phenyl substituent on the oximino carbon (*i.e.* **3a**). The oximes **3b** and **4b**, with alkyl substitution at that position, also undergo the cyclization as the sole process, although less efficiently. Associated with this we have published a preliminary account of analogous cyclizations in the sensitized irradiation of β,γ-unsaturated hydrazone derivatives **8** that afford dihydropyrazoles **9**.[6] The present pub-

† *Permanent address*: Department of Chemistry, The University of Dundee, UK DD1 4HN

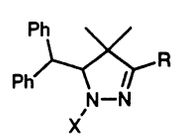
lication details our studies to establish the features within these types of molecules that control the outcome of these two cyclizations.

Results and discussion

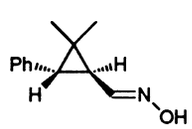
The present study was aimed at determining the influence of changes in substitution at C-1 and C-4, in the acyclic oximes **3** and changes in ring size in the cyclic oximes **4**. The compounds selected for this study were the oximes **3c**, **3d**, **3e**, **4a** and **4c**. The synthesis of the oximes **3d**[7] and **3e**[1] has been reported by us. The oxime **3c** was readily synthesized by standard oximation procedures from the corresponding carbonyl compound described previously in the literature.[8] Acetophenone-sensitized irradiation of the ketoxime **3c** for 1 h brought about the formation of **5c** in 15% yield and starting material **3c** (72%) as a mixture of *E*/*Z*-isomers of the C–C double bond. This result shows that the change in substitution in C–4 from diphenyl in **3a** to monophenyl in **3c** does not affect the outcome of the reaction adversely. The formation of the dihydroisoxazole **5c** fits within the mechanism shown in Scheme 1. However, under the same experimental conditions, the aldoxime **3d** undergoes an ADPM rearrangement exclusively affording the cyclopropane **10**. This compound was unequivocally identified by conversion into the corresponding oxime acetate previously described by us.[7] Regardless of the marked change in behaviour between **3c** and **3d** these results are in agreement with our previous findings. As mentioned above aldoximes in which the biradical intermediate is stabilized by conjugation with phenyl rings undergo ADPM rearrangement while the phenyl ketoxime **3a**, with a phenyl substituent at C-1, gives the dihydroisoxazole **5a**. However, the successful ADPM reactivity of **3d** casts doubts on the lack of reactivity of the aldoxime **3e**, previously reported by us,[1] and a reinvestigation of the photoreactivity of this compound was necessary. A careful analysis of the crude reaction mixture obtained from the acetophenone-sensitized irradiation of **3e**, for 1 h, demonstrated that this compound is photochemically reactive contrary to our previous report. This treatment yields the cyclopropyl oxime **11a** in 10% yield, the dihydroisoxazole **5d** in 8% yield in addition to recovered starting material (58%).



8a R = Me, X = Ts
8b R = H, X = Ts
8c R = H, X = Bz
8d R = H, X = Ac
8e R = Ph, X = Ts



9a R = Me, X = Ts
9b R = H, X = Ts
9c R = H, X = Bz
9d R = H, X = Ac



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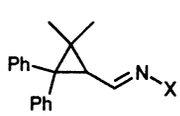


11a X = OH
11b X = NHTs
11c X = NHBz
11d X = NHAc

The differences observed in the results from this series of compounds can be interpreted in terms of SET involvement or the lack of it. Thus we observe a gradation in reactivity in this series. The cyclization of the original compound **3a** shows that the phenylhydroxyimino moiety is a good electron acceptor and the diphenylvinyl group is well known to be a good donor.[9] Thus SET is favoured and cyclization (see Scheme 1) yields the dihydroisoxazole **5a** comparatively efficiently (38% within 10 min).[5] In the oxime **3c** the electron-accepting ability of the hydroxyimino group is unchanged but the vinyl moiety is less efficient in electron transfer reactions but is still able to undergo the SET[10] and as a result **5c** is formed less efficiently. Decreasing the electron-accepting capacity of the hydroxyimino group in **3d** and retaining the poorer electron-donating phenylvinyl group provides a situation where electron transfer apparently does not take place and the ADPM process takes over affording the cyclopropyl oxime **10**. In derivative **3e** the hydroxyimino group remains the same but the vinyl substituent is now the good electron-donating diphenylvinyl system. With this compound a balance between electron transfer, affording **5d**, and ADPM reactivity giving **11a** is observed. Thus it is clear that ketoxime derivatives show a preference for the electron transfer process and the formation of dihydroisoxazoles while the aldoxime derivatives follow the ADPM path preferentially.

Table 1 Yield of photoproducts

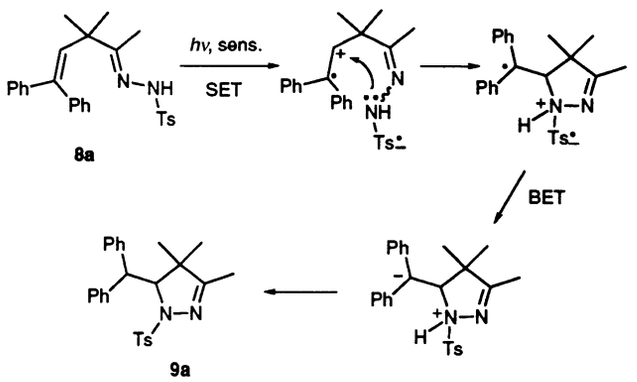
Starting compd.	ADPM product (%)	Five membered-ring heterocycle (%)
3c	—	**5c** (15)
3d	**10** (19)	—
3e	**11a** (10)	**5d** (8)
4a	—	**6a** (20)
4c	—	**6c** (12)
8a	—	**9a** (75)
8b	**11b** (7)*	**9b** (18)
8c	**11c** (22)	**9c** (11)
8d	**11d** (68)*	**9d** (1)
12b	**13b** (68)	—
12c	**13c** (46)	—

* Isolated as the corresponding aldehyde.

The capacity for the ketoximes to undergo SET and cyclization to dihydroisoxazoles is also observed with the derivatives **4a** and **4c**. These two compounds are readily prepared by reaction of the corresponding 1-methyl-2-oxocycloalkanecarbaldehyde[11] with benzyltriphenylphosphonium ylide, followed by oximation. Brief irradiation of both of these affords the corresponding dihydroisoxazoles **6a** and **6c** in 20 and 12% yields, respectively. It is worthwhile noting that prolonged irradiation of these oximes and also of the oximes **3**, does not increase the yield of product markedly. In qualitative terms there is little variation in the apparent efficiency of the reaction of the oximes **4a** and **4c**, compared with the previously reported cyclization of the oxime **4b** that gives **6b** in 20% yield.[5] Thus ring size does not appear to influence the cyclization process.

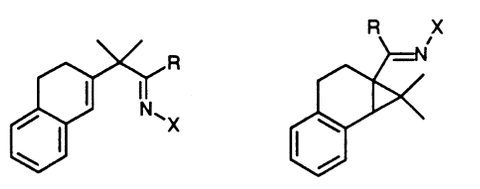
The foregoing demonstrates that if SET takes place then cyclization involving the oxygen of the oxime to the cation centre is a viable process. It should, therefore, be possible to observe analogous reactivity with other derivatives of β,γ-unsaturated carbonyl compounds such as the hydrazones. This was demonstrated previously by us and the results were published in a preliminary form.[6] Since the best yield for the formation of dihydroisoxazoles in the oxime examples took place with the phenyl ketone derivative **3a**, it was logical to study the reactivity of the corresponding hydrazone derivative **8e**. All the attempts to synthesize this compound by condensation of the corresponding carbonyl compound with tosylhydrazide were unsuccessful. This could be due to the low reactivity of the phenyl ketone towards nucleophilic attack. However, the hydrazone derivatives **8a–d** were obtained in good yield by condensation between the corresponding carbonyl compounds and hydrazine derivatives. Acetophenone-sensitized irradiation of **8a** follows an analogous reaction path of the oxime cyclization and yields the dihydropyrazole **9a** in 75% yield. The success with this reaction suggests that the tosylhydrazone moiety is an even better electron acceptor than is the oxime. When the aldehydo derivative **8b** was irradiated the reactivity observed is also in agreement with our earlier observations with the oxime derivatives

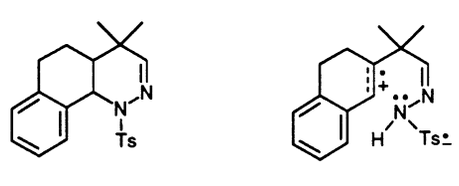
and one of the products of the reaction is the dihydropyrazole **9b** obtained in 18% yield. The reaction, however, also affords the ADPM product, the cyclopropane **11b**, in 9% yield. Thus it is obvious that there is a partitioning of the reaction between the electron transfer path to the dihydropyrazole and the ADPM path to the cyclopropane. In order to explain the formation of dihydropyrazoles we propose a mechanism involving SET from the alkene moiety to the substituent on the terminal nitrogen, as shown in Scheme 2 for tosylhydrazone **8a**. Cyclization within the resultant zwitterionic biradical affords the heterocyclic product. This mechanism provides an explanation for the different yields of dihydropyrazoles obtained in the irradiation of **8a** and **8b** and those obtained in the irradiation of **8c** and **8d**.[6] Thus, with the tosyl derivative **8a** the yield is highest of all, the benzoyl derivative **8c** gives a reduced yield of the dihydropyrazole **9c** (11%) and the acetyl derivative **8d** affords only a trace of **9d** (1%). Interestingly, as the ability of the hydrazone substituent to accept an electron decreases the yield of the ADPM product **11c** and **11d**, respectively, increases to 22% with **8c** and 68% with **8d**.



Scheme 2

The study with the oxime derivatives has shown that the best yields of heterocyclic products are obtained with the phenyl ketone derivatives. However, the oxime **12a** is an exception to this generalization. The oxime **12a**, is readily synthesized by methylation of 2-(3,4-dihydro-2-naphthyl)acetonitrile[12] with potassium *tert*-butoxide and methyl iodide, followed by reaction of the methylated nitrile with phenyllithium to obtain the corresponding ketone. Oximation of this yields oxime **12a**. Acetophenone-sensitized irradiation of **12a** affords no dihydroisoxazole and only the ADPM process takes place affording cyclopropane **13a** in 20% yield. The same preference for ADPM reactivity is also shown for the ketohydrazone derivative **12b** that affords **13b** efficiently in 68% yield. The aldehyde derivative **12c** also undergoes the ADPM affording **13c**. The ADPM rearrangement of the keto derivatives **12a** and **12b** was totally unexpected since in our experience related β,γ-unsaturated keto derivatives are unreactive by this mode. The conversion of **12a** into **13a** is the first example of an ADPM rearrangement of a phenyl ketone derivative. There is no evidence in the photoreactions of **12a** and **12b** for SET involvement analogous to that described earlier. However, **12c**, in addition to the cyclopropane **13c**, also gives a heterocyclic compound formed in 9% yield. Analysis of the spectroscopic data identifies this as the hexahydrophenanthroline **14**. We propose that this compound is formed by an SET process to yield a zwitterion such as **15**, within which cyclization affords the hexahydrophenanthroline **14**. The formation of **14** containing a six-membered ring was surprising in the light of our previous results. The usual cyclization mode followed within the zwitterionic biradical precursors involved an *exo* attack with the exclusive formation of a five-membered ring.[5] Cyclization of the zwitterionic biradical **15** involves an *endo* ring closure. Such a change in the cyclization mode could be the result of the structural constraints of the dihydronaphthalene moiety.





The above results demonstrate that acyclic β,γ-unsaturated ketoximes **3a–d** undergo cyclization to dihydroisoxazoles on triplet-sensitized irradiation. Similarly tosylhydrazones **8a-b**, benzoylhydrazone **8c** and acetylhydrazone **8d** from acyclic β,γ-unsaturated carbonyl compounds yield dihydropyrazoles **9** under analogous reaction conditions. Both reactions are thought to proceed *via* an intramolecular SET mechanism taking place from the alkene moiety to the hydroxyimino group, in the case of the oximes, or to the acetyl, the benzoyl or the tosyl groups, in the case of the hydrazone derivatives. This interpretation gives justification to the dependency of the efficiency of the reaction on the nature of the substituent on the terminal nitrogen. Thus, in qualitative terms, the efficiency increases from acetyl to benzoyl to tosyl in an order that it is coincident with the electron-accepting capacities of these groups. When the efficiency of the SET process diminishes the ADPM rearrangement competes with the cyclization. This situation is observed in the aldehyde derivatives **3d**, **3e**, **8b**, **8c** and **8d**. However, when the alkene moiety is part of a dihydronaphthalene unit, as in compounds **12**, the reactivity observed is entirely different. In this instance the predominant reaction path for both β,γ-unsaturated oximes and hydrazone derivatives is the ADPM rearrangement regardless of whether the precursor carbonyl is an aldehyde or a ketone. In one case only '**12c**' the formation of the phenanthroline **14**, resulting from an *endo* cyclization, was observed as a very minor product, in addition to the cyclopropyl derivative **13c** resulting from the ADPM rearrangement. The reactivity observed for the dihydronaphthalene derivatives could be due to the particular characteristics of the π-π* triplet excited state of this chromophore, as have been demonstrated by Caldwell *et al.*[13] The unusual short life time of the excited state in this instance was interpreted as a result of the planarity of the excited double bond. This factor could be responsible for the absence of cyclizations and also for the efficient ADPM rearrangement of these systems. However it cannot be ruled out that some other undetermined structural features present in these systems could also account for the observed reactivity. Our results show that compounds that were previously considered of little synthetic utility, such as β,γ-unsaturated oximes and hydrazone derivatives, can undergo novel and synthetically useful photochemical reactions, namely: ADPM rearrangement and/or cyclizations to different types of heterocycles depending on the substitution pattern present in the β,γ-unsaturated system.

Experimental

Melting points were determined on a Buchi 530D apparatus in open capillaries and are uncorrected. IR spectra were recorded

on a Perkin-Elmer 781 spectrophotometer as liquid films, unless otherwise stated and band positions are reported in wavenumbers (cm^{-1}). NMR spectra were run at the Servicio de RMN de la Universidad Complutense de Madrid. ^{1}H NMR spectra: Varian VXR-300S (300 MHz) and Bruker AC-250F (250 MHz), $CDCl_3$ as solvent, TMS as internal standard and coupling constants *J* are given in Hz. ^{13}C NMR spectra: Varian VXR-300S (75 MHz) and Bruker AC-250F (62 MHz), $CDCl_3$ (δ 77.0) as internal standard. UV–VIS spectra were recorded for solutions in CH_2Cl_2 using a Perkin Lambda 3B spectrophotometer. Mass spectra were run at the Chemistry Department, University of Dundee using a VG 11-250J mass spectrometer. Combustion analyses were carried out by the Servicio de Microanálisis de la Universidad Complutense de Madrid. Column chromatography was performed using silica gel 60 (40-63 mm) (Merck). Commercially available starting materials and reagents were purchased from the Aldrich Chemical Co. Ether refers to diethyl ether.

2,2-Dimethyl-4-phenylbut-3-enal oxime **3d**,[7] 2,2-dimethyl-4,4-diphenylbut-3-enal oxime **3e**,[1] 2,2-dimethyl-4,4-diphenylbut-3-enal benzoylhydrazone **8c**[14] and 2,2-dimethyl-4,4-diphenylbut-3-enal acetylhydrazone **8d**[14] were prepared as previously described.

Synthesis of 2-methyl-2-(2-phenylvinyl)cycloheptanone

A solution of butyllithium (solution 1.6 mol dm^{-3} in hexane; 36.5 cm^3, 0.06 mol) was slowly added dropwise to a solution of benzyl(triphenyl)phosphonium chloride (22.5 g, 0.06 mol) in anhydrous THF (100 cm^3), at 0 °C under argon. Then, the mixture was refluxed for 1 h. After cooling, the red reaction mixture was treated with a solution of 1-methyl-2-oxocycloheptanecarbaldehyde[11] (6 g, 0.04 mol) in THF (50 cm^3), added at room temperature. The mixture was stirred for 12 h, hydrolysed with saturated aqueous ammonium chloride and extracted with ether. The extract was dried ($MgSO_4$), filtered and evaporated to dryness. Flash chromatography of the crude product using hexane–ether (8:2) as eluent gave a 1:1 mixture of *Z*:*E* isomers of the *title compound* as a yellow oil (7.1 g, 80%); ν_{max}/cm^{-1} 1700 (CO); δ_H(250 MHz) 1.0 (1.5 H, s, Me of *E* isomer), 1.1 (1.5 H, s, Me of *Z* isomer), 1.2–2.5 (10 H, m, 5 CH_2), 5.4 (0.5 H, d, *J* 12.4, PhCH=C*H* of *Z* isomer), 6.0, 6.2 (1 H, AB, *J* 16.5, PhC*H*=C*H* of *E* isomer), 6.3 (0.5 H, d, *J* 12.4, PhC*H*=CH of *Z* isomer) and 6.8–7.5 (5 H, m, aryl H); δ_C(75 MHz) 23.7 (Me), 24.2 (Me), 24.5, 24.7, 25.9, 26.7, 29.9, 30.7, 37.2, 40.5, 40.8, 40.9 (CH_2), 53.6 (quaternary C of *E* isomer), 53.9 (quaternary C of *Z* isomer), 126.0–136.8 (aryl and vinyl C), 214.2 (C=O of *E* isomer) and 214.4 (C=O of *Z* isomer); *m*/*z* 228 (M^+, 100%), 200 (8), 185 (25), 157 (67), 143 (95), 129 (76), 109 (20), 91 (36), 77 (14) and 67 (13) (Found: C, 84.2; H, 8.8. $C_{16}H_{20}O$ requires C, 84.22; H, 8.78%).

Synthesis of 2-methyl-2-(2-phenylvinyl)cyclopentanone

A solution of benzyl(triphenyl)phosphonium chloride (14.2 g, 37 mmol) in 1,2-dimethoxyethane (25 cm^3) was added dropwise to a stirred suspension of NaH (60% dispersion; 1.5 g, 0.03 mol) in the same solvent (15 cm^3). Then 1-methyl-2-oxocyclopentanecarbaldehyde[11] (4 g, 32 mmol) was added slowly to the mixture, the temperature of which was kept <35 °C. The mixture was stirred for 4 h at room temperature when the deposition of a thick gelatinous precipitate indicated completion of the reaction. The mixture was poured into water and extracted with chloroform. The extract was dried ($MgSO_4$), filtered and concentrated to dryness. Flash chromatography of the residue using hexane–ether (8:2) as eluent gave a 1:1 mixture of *Z*:*E* isomers of the *title compound* (4.24 g, 66%) as a yellow oil; ν_{max}/cm^{-1} 1720; δ_H(250 MHz) 1.1 (1.5 H, s, Me of *E* isomer), 1.2 (1.5 H, s, Me of *Z* isomer), 1.1–2.3 (6 H, m, 3CH_2), 5.8 (0.5 H, d, *J* 12.4, PhCH=C*H* of *Z* isomer), 6.1, 6.3 (2 H, AB, *J* 16.5, PhC*H*=C*H* of *E* isomer), 6.5 (0.5 H, d, *J* 12.4, PhC*H*=CH of *Z* isomer), 7.1–7.8 (5 H, m, aryl H); δ_C(62 MHz), 23.0 (Me of *E* isomer), 23.7 (Me of *Z* isomer), 18.8, 18.9, 36.7, 36.8, 37.3 (CH_2), 50.8 (quaternary C of *Z* isomer), 51.4 (quaternary C of *E* isomer), 126.1–137.9 (aryl and vinyl C), 220.1 (CO of *E* isomer) and 221.0 (CO of *Z* isomer).

Synthesis of 2-(3,4-dihydro-2-naphthyl)-2-methyl-1-phenylpropan-1-one

2-(3,4-Dihydro-2-naphthyl)-2-methylpropanonitrile. A solution of 2-(3,4-dihydro-2-naphthyl)acetonitrile[12] (1.54 g, 9.1 mmol) and methyl iodide (7.65 g, 53 mmol) in anhydrous ether (30 cm^3) was added to a suspension of potassium *tert*-butoxide (3.95 g, 35 mmol) in ether (40 cm^3) at −78 °C under nitrogen. The mixture was stirred at −78 °C for 1 h and then at room temperature for an additional 1 h. The solution was then quenched with water and extracted with ether. The extract was washed successively with aqueous NH_4Cl, aqueous NaCl and water and then dried ($MgSO_4$), filtered and evaporated to dryness to yield the *title compound* (1.72 g, 96%) as an oil which was used in the next step without further purification; ν_{max}/cm^{-1} 2220 (CN); δ_H(300 MHz) 1.5 (6 H, s, 2Me), 2.3 (2 H, m, CH_2), 2.7 (2 H, m, CH_2), 6.5 (1 H, s, vinyl H) and 7.0–7.1 (4 H, m, aryl H); δ_C(75 MHz) 23.9 (CH_2), 26.0 (2Me), 28.3 (CH_2), 37.9 (quaternary C), 123.1 (vinyl C), 123.9 (CN) and 126.7–139.4 (aryl and vinyl C); *m*/*z* 197 (M^+, 42%), 182 (100) and 129 (45) (Found: M^+, 197.1199. $C_{14}H_{15}N$ requires *M*, 197.1201).

A solution of the above propanonitrile (850 mg, 4.31 mmol) in anhydrous ether (9 cm^3) was added slowly dropwise to a solution of phenyllithium (solution 2 mol dm^{-3} in hexane; 4.4 cm^3, 8.8 mmol) in ether (9 cm^3) at 0 °C under argon. The reaction mixture was stirred at 0 °C for 3 h and then at room temperature for an additional 1 h. A solution of H_2SO_4 (6 mol dm^{-3}; 7 cm^3) in dioxane (12 cm^3) was added to the mixture which was then heated to 50–60 °C for 2 h. The organic phase was separated and the aqueous phase was neutralized with aqueous NaOH (10%). The aqueous phase was extracted with ether and the combined organic extracts were dried ($MgSO_4$), filtered and evaporated to dryness. The residue was purified by flash chromatography using hexane–ether (99:1) as eluent to yield the *title compound* (710 mg, 60%) as an oil; ν_{max}/cm^{-1} 1680 (CO); δ_H(300 MHz) 1.4 (6 H, s, 2Me), 2.1 (2 H, m, CH_2), 2.6 (2 H, m, CH_2), 6.6 (1 H, s, vinyl H), 7.0–7.3 (7 H, m, aryl H) and 8.0 (2 H, m, aryl H); δ_C(75 MHz) 25.2 (2Me), 25.4, 28.1 (CH_2), 52.7 (quaternary C), 121.3 (vinyl C), 126.1–136.7 (aryl C), 145.3 (vinyl C) and 203.8 (CO); *m*/*z* 276 (M^+, 3%), 171 (100) and 77 (6) (Found: M^+, 276.1514. $C_{20}H_{20}O$ requires *M*, 276.1509.)

Standard method for the synthesis of oximes

The corresponding aldehyde, hydroxylamine hydrochloride and pyridine were refluxed in EtOH (50 cm^3) for 1–6 h. The aldehyde/hydroxylamine/pyridine ratio was 1:1.2:1.2 for all the experiments. The solvent was evaporated and the crude product was dissolved in ether, washed with 10% aqueous HCl, water and brine. The oximes were isolated and purified by flash chromatography using hexane–ether as eluent.

2-Methyl-2-(2-phenylvinyl)cyclopentanone oxime 4a. From 2-methyl-2-(2-phenylvinyl)cyclopentanone (1.2 g, 6 mmol) a 3:2 mixture of *Z*:*E* isomers of the oily oxime **4a** (0.98 g, 76%) was obtained; ν_{max}/cm^{-1} 3250 (OH) and 1615 (C=N); λ_{max}/nm 247 (ε 8100 $dm^3\ mol^{-1}\ cm^{-1}$); δ_H(250 MHz) 1.2 (1.8 H, s, Me of *Z* isomer), 1.4 (1.2 H, s, Me of *E* isomer), 1.6–2.6 (6 H, m, 3 CH_2), 5.8 (0.6 H, d, *J* 12.3, PhCH=C*H* of *Z* isomer), 6.3, 6.4 (0.8 H, AB, *J* 16.3, PhC*H*=C*H* of *E* isomer), 6.5 (0.6 H, d, *J* 12.3, PhC*H*=CH of *Z* isomer), 7.1–7.3 (5 H, m, aryl H), 9.7 (0.6 H, br s, OH of *Z* isomer) and 9.8 (0.4 H, br s, OH of *E* isomer); δ_C(75 MHz) 24.3 (Me of *E* isomer), 26.0 (Me of *Z* isomer), 20.6, 20.7, 26.3, 26.8, 39.6, 39.7 (CH_2), 47.8 (quaternary C of *Z* isomer), 48.5 (quaternary C of *E* isomer), 126.0–129.2, 135.1, 137.0, 137.2, 138.0 (aryl and vinyl C), 169.2 (C=N of *E* isomer) and 170.5 (C=N of *Z* isomer); *m*/*z* 215 (M^+, 46%), 198 (100), 170 (48), 113 (35) and 91 (60) (Found: M^+, 215.1304. $C_{14}H_{17}NO$ requires *M*, 215.1306).

2-Methyl-2-(2-phenylvinyl)cycloheptanone oxime 4c. From 2-methyl-2-(2-phenylvinyl)cycloheptanone (2.5 g, 11 mmol), the oxime **4c** (2.4 g, 90%) was obtained as a white solid, consisting of a 1:1 mixture of *Z*:*E* isomers, mp 75–77 °C (from hexane); ν_{max}/cm^{-1} 3250 (OH); λ_{max}/nm 249 (1200); δ_H(250 MHz) 1.1 (1.5 H, s, Me of *Z* isomer), 1.2 (1.5 H, s, Me of *E* isomer), 1.2–1.7 (8 H, m, 4 CH_2), 2.1 (1 H, m, CH_2 of *Z* isomer), 2.7 (1 H, m, CH_2 of *E* isomer), 5.6 (0.5 H, d, *J* 12.5, PhCH=C*H* of *Z* isomer), 6.1, 6.2 (1 H, AB, *J* 16.3, PhC*H*=C*H* of *E* isomer), 6.5 (0.5 H, d, *J* 12.5, PhC*H*=CH of *Z* isomer), 7.0–7.3 (5 H, m, aryl H), 9.7 (0.5 H, br s, OH of *Z* isomer) and 10.1 (0.5 H, br s, OH of *E* isomer); δ_C(75 MHz) 23.3, 23.6, 24.5 (CH_2), 24.8 (Me), 25.2 (CH_2), 25.4 (Me), 25.6, 25.9, 30.3, 30.7, 39.6, 42.6 (CH_2), 45.9 (quaternary C of *Z* isomer), 46.0 (quaternary C of *E* isomer), 126.0–128.9, 136.5, 137.0, 137.2, 138.0 (aryl and vinyl C), 164.8 (C=N of *Z* isomer) and 165.5 (C=N of *E* isomer); *m*/*z* 243 (M^+, 74), 228 (91), 200 (100), 186 (29), 143 (30), 129 (48), 115 (28), 91 (60), 77 (25) and 767 (23) (Found: C, 79.0; H, 8.6; N, 5.6. $C_{16}H_{21}NO$ requires C, 79.03; H, 8.64; N, 5.76%).

(*E*)-2,2-dimethyl-1,4-diphenylbut-3-en-1-one oxime 3c. From (*E*)-2,2-dimethyl-1,4-diphenylbut-3-en-1-one[8] (1.47 g, 5.9 mmol) the oxime **3c** (0.68 g, 44%) was obtained as a white solid, mp 151–153 °C (from hexane); ν_{max}(KBr)/cm^{-1} 3260 (OH); λ_{max}/nm 254 (18 000); δ_H(250 MHz) 1.3 (6 H, s, 2Me), 6.2, 6.3 (2 H, AB, *J* 16.3, vinyl H), 7.1–7.4 (10 H, m, aryl H) and 7.8 (1 H, br s, OH); δ_C(62 MHz) 25.9 (2Me), 43.0 (quaternary C), 126.4–137.3 (aryl and vinyl C) and 164.8 (C=N); 265 (M^+, 100%), 250 (38), 248 (63), 145 (33), 131 (37) and 91 (36) (Found: C, 81.3; H, 7.3; N, 5.3. $C_{18}H_{19}NO$ requires C, 81.51; H, 7.17; N, 5.28%).

2-(3,4-Dihydro-2-naphthyl)-2-methyl-1-phenylpropanone oxime 12a. From 2-(3,4-dihydro-2-naphthyl)-2-methyl-1-phenylpropanone (310 mg, 1.12 mmol), the oxime **12a** (209 mg, 64%) was obtained as a white solid, mp 195–197 °C (from hexane); ν_{max}/cm^{-1} 3400 (OH); λ_{max}/nm 274 (18 000); δ_H(300 MHz) 1.3 (6 H, s, 2Me), 1.5 (1 H, s, OH), 2.4 (2 H, m, CH_2), 2.8 (2 H, m, CH_2), 6.2 (1 H, s, vinyl H) and 6.9–7.3 (9 H, m, aryl H); δ_C(75 MHz) 24.3 (CH_2), 25.1 (2Me), 28.7 (CH_2), 45.7 (quaternary C), 122.6–132.7, 134.5, 134.7, 144.1 (aryl and vinyl C) and 163.9 (C=N); *m*/*z* 291 (M^+, 100%), 274 (85), 234 (51), 171 (49), 151 (56), 129 (41) and 113 (41) (Found: M^+, 291.1627. $C_{20}H_{21}NO$ requires *M*, 291.1618) (Found: C, 82.6; H, 7.5; N, 4.9. $C_{20}H_{21}NO$ requires C, 82.44; H, 7.27; N, 4.81%).

Synthesis of 3,3-dimethyl-5,5-diphenylpent-4-en-2-one tosylhydrazone 8a

3,3-Dimethyl-5,5-diphenylpent-4-en-2-one[15] (0.3 g, 1.1 mmol), toluene-*p*-sulfonylhydrazide (0.23 g, 1.2 mmol) and zinc chloride (*ca.* 20 mg) were refluxed in toluene (60 cm^3) for 8 h, with azeotropic removal of water by a Dean and Stark trap. The mixture was then cooled, the catalyst was filtered off and the solution evaporated to dryness. Flash chromatography of the residue using hexane-ethyl acetate (8:2) as eluent afforded the desired tosylhydrazone **8a** (0.37 g, 78%) as a white solid, mp 176–177 °C (from EtOH); ν_{max}/cm^{-1} 3090 (NH), 1630 (C=N); λ_{max}/nm 230 (24 000); δ_H(300 MHz) 1.2 (6 H, s, 2Me), 1.3 (3 H, s, MeCN), 2.4 (3 H, s, ArMe), 5.9 (1 H, s, vinyl H) and 6.8–7.8 (15 H, m, aryl H and NH); δ_C(75 MHz) 13.7 (MeCN), 21.5 (ArMe), 27.8 (2Me), 45.1 (quaternary C), 127.0–143.7 (aryl and vinyl C) and 161.8 (C=N); *m*/*z* 432 (M^+, 1), 265 (100), 167 (19), 155 (38) and 91 (65) (Found: C, 72.2; H, 6.34; N, 6.5; S, 7.0. $C_{26}H_{28}N_2O_2S$ requires C, 72.23; H, 6.48; N, 6.48; S, 7.41%).

Synthesis of 2,2-dimethyl-4,4-diphenylbut-3-enal tosylhydrazone 8b

2,2-Dimethyl-4,4-diphenylbut-3-enal[7] (0.8 g, 3.2 mmol) and toluene-*p*-sulfonylhydrazide (0.6 g, 3.2 mmol) were dissolved in methylene dichloride (50 cm^3) and the solution was stirred at room temperature in the presence of $MgSO_4$ for 4 h. Conventional work-up, followed by flash chromatography using hexane–ether (7:3) as eluent afforded the desired tosylhydrazone **8b** (0.8 g, 67%) as a white solid, mp 103–105 °C (from EtOH); ν_{max}/cm^{-1} 3190 (NH) and 1640 (C=N); λ_{max}/nm 215 (6300); δ_H(300 MHz) 1.2 (6 H, s, 2Me), 2.4 (3 H, s, ArMe), 6.0 (1 H, s, vinyl H), 6.6 (1 H, s, CH=N) and 6.9–7.9 (15 H, m, aryl H and NH); δ_C(75 MHz) 21.3 (ArMe), 26.9 (2Me), 40.6 (quaternary C), 126.6–143.6 (aryl and vinyl C) and 157.5 (C=N); *m*/*z* 418 (M^+, 13), 263 (42), 234 (51), 219 (91), 167 (100), 146 (63), 91 (64), 77 (16) and 65 (26) (Found: C, 71.4; H, 6.3; N, 6.7; S, 7.9. $C_{25}H_{26}N_2O_2S$ requires C, 71.78; H, 6.21; N, 6.69; S, 7.65%).

Synthesis of 2-(3,4-dihydro-2-naphthyl)-3-methylbutan-2-one tosylhydrazone 12b

The same procedure used for the synthesis of **8a** was followed in this case. Thus, 2-(3,4-dihydro-2-naphthyl)-3-methylbutan-2-one[16] (400 mg, 1.87 mmol) and toluene-*p*-sulfonylhydrazide (382 mg, 2.05 mmol) gave, after flash chromatography using hexane–ethyl acetate (9:1) as eluent, the desired tosylhydrazone **12b** as a white solid (0.41 g, 57%), mp 173–174 °C (from EtOH); ν_{max}/cm^{-1} 3210 (NH) and 1600 (C=N); λ_{max}/nm 273 (14 000) and 265 (14 400); δ_H(300 MHz) 1.2 (6 H, s, 2Me), 1.6 (3 H, s, MeCN), 1.7 (2 H, m, CH_2), 2.4 (3 H, s, ArMe), 2.5 (2 H, m, CH_2), 6.2 (1 H, s, vinyl H), 7.0 (4 H, m, aryl H), 7.2 (2 H, d, *J* 8.3, aryl H), 7.6 (1 H, br s, NH) and 7.8 (2 H, d, *J* 8.3, aryl H); δ_C(75 MHz) 12.4 (MeCN), 21.5 (ArMe), 23.77 (2Me), 23.81 (CH_2), 28.2 (CH_2), 47.6 (quaternary C), 121.9 (vinyl C), 125.6–145.0 (aryl and vinyl C) and 161.0 (C=N); *m*/*z* 382 (M^+, 33%), 227 (25), 198 (36) and 68 (100) (Found: C, 68.8; H, 6.7; N, 7.4. $C_{22}H_{26}N_2O_2S$ requires C, 69.06; H, 6.85; N, 7.32%).

Synthesis of 2-(3,4-dihydro-2-naphthyl)-2-methylpropanal tosylhydrazone 12c

The same procedure used for the synthesis of **8b** was followed in this case. Thus, from 2-(3,4-dihydro-2-naphthyl)-2-methylpropanal[16] (0.56 g, 2.8 mmol) the desired tosylhydrazone **12c** was obtained as a white solid (760 mg, 73%), mp 177–178 °C (from EtOH); ν_{max}/cm^{-1} 3180 (NH) and 1610 (C=N); λ_{max}/nm 229 (24 200); δ_H(250 MHz) 1.2 (6 H, s, 2Me), 1.9 (2 H, t, *J* 8.1, CH_2), 2.4 (3 H, s, ArMe), 2.5 (2 H, t, *J* 7.6, CH_2), 6.1 (1 H, s, vinyl H), 6.9 (1 H, s, CH=N), 6.7–7.4 (6 H, m, aryl H) and 7.8 (2 H, *J* 8.3, aryl H); δ_C(63 MHz) 21.8 (ArMe), 23.7 (2Me), 23.9 (CH_2), 28.4 (CH_2), 43.5 (quaternary C), 122.4 (vinyl C), 126.2–144.3 (aryl and vinyl C) and 157.1 (C=N); *m*/*z* 354 ($M^+ - 15$, 0.7) and 91 (100) (Found: C, 68.1; H, 6.5; N, 7.6. $C_{21}H_{24}N_2O_2S$ requires C, 68.45; H, 6.56; N, 7.60%).

Preparative photolyses

The photolyses were carried out in an immersion-well apparatus with a Pyrex filter and a 400-W medium-pressure Hg arc lamp. Solutions of the compounds and the sensitizer in anhydrous benzene or methylene dichloride (420 cm^3) were purged with argon for 1 h and irradiated under a positive pressure of argon for the times shown. After completion of the irradiation the solvent and the sensitizer were removed under reduced pressure and the products were separated by flash chromatography.

Acetophenone-sensitized irradiation of the oxime 3e. This compound (350 mg, 1.32 mmol) and acetophenone (5.6 g) were irradiated in methylene dichloride for 1 h. After removal of the solvent and the sensitizer, flash chromatography using hexane-ether (9:1) gave unchanged **3e** (204 mg, 58%), a 3:2 mixture of *Z*:*E* isomers of the cyclopropyloxime **11a** (36 mg, 10%) as a white solid mp 145–46 °C; ν_{max}(KBr)/cm^{-1} 3250 (OH) and 1650 (CH); δ_H(300 MHz) 1.09 (1.2 H, s, Me of *E* isomer), 1.11 (1.8 H, s, Me of *Z* isomer), 1.29 (1.2 H, s, Me of *E* isomer), 1.32 (1.8 H, s, Me of *Z* isomer), 2.4 (0.4 H, d, *J* 9.8, CH of *E* isomer), 2.9 (0.6 H, d, *J* 8.6, CH of *Z* isomer), 6.4 (0.6 H, d, CH=N of *Z* isomer) and 7.1–7.5 (10.4 H, m, aryl H and CH=N of *E* isomer); δ_C(75 MHz) 20.4 (Me of *Z* isomer), 20.6 (Me of *E* isomer), 25.0 (Me of *E* isomer), 25.3 (Me of *Z* isomer), 28.1 (*C*Me$_2$ of *E* isomer), 28.5 (*C*Me$_2$ of *Z* isomer), 29.4 (CH of *E* isomer),

33.3 (CH of *Z* isomer), 46.6 (*C*Ph_2 of *E* isomer), 48.0 (*C*Ph_2 of *Z* isomer), 126.1–144.3 (aryl C), 151.0 (CN of *E* isomer) and 152.5 (CN of *Z* isomer). This compound was further characterized by transformation into the corresponding acetate.[17] Further elution afforded the dihydroisoxazole **5d** (30 mg, 8%) as an oil; ν_{max}(KBr)/cm^{-1} 1610; δ_H(300 MHz), 0.9 (3 H, s, Me), 1.0 (3 H, s, Me), 4.2 (1 H, d, *J* 11.0, $CHPh_2$), 4.8 (1 H, d, *J* 11.0, OCH), 6.9 (1 H, s, CH=N) and 7.0–7.4 (10 H, m, aryl H); δ_C(75 MHz) 19.4 (Me), 24.9 (Me), 51.2 ($CHPh_2$), 88.4 (CHO), 126.6–128.7 (aryl C) and 157.8 (CN); *m*/*z* 264 ($M^+ - 1$, 1%), 167 (100) and 165 (18) (Found: $M^+ - 1$, 264.1392. $C_{18}H_{18}NO$ requires *M*, 264.1384).

Acetophenone-sensitized irradiation of the oxime 4a. This compound (296 mg, 1.37 mmol) and acetophenone (2.7 g) in methylene dichloride were irradiated for 15 min. After removal of the solvent and the sensitizer, flash chromatography using hexane–ether (9:1) gave unchanged **4a** (220 mg, 74%) and the dihydroisoxazole **6a** (60 mg, 20%) as a colourless oil; ν_{max}(KBr)/cm^{-1} 1645 (C=N); δ_H(300 MHz) 1.5 (3 H, s Me), 1.6–2.4 (6 H, m, 3 CH_2), 4.0 (1 H, dd, *J* 6.7 and 5.5, ABX CH_2), 4.1 (1 H, dd, *J* 9.1 and 6.7, ABX CH_2), 4.2 (1 H, dd, *J* 9.1 and 5.5, CH) and 7.0–7.3 (5 H, m, aryl H); δ_C(75 MHz) 18.2 (Me), 24.9, 31.2, 35.6 (CH_2), 52.5 (quaternary C), 85.7 (CH), 126.5–129.7, 138.1 (aryl C) and 168.0 (C=N); *m*/*z* 215 (M^+, 45%), 198 (100), 170 (47), 129 (67), 115 (34) and 91 (61) (Found: M^+, 215.1300. $C_{14}H_{17}NO$ requires *M*, 215.1306).

Acetophenone-sensitized irradiation of the oxime 4c. This compound (400 mg, 1.6 mmol) and acetophenone (2 g), in methylene dichloride were irradiated for 22 min. After removal of the solvent and the sensitizer, flash chromatography using hexane–ether (9:1) gave unchanged **4c** (273 mg, 68%) and the dihydroisoxazole **6c** (47 mg, 12%) as a white solid, mp 118–120 °C (from hexane); ν_{max}(KBr)/cm^{-1} 1660 (CN); δ_H(300 MHz) 1.1 (3 H, s Me), 1.4–2.3 (10 H, m, 5CH_2), 2.7 (1 H, dd, *J* 14.3 and 4.0, ABX CH_2), 3.1 (1 H, dd, *J* 14.3 and 9.2, ABX CH_2), 4.4 (1 H, dd, *J* 9.2 and 4.0, CH) and 7.1–7.8 (5 H, m, aryl H); δ_C(75 MHz) 19.2 (Me), 23.9, 25.7, 28.9, 31.3, 33.9, 35.6 (CH_2), 54.5 (quaternary C), 87.1 (CH), 126.5–129.2, 133.5, 138.3 (aryl C) and 168.6 (C=N); *m*/*z* 243 (M^+, 1), 105 (10), 91 (11) and 84 (100) (Found: C, 79.4; H, 8.6; N, 5.8. $C_{16}H_{21}NO$ requires C, 79.03; H, 8.74; N, 5.76%).

Acetophenone-sensitized irradiation of the oxime 3c. The *E*-oxime **3c** (350 mg, 1.32 mmol) and acetophenone (2 g) were irradiated in methylene dichloride for 1 h. After removal of the solvent and the sensitizer, flash chromatography using hexane–ether (95:5) gave the dihydroisoxazole **5c** as a white solid (52 mg, 13%), mp 125–127 °C (from hexane); ν_{max}(KBr)/cm^{-1} 1610 (CN); δ_H(300 MHz) 1.2 (3 H, s, Me), 1.3 (3 H, s, Me), 2.8 (1 H, dd, *J* 14.7 and 4.2, ABX CH_2), 3.0 (1 H, dd, *J* 14.7 and 9.1, ABX CH_2), 4.3 (1 H, dd, *J* 9.1 and 4.2, CH), 7.2–7.4 (8 H, m, aryl H) and 7.6 (2 H, m, aryl H); δ_C(75 MHz) 19.5 (Me), 23.7 (Me), 34.2 (CH_2), 51.0 (quaternary C), 91.1 (CH), 126.4–129.5, 137.6 (aryl C) and 165.5 (C=N) (Found: C, 81.8; H, 7.4; N, 5.6. $C_{18}H_{19}NO$ requires C, 81.51; H, 7.17; N, 5.28%). Further elution gave the oxime **3c** (251 mg, 72%) as a 1:1 mixture of *Z*:*E* isomer of the C=C bond; δ_H(300 MHz) 1.1 (3 H, s, 2Me of *Z* isomer), 1.3 (3 H, s, 2Me of *E* isomer), 5.5 (0.5 H, d, *J* 12.6 PhCH=C*H* of *Z* isomer), 6.2, 6.3 (1 H, AB, *J* 16.3, PhC*H*=C*H* of *E* isomer), 6.5 (0.5 H, d, *J* 12.6, PhC*H*=CH of *Z* isomer), 7.0–7.3 (10 H, m, aryl H) and 7.8, 8.0 (1 H, br, s, OH); δ_C(75 MHz) 25.9 (Me), 27.5 (Me), 42.8 (quaternary C), 43.0 (quaternary C), 126.1–137.3 (aryl and vinyl C) and 161.8, 163.8 (CN).

Acetophenone-sensitized irradiation of the oxime 3d. The oxime **3d** (312 mg, 1.65 mmol) and acetophenone (2 g) were irradiated in methylene dichloride for 1 h. After removal of the solvent and the sensitizer, flash chromatography using hexane-ether (95:5) as eluent gave **3d** (132 mg, 42%) as a 1:1 mixture of *Z*:*E* isomers of the C=C bond; δ_H(300 MHz) 1.1, 1.2 (6 H, s, 2Me), 5.5 (0.5 H, d, *J* 12.2, PhCH=C*H* of *Z* isomer), 6.1, 6.3 (1 H, AB, *J* 16.2, vinyl H of *E* isomer), 6.5 (0.5 H, d, *J* 12.2, PhC*H*=CH of *Z* isomer), 7.0–7.5 (5 H, m, aryl H) and 8.2, 8.6 (1 H, br s, OH) and the cyclopropane **10** (58 mg, 19%) as a white solid, mp 124–126 °C (from hexane); ν_{max}(KBr)/cm^{-1} 3100 (OH) and 1610; δ_H(300 MHz) 0.9 (3 H, s, Me), 1.3 (3 H, s, Me), 2.3 (1 H, d, *J* 5.5, CH), 2.5 (1 H, dd, *J* 8.5, 5.5, CH), 6.6 (1 H, d, *J* 8.5, CH=N) and 7.2–7.3 (5 H, m, aryl H); δ_C(75 MHz) 21.6 (Me), 22.8 (Me), 29.5 (quaternary C), 36.1 (CH), 38.1 (CH), 126.2–128.8 (aryl C) and 152.3 (CN). This compound was further characterized by transformation into the corresponding acetate.[7]

Acetophenone-sensitized irradiation of the oxime 12a. This compound (200 mg, 0.69 mmol) and acetophenone (7.7 g) in methylene dichloride were irradiated for 20 min. After removal of the solvent and the sensitizer, flash chromatography of the residue using hexane-ether (95:5) gave the cyclopropyl oxime **13a** (40 mg, 20%) as a white solid, mp 202–204 °C (from hexane); ν_{max}/cm^{-1} 3300 (OH) and 1610 (C=N); δ_H(300 MHz) 0.8 (3 H, s, Me), 1.1 (3 H, s, Me), 1.5 (1 H, s, OH), 1.7 (1 H, s, CH), 2.3 (2 H, m, CH_2), 2.6 (1 H, m, 1/2 CH_2), 3.0 (1 H, m, 1/2 CH_2) and 7.1–7.3 (9 H, m, aryl H); δ_C(75 MHz) 14.2 (Me), 22.7 (Me), 28.7 (CH_2), 29.8 (CH_2), 30.4 (quaternary C), 31.7 (CH), 32.2 (quaternary C), 126.2–128.9 (aryl C) and 179.0 (C=N); *m*/*z* 274 ($M^+ - 17$, 19), 232 (64), 173 (100) and 145 (46) (Found: C, 82.3; H, 7.0; N, 4.6. $C_{20}H_{21}NO$ requires C, 82.44; H, 7.27; N, 4.81%). Further elution afforded unchanged **12a** (110 mg, 55%).

Acetophenone-sensitized irradiation of the tosylhydrazone 8a. This compound (300 mg, 0.69 mmol) and acetophenone (3 g) were irradiated in benzene for 50 min. After removal of the solvent and the sensitizer, flash chromatography of the residue using hexane–ether acetate (8:2) gave unchanged **8a** (50 mg, 16%) and the dihydropyrazole **9a** (225 mg, 75%) as a white solid, mp 125–126 °C (from EtOH); ν_{max}(KBr)/cm^{-1} 1620 (C=N); δ_H(300 MHz) 0.8 (3 H, s, Me), 1.0 (3 H, s, Me), 1.9 (3 H, s, MeCN), 2.3 (3 H, s, MeAr), 3.9 (1 H, d, *J* 10.0, $CHPh_2$), 5.0 (1 H, d, *J* 10.0, NCH) and 7.1–7.3 (14 H, m, aryl H); δ_C(75 MHz) 12.2, 20.0, 21.4, 26.8 (Me), 52.7 (CMe_2), 53.5 (CPh_2), 68.5 (CH-N), 126.1–143.5 (aryl C) and 170.0 (CN); *m*/*z* 433 (M^++1, 1%), 265 (100), 176 (31), 165 (25), 155 (48), 91 (88), 65 (14) and 41 (11) (Found: C, 71.5; H, 6.7; N, 6.3. $C_{26}H_{28}N_2O_2S$. 1/2 EtOH requires C, 71.21; H, 6.81; N, 6.15%).

Acetophenone-sensitized irradiation of the tosylhydrazone 8b. This compound (496 mg, 1.2 mmol) and acetophenone (15 g) were irradiated in benzene for 30 min. After removal of the solvent and the sensitizer, flash chromatography of the residue using hexane–ethyl acetate (8:2) gave unchanged **8b** (339 mg, 70%) and a mixture of the tosylhydrazone **11b** and the dihydropyrazole **9b** (121 mg (27%). This mixture was hydrolysed following the method described by Reese and co-workers.[18] Thus, to an ice cooled solution of the mixture of **11b** and **9b** in MeOH (20 cm^3), was added a solution of H_2O_2 (0.2 cm^3, 1.68 mmol) and K_2CO_3 (55 mg, 0.56 mmol) in water (10 cm^3). After the solution had been stirred for 6 h, it was adjusted to pH 8 with H_3PO_4 and extracted with methylene dichloride. The organic layer was dried ($MgSO_4$), filtered and evaporated to dryness. Flash chromatography of the residue using hexane-ether (9:1) as eluent afforded 2,2-dimethyl-3,3-diphenylcyclopropanecarbaldehyde[19] (20 mg, 7%) and the dihydropyrazole **9b** (91 mg, 18%) as a white solid mp 122–124 °C; ν_{max}(KBr)/cm^{-1} 1640 (C=N); δ_H(300 MHz) 0.8 (3 H, s, Me), 1.0 (3 H, s, Me), 2.3 (3 H, s, MeAr), 4.0 (1 H, d, *J* 11.0, $CHPh_2$), 4.8 (1 H, d, *J* 11.0, NCH), 6.8 (1 H, s, CH=N) and 7.0–8.0 (14 H, m, aryl H); δ_C(75 MHz) 20.1 (Me), 21.8 (ArMe), 27.2 (Me), 52.2 (CPh_2), 53.4 (CMe_2), 76.8 (CHN), 126.3–143.8 (aryl C) and 163.0 (CN); *m*/*z* 418 (M^+, 1%), 251 (63), 167 (16), 165 (15), 155 (65) and 91 (100) (Found: C, 71.5; H, 6.2; N, 6.5; S, 7.9. $C_{25}H_{26}N_2O_2S$ requires C, 71.78; H, 6.21; N, 6.69; S, 7.65%).

Acetophenone-sensitized irradiation of the benzoylhydrazone 8c. This compound (850 mg, 2.3 mmol) and acetophenone (30 g) in methylene dichloride were irradiated for 45 min. After removal of the solvent and the sensitizer, flash chromatography

of the residue using hexane–ethyl acetate (7:3) gave dihydropyrazole **9c** as a white solid (92 mg, 11%), mp 193–194 °C (from EtOH); ν_{max}/cm^{-1} 3210 (OH), 1655 (CO) and 1600 (C=N); δ_H(300 MHz) 1.0 (3 H, s, Me), 1.2 (3 H, s, Me), 4.2 (1 H, d, *J* 11.0, $CHPh_2$), 5.4 (1 H, d, *J* 10.0, CH−N), 6.7 (1 H, s, CH=N) and 7.5–7.0 (15 H, m, aryl H); δ_C(63 MHz) 19.4, 27.0 (Me), 50.1 (quaternary C), 51.5 ($CHPh_2$), 65.8 (CH−N), 122.9–141.4 (aryl C), 158.1 (C=N) and 167.6 (CO); *m*/*z* 368 (M^+, 1%), 201 (68), 167 (15), 165 (18), 105 (100) and 77 (53) (Found C, 81.8; H, 6.4; N, 7.7. $C_{25}H_{24}N_2O$ requires C, 81.53; H, 6.51; N, 7.60%). Further elution gave the benzoylhydrazone **8c** (527 mg, 62%) and cyclopropylbenzoylhydrazone **11c** (184 mg, 22%).[14]

Acetophenone-sensitized irradiation of the acetylhydrazone 8d. This compound (268 mg, 0.8 mmol) and acetophenone (12 g) in benzene were irradiated for 2 h. After removal of the solvent and the sensitizer, the crude photolysate was hydrolysed by adding to it a solution of sulfuric acid 10%; (aqueous solution: 20 cm^3) in THF (60 cm^3). After being stirred for 12 h, the mixture was extracted with ether. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), filtered and evaporated to dryness. Flash chromatography of the residue using hexane as eluent gave 2,2-dimethyl-4,4-diphenyl-3-butenal (55 mg, 24%), 2,2-dimethyl-3,3-diphenylcyclopropanecarbaldehyde[19] (155 mg, 68%) and dihydropyrazole **9d** (4 mg, 1%); δ_H(300 MHz) 1.0 (3 H, s, Me), 1.1 (3 H, s, Me), 1.8 (3 H, s, MeCO), 4.0 (1 H, d, *J* 11.0, $CHPh_2$), 4.9 (1 H, d, *J* 11.0, CH−N) and 7.4–7.0 (11 H, m, aryl H and CH=N).

Acetophenone-sensitized irradiation of the tosylhydrazone 12b. This compound (204 mg, 0.53 mmol) and acetophenone (6 g) in methylene dichloride were irradiated for 15 min. After removal of the solvent and the sensitizer, flash chromatography of the residue using hexane–ether (8:2) gave the cyclopropyl tosylhydrazone **13b** as a white solid (141 mg, 68%), mp 187–189 °C (from EtOH); ν_{max}/cm^{-1} 3210 (NH), 1620 (C=N); δ_H(300 MHz) 0.56 (3 H, s, Me), 0.65 (3 H, s, Me), 1.6 (1 H, m, 1/2 CH_2), 1.7 (3 H, s, MeCN), 1.8 (1 H, m, 1/2 CH_2), 2.1 (1 H, s, CH), 2.25 (1 H, m, 1/2 CH_2), 2.28 (3 H, s, MeAr), 2.5 (1 H, m, 1/2 CH_2), 6.9 (4 H, m, aryl H), 7.1 (2 H, d, *J* 8.3, aryl H), 7.4 (1 H, br s, NH) and 7.7 (2 H, d, *J* 8.3, aryl H); δ_C(63 MHz) 16.0, 17.7, 21.7, 22.7 (Me), 24.2, 28.2 (CH_2), 29.0 (CH), 29.4 (quaternary C), 36.8 (quaternary C), 125.7–144.1 (aryl C) and 159.3 (C=N); *m*/*z* 380 ($M^+ - 2$, 3%), 227 (93), 212 (40), 198 (56), 155 (62), 138 (54), 129 (58), 89 (100) and 77 (35). We have not been able to obtain acceptable microanalytical data for compound **13b**. Attempts to purify this compound by recrystallization in ethanol and by column chromatography on silica gel were unsuccessful due to partial decomposition.

Acetophenone-sensitized irradiation of the tosylhydrazone 12c. This compound (215 mg, 0.58 mmol) and acetophenone (2 g) in methylene dichloride were irradiated for 7 min. After removal of the solvent and the sensitizer, flash chromatography of the residue using hexane–ether (9:1) gave the hexahydrophenanthroline **14** (20 mg, 9%) as a white solid, mp 179–180 °C (from EtOH); ν_{max}/cm^{-1} 1610 (C=N); δ_H(250 MHz) 0.3 (3 H, s, Me), 0.9 (3 H, s, Me), 1.4–1.6 (1 H, m, 1/2 CH_2), 1.8 (1 H, m, CH), 2.0 (1 H, m, 1/2 CH_2), 2.4 (3 H, s, MeAr), 2.5–2.7 (2 H, m, CH_2), 4.9 (1 H, d, *J* 5.7, CH−N), 7.0 (1 H, s, CH=N) 7.0–7.3 (6 H, m, aryl H) and 7.7 (2 H, d, *J* 8.3, aryl H); δ_C(63 MHz) 20.3 (CH_2), 20.4 (Me), 21.6 (Me), 26.3 (CH_2), 27.6 (ArMe), 33.3 (quaternary C), 37.3, 54.8 (CH), 126.1–143.7 (aryl C) and 152.2 (C=N); *m*/*z* 368 (M^+, 3%), 304 (6), 213 (43), 129 (30), 85 (57) and (100) (Found C, 68.4; H, 6.3; N, 7.4; S, 8.4. $C_{21}H_{24}N_2O_2S$ requires C, 68.45; H, 6.56; N, 7.60; S, 8.70). Further elution gave an inseparable 3:7 mixture of tosylhydrazone **12c** and cyclopropane **13c** (142 mg). This compound was characterized by independent synthesis. Thus, a mixture of the corresponding aldehyde[20] (102 mg, 0.51 mmol) and toluene-*p*-sulfonylhydrazide (95 mg, 0.51 mmol) in methylene dichloride (20 cm^3) was stirred for 12 h. Conventional work-up afforded the desired cyclopropane **13c** (169 mg, 90%) as a white solid, mp 175–176 °C (from EtOH); ν_{max}/cm^{-1} 3190 (NH) and 1610 (C=N); δ_H(300 MHz) 0.8 (3 H, s, Me), 1.2 (3 H, s, Me), 1.6 (2 H, m, CH_2), 2.0 (1 H, s, CH), 2.4 (3 H, s, MeAr), 2.6 (2 H, m, CH_2) and 7.0–7.9 (9 H, m, aryl H and CH=N); δ_C(63 MHz) 18.9 (Me), 21.7 (Me), 22.2 (CH_2), 23.4 (Me), 28.5 (CH_2), 31.9 (quaternary C), 32.5 (quaternary C), 33.2 (CH), 126.1-144.2 (aryl C) and 157.3 (C=N).

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