A study on the scope of the photochemical 1,3-migration of oximino groups in β,γ-unsaturated oximes and oxime derivatives

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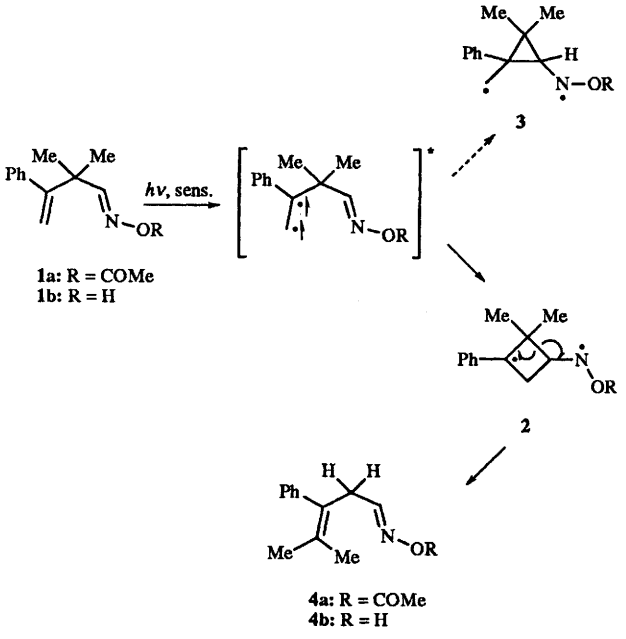
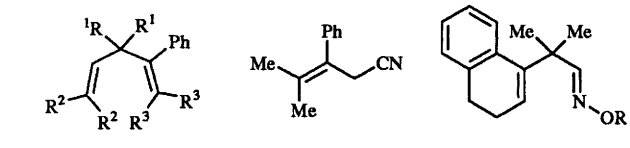
While the aza-di-π-methane rearrangement is the normal photoreactive behaviour of β,γ-unsaturated imines and oxime acetates, the results obtained in this study show that 1,3-migrations of acetoxyimino groups in β,γ-unsaturated oxime acetates takes place only when all the parameters are correct. The rearrangement takes place when there is a quaternary carbon separating the two π-systems and when one of the radical centres in the intermediate cyclobutyl 1,4-biradical is stabilized by conjugation with a phenyl ring. Suppression of the free rotor effect also helps to promote the reaction. These criteria are fulfilled in compounds 1a and 7a. The reaction was extended to the β,γ-unsaturated oximes 1b and 7b where again the 1,3-migration of the oximino group took place.

Previously we reported the first example of a 1,3-migration of an acetoxyimino group occurring on sensitized irradiation of the oxime acetate of 2,2-dimethyl-3-phenylbut-3-enal **1a**. Acetophenone-sensitized irradiation of **1a** for 1 h brought about smooth and efficient conversion into a new compound **4a** in 62% yield. The yield of **4a** can be increased to 81% after irradiation for 5 h. This novel product **4a** was readily identified as the oxime acetate of 4-methyl-3-phenylpent-3-enal.[1] No evidence was obtained for the operation of the aza-di-π-methane reaction mode. The formation of **4a** is the first example of a 1,3-migration of a C=N group in a 1-aza-1,4-diene system.

It is likely, based on the relative triplet energies of the phenylvinyl group and the C=N moiety, that the phenylvinyl group will be the terminus for the triplet energy transfer from acetophenone. That being the case, excitation of the C=N group was considered to be unlikely. This eliminates the possibility of the rearrangement arising from Norrish Type I-like bond fission of the C=N group and subsequent 1,3-migration.[2] Reactivity of this type is common in other systems such as β,γ-unsaturated ketones.[3] A simple mechanism to account for the observed rearrangement is illustrated in Scheme 1, where the cyclobutyl 1,4-biradical **2**, with stabilization by the phenyl group, is to be preferred to the alternative 1,4-biradical **3**, formed by the aza-di-π-methane bridging process. The resultant bond fission within the biradical **2** yields the final product whereby the 1,3-migration of the oxime acetate function has occurred. The substitution pattern is obviously important in controlling the outcome of the reaction and in the suppression of alternative reaction modes such as the ADPM rearrangement. It is interesting to note that the 1,4-diene **5a**, with a similar substitution pattern on one of the vinyl moieties, undergoes the di-π-methane rearrangement on direct irradiation.[4a] However, acetophenone-sensitized irradiation of **5a** affords a rearrangement product **5b** where a vinyl group has undergone a 1,3-migration. The mechanism proposed by us for the rearrangement of **1a** is substantially the same as that proposed by Zimmerman and his co-workers for the conversion of diene **5a**.[4b]

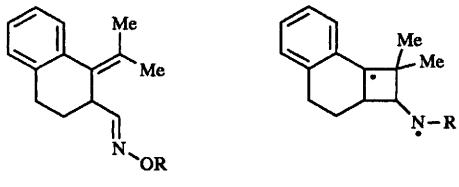


Scheme 1



5a: R^1 = Me, R^2 = Ph, R^3 = H
5b: R^1 = H, R^2 = Ph, R^3 = Me

7a: R = COMe
7b: R = H



8a: R = COMe
8b: R = H

9a: R = COMe
9b: R = H

Results and discussion

The current report details our attempts to establish the parameters that control the 1,3-migration in 1-aza-1,4-diene systems. If the only controlling feature in the process is the stability of the cyclobutyl 1,4-biradical **2** then it should be possible to approach this same biradical by irradiation of the 1-

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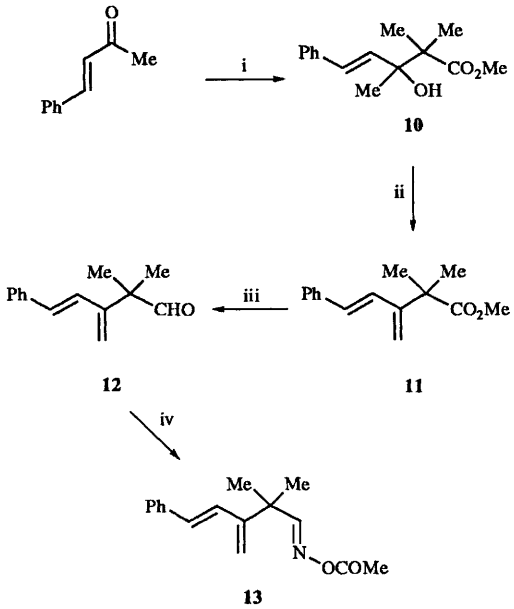
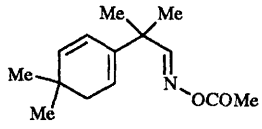
aza-1,4-diene **4a**. However, it was established readily that the irradiation of **4a**, under conditions identical with those used for the irradiation of **1a**, did not bring about the 1,3-migration. The products isolated from this reaction were identified as the *E*/*Z* isomers of the starting material **4a** and the nitrile **6** formed by thermal elimination of acetic acid from **4a**. The absence of the 1,3-rearrangement product **1a** demonstrates that the rearrangement of **1a** into **4a** is a one-way process or, in other words, a photostationary state favouring one component exclusively. The lack of reversibility can be understood because, although both the alkene moieties in **1a** and **4a** have the same capacity to accept triplet energy from the sensitizer, the absence of a quaternary carbon between the two π-systems could surpress the formation of intermediate **2**. There is also the possibility that **2** is formed on irradiation of **4a**, but breaks down in favour of **4a** rather than **1a**. The substitution in the central carbon atom is a well established structural feature controlling the photochemical reactivity of 1,4-dienes in the di-π-methane rearrangement.[5]

From the foregoing, it was clear that the key features for the successful operation of the 1,3-migration were the stability of the cyclobutyl 1,4-biradical and the presence of a quaternary carbon between the two π-systems. Compound **7a** incorporates both a quaternary carbon and a means of stabilizing the cyclobutyl biradical. In addition, the possibility of free-rotor deactivation of the excited state is eliminated since the phenylvinyl moiety is part of a ring system. The irradiation of **7a**, for 30 min, using acetophenone as sensitizer, brought about conversion into a single photoproduct in 80% yield. The identity of this compound was established readily as the 1,3-migrated product **8a**. This product is formed by the same path as that for the formation of **4a** from **1a**. Again, it is presumed that the stability of the cyclobutyl 1,4-biradical **9a** is the controlling feature. This intermediate undergoes ring-opening to yield the final product. In qualitative terms, the rearrangement of **7a** is more efficient than that reported for **1a**, affording **8a** in higher yields with shorter irradiation times. This enhanced efficiency could be the result both of the suppression of free rotor deactivation of the triplet state and of enhanced overlap of the cyclobutyl radical with the benzene ring due to the planarity of that part of the molecule. An alternative method for the stabilization of the cyclobutyl 1,4-biradical, using a styryl group, was incorporated in **13**. It was considered likely that the cyclobutyl radical would be stabilized as effectively by a styryl group as by a phenyl. The compound was synthesized by the route outlined in Scheme 2. Irradiation of **13** using *m*-methoxyacetophenone as sensitizer for 1.5 h yields only a 1:1 mixture of *Z*:*E*-isomers of the styryl double bond. No evidence was obtained for the operation of the 1,3-migration in this instance. It is interesting to note that the transfer of triplet energy from the sensitizer to the styryl moiety of the reactant molecule had taken place as evidenced by the isomerization of the double bond. The absence of any reaction other than this suggests that an efficient energy-wasting step, the free rotor process, was operative.



Scheme 2 *Reagents:* i, isopropylcyclohexylamine–LiBu–Me_2CH-CO_2Me; ii, P_2O_5; iii, (*a*) $LiAlH_4$, (*b*) PCC; iv, (*a*) NH_2OH–HCl, (*b*) MeCOCl–pyridine

From the previous result it is clear that the free rotor effect can be an effective method for deactivation of the excited state. Incorporation of the double bond into a ring would overcome this and still permit stabilization of the 1,4-biradical by conjugation with a vinyl group. Thus compound **14** was chosen



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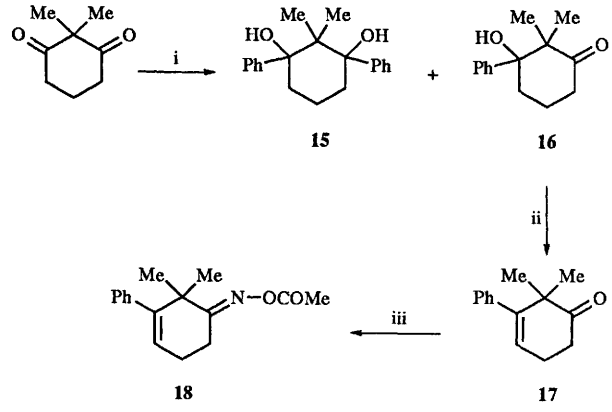
as the next reactant and its synthesis was carried out from 4,4-dimethylcyclohex-2-enone by a method similar to that used for the synthesis of **13** (Scheme 2). However, again no evidence for rearrangement was detected on irradiation of the azatriene **14** for either a short time with acetophenone as sensitizer or prolonged irradiation using phenanthrene. Only highly polar material was obtained in both of these experiments. Phenanthrene was used to eliminate the possibility that the decomposition was the result of hydrogen abstraction reactions that might have occurred in the acetophenone excitation experiment. However no difference was encountered. Compound **14** is thermally unstable, therefore it may be that this instability is the reason for the failure to observe rearrangement, although it could also be argued that the resultant cyclobutyl 1,4-biradical was not sufficiently stable to permit the bonding required for the rearrangement.

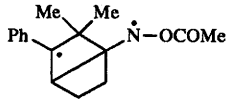
The next candidate for study reverted to the original substitution pattern with a phenyl group on the vinyl moiety. In this instance all the positive features, a quaternary carbon separating the two π-systems, the absence of free rotor deactivation and the possibility of cyclobutyl 1,4-biradical stabilization by a phenyl group, were incorporated into molecule **18**. This was synthesized according to Scheme 3.



Scheme 3 *Reagents:* i, PhLi; ii, P_2O_5; iii, (*a*) NH_2OH–HCl, (*b*) MeCOCl–pyridine

Acetophenone- or acetone-sensitized irradiation of this compound also failed to bring about rearrangement. It is not impossible within this molecule that stabilization of the cyclobutyl 1,4-biradical is inefficient because of steric constraint within the bicyclic 1,4-biradical intermediate **19** that prevents overlap of the phenyl ring with the radical centre.

Recently we have demonstrated that in some instances it is possible to observe rearrangement reactions, notably the aza-di-π-methane process,[6] or cyclizations to dihydroisoxazoles,[7] with oximes. Photoreactions of this sort with oximes were unprecedented since it has long been proposed that β,γ-unsaturated oximes were unreactive. Thus, it was of some importance to establish whether or not it was possible to observe 1,3-migration reactions with oximes. Sensitized-irradiation of the oxime **1b** resulted in the formation of a complex



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mixture of products from which a low yield of the corresponding rearranged oxime **4b** was isolated. It is clear in this example that the rearrangement of the oxime is inefficient and alternative reaction modes are operative. This is not so with the oxime **7b**. In this instance brief acetophenone-sensitized irradiation brings about efficient 1,3-migration to yield the isomeric oxime **8b** in 86% yield. This is the first example of a 1,3-migration of a hydroxyimino group within a β,γ-unsaturated oxime.

The results presented by us show that the 1,3-migration of a hydroxyimino or acetoxyimino group in a β,γ-unsaturated oxime or oxime acetate takes place only when all the parameters are correct. Thus, the molecules undergoing the rearrangement should have a quaternary carbon separating the two π-systems and stabilization of one of the radical centres in the cyclobutyl 1,4-biradical by conjugation with a phenyl ring. Suppression of the free rotor effect also helps to promote the reaction. These criteria are fulfilled in compounds **1a**, **7a** and **7b**. It is interesting to note that for decades β,γ-unsaturated oximes were considered to be photochemically inert. Thus, in our opinion, one of the most important findings in this study is the discovery of another new unprecedented photochemical rearrangement in such systems, although restricted to a very limited number of compounds of this type.

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. ^1H 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 or ethanol 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.

Synthesis of the oxime acetate 7a and oxime 7b

2-(3,4-Dihydro-1-naphthyl)-2-methylpropanol. A solution of ethyl 2-(3,4-dihydro-1-naphthyl)-2-methylpropanoate[8] (2.3 g, 10 mmol) in dry ether (70 cm^3) was added slowly dropwise and at 0 °C to a stirred suspension of lithium aluminium hydride (0.36 g, 9.5 mmol) in dry ether (50 cm^3). The resulting mixture was kept at room temperature until disappearance of the starting material (monitored by TLC). The residual lithium aluminium hydride was decomposed by addition to the mixture of acetone followed by aqueous NH_4Cl. The organic layer was separated, washed with brine, dried ($MgSO_4$), filtered and evaporated to dryness, to give the *title compound* (1.8 g, 89%) as an oil; ν_{max}/cm^{-1} 3380 (OH) and 1620 (C=C); δ_H(300 MHz) 1.3 (6 H, s, 2 Me), 1.6 (1 H, br s, OH), 2.2 (2 H, m, CH_2), 2.6 (2 H, m, CH_2), 3.7 (2 H, d, J 3, CH_2OH), 6.2 (1 H, t, J 5.1, CH=C), 7.1–7.2 (3 H, m, aryl H) and 7.5 (1 H, m, aryl H); δ_C(75 MHz) 23.4 (CH_2), 26.1 (2 Me), 29.0 (CH_2), 40.7 (quaternary C), 70.5 (CH_2O), 124.9, 125.6, 126.1, 127.8, 128.0, 134.0, 138.4 and 140.2 (aryl and vinyl C); m/z 202 (M^+, 46%), 171 (100), 156 (25), 143 (54), 141 (30), 129 (84), 115 (34), 91 (12) and 77 (8) (Found: M^+, 202.1350. $C_{14}H_{18}O$ requires M, 202.1358).

2-(3,4-Dihydro-2-naphthyl)-2-methylpropanal. The above alcohol (1.8 g, 8.9 mmol) and pyridinium chlorochromate (2.8 g, 12.8 mmol) were allowed to react in methylene dichloride at room temperature for 24 h. The crude reaction mixture was filtered through silica gel to remove highly polar material and the filtrate evaporated to give the *title compound* as an oil which was used in the next step without further purification; ν_{max}/cm^{-1} 2790, 2700, 1720 (CO) and 1620 (C=C); δ_H(300 MHz) 1.4 (6 H, s, 2 Me), 2.3 (2 H, m, CH_2), 2.7 (2 H, m, CH_2), 6.2 (1 H, t, J 4.5, CH=C), 7.0–7.2 (4 H, m, aryl H) and 9.5 (1 H, s, CHO); δ_C(75 MHz) 22.1 (2 Me), 23.3, 28.3 (CH_2), 50.3 (quaternary C), 124.0, 126.1, 126.6, 127.8, 133.2, 137.4, 137.9 (aryl and vinyl C) and 205.0 (CO); m/z 200 (M^+, 29%), 171 (90), 169 (73), 143 (49), 141 (61), 129 (100), 128 (81), 115 (61), 91 (24) and 77 (19) (Found: M^+, 200.1194. $C_{14}H_{16}O$ requires M, 200.1201).

2-(3,4-Dihydro-1-naphthyl)-2-methylpropanal oxime 7b. The aldehyde synthesized above (1.24 g, 6.2 mmol), hydroxylamine hydrochloride (0.52 g, 7.4 mmol) and pyridine (0.74 cm^3, 7.4 mmol) were heated at reflux in ethanol (25 cm^3) for 3 h. After work-up, flash chromatography of the crude product using hexane–ether (9:1) as eluent gave the *oxime* **7b** (1.2 g, 90%) as a white solid, mp 120–121 °C (from hexane); ν_{max}(KBr)/cm^{-1} 3250 (OH); δ_H(300 MHz) 1.5 (6 H, s, 2 Me), 2.2 (2 H, m, CH_2), 2.7 (2 H, m, CH_2), 6.1 (1 H, t, J 4.6, CH=C), 7.1–7.5 (4 H, m, aryl H), 7.5 (1 H, s, CH=N) and 8.4 (1 H, br s, OH); δ_C(75 MHz) 23.3 (CH_2), 26.5 (2 Me), 28.5 (CH_2), 40.4 (quaternary C), 125.2, 125.7, 125.9, 126.2, 127.5, 133.5, 137.7, 140.5 (aryl and vinyl C) and 159.0 (C=N); m/z 215 (M^+, 14%), 200 (65), 198 (11), 182 (20), 141 (20), 128 (40), 115 (25), 91 (100) and 77 (13) (Found: C, 78.3; H, 8.1; N, 6.8. $C_{14}H_{17}NO$ requires C, 78.10; H, 7.96; N, 6.51%).

Oxime acetate 7a. Acetyl chloride (0.48 cm^3, 6.7 mmol) was added to a solution of the oxime **7b** (1.2 g, 5.6 mmol) in pyridine (3 cm^3) at 0 °C. The mixture was stirred for 2 h at room temperature and then diluted with ether. The pyridine was removed by washing successively with 10% aqueous HCl, saturated aqueous $NaHCO_3$ and brine. The combined organic phases were dried ($MgSO_4$), filtered and evaporated to dryness. Flash chromatography with hexane–ether (8:2) as eluent gave the *oxime acetate* **7a** (0.64 g, 45%) as a white solid, mp 62–64 °C (from hexane); ν_{max}(KBr)/cm^{-1} 1760 (CO) and 1610 (C=N); λ_{max}(EtOH)/nm 259 (ε/dm^3 mol^{-1} cm^{-1} 6700); δ_H(300 MHz) 1.5 (6 H, s, 2 Me), 2.1 (3 H, s, COMe), 2.2 (2 H, m, CH_2), 2.7 (2 H, m, CH_2), 6.1 (1 H, t, J 4.8, CH=C), 7.1–7.2 (3 H, m, aryl H), 7.5 (1 H, m, aryl H) and 7.7 (1 H, s, CH=N); δ_C(75 MHz) 19.5 (COMe), 23.3 (CH_2), 26.1 (2Me), 28.4 (CH_2), 41.2 (quaternary C), 124.7, 126.0, 126.4, 126.5, 127.7, 133.4, 137.6, 139.7 (aryl and vinyl C), 166.5 (C=N) and 168.6 (C=O); m/z 257 (M^+, 3%), 200 (53), 198

(62), 197 (36), 182 (32), 155 (31), 141 (24), 129 (100), 127 (20) and 115 (27) (Found: C, 74.6; H, 7.3; N, 5.3. $C_{16}H_{19}NO_2$ requires C, 74.68; H, 7.44; N, 5.44%).

Synthesis of the oxime acetate 13

Methyl (*E*)-3-hydroxy-2,2,3-trimethyl-5-phenylpent-4-enoate 10. A *solution* of butyllithium (solution 1.6 mol dm^{-3} in hexane; 42.5 cm^3, 68 mmol) was slowly added dropwise to a solution of isopropylcyclohexylamine (11.2 cm^3, 68 mmol) in anhydrous THF (100 cm^3) at −78 °C under argon. After the addition was complete, the solution was stirred for 15 min and then treated with methyl isobutyrate (7.8 cm^3, 68 mmol), added dropwise to the mixture. After 20 min, a solution of 4-phenylbut-3-en-2-one (10 g, 68 mmol) in 30 cm^3 of dry THF was also added dropwise to the mixture. After being stirred at −78 °C for 2 h, the reaction mixture was worked up by acidification with 20% hydrochloric acid and extracted with ether (×3). The extracts were washed with brine, dried ($MgSO_4$), filtered and evaporated to dryness. Distillation of the crude material gave the *ester* **10** (10.5 g, 63%) as an oil, bp 87–89 °C/0.7 mmHg; ν_{max}/cm^{-1} 3480 (OH) and 1720 (CO); δ_H(250 MHz) 1.27 (3 H, s, Me), 1.30 (3 H, s, Me), 1.34 (3 H, s, Me), 3.7 (3 H, s, OMe), 4.0 (1 H, br s, OH), 6.3 (1 H, d, *J* 16, CH=C), 6.7 (1 H, d, *J* 16, CH=C) and 7.1–7.4 (5 H, m, aryl H); δ_C(62 MHz) 21.35, 21.32, 23.6 (3 Me), 50.0 (quaternary C), 52.2 (OMe), 75.7 (COH), 126.5, 127.4, 128.0, 128.5, 129.3, 129.4, 132.4, 137.0 (aryl and vinyl C) and 178.7 (CO); *m/z* 248 (M^+, 15%), 147 (100), 129 (30), 103 (13) and 77 (10) (Found: M^+, 248.141 25. $C_{15}H_{20}O_3$ requires *M*, 248.141 20).

Methyl (*E*)-2,2-dimethyl-3-methylidene-5-phenylpent-4-enoate 11. P_2O_5 (2.8 g, 20 mmol) was added to a solution of the ester **10** (4 g, 16 mmol) and a catalytic amount of hydroquinone dissolved in dry ether (100 cm^3). The reaction mixture was refluxed for 4 h after which time the hydroxy ester had disappeared (analysis by TLC). The P_2O_5 formed a dark, viscous deposit on the walls of the flask. The mixture was allowed to cool to room temperature after which it was filtered through silica gel to remove highly polar material and the filtrate evaporated to dryness. The residue was purified by flash chromatography using hexane–ether (9:1) as eluent yielding the ester **11** (2.7 g, 73%) as an oil. In order to avoid further polymerization it is necessary to store this product in a CH_2Cl_2 solution and in the presence of a catalytic amount of hydroquinone as stabilizer; ν_{max}/cm^{-1} 1730 (CO); δ_H(250 MHz) 1.4 (6 H, s, 2 Me), 3.6 (3 H, s, OMe), 5.0 (1 H, s, CH_2=C), 5.3 (1 H, s, CH_2=C), 6.5 (1 H, d, *J* 16.4, CH=C), 6.6 (1 H, d, *J* 16.4, CH=C) and 6.8–7.3 (5 H, m, aryl H); δ_C(62 MHz) 25.6 (2 Me), 46.7 (quaternary C), 52.4 (OMe), 111.2, 126.7, 127.8, 128.3, 128.7, 130.0, 137.3, 149.6 (aryl and vinyl C) and 177.4 (CO).

(*E*)-2,2-Dimethyl-3-methylidene-5-phenylpent-4-en-1-ol. The procedure used for the synthesis of 2-(3,4-dihydro-1-naphthyl)-2-methylpropanol was followed in this case. Thus, from lithium aluminium hydride (0.32 g, 8.4 mmol) and **11** (1.94 g, 8.4 mmol), the *title compound* was obtained as an oil (1.38 g, 81%); ν_{max}/cm^{-1} 3400 (OH) and 1630 (C=C); δ_H(250 MHz) 1.1 (6 H, s, 2 Me), 1.4 (1 H, br s, OH), 3.4 (2 H, s, CH_2), 4.9 (1 H, d, *J* 1.1, CH_2=C), 5.3 (1 H, d, *J* 1.1, CH_2=C), 6.69 (1 H, d, *J* 16, CH=C), 6.76 (1 H, d, *J* 16, CH=C) and 7.1–7.4 (5 H, m, aryl H); δ_C(62 MHz) 24.2, (2 Me), 41.1 (quaternary C), 70.5 (CH_2), 111.3, 126.6, 127.7, 128.7, 130.6, 137.3, 151.8 (aryl and vinyl C); *m/z* 202 (M^+, 11%), 185 (18), 155 (24), 129 (100), 105 (28), 91 (25) and 77 (22).

(*E*)-2,2-Dimethyl-3-methylidene-5-phenylpent-4-enal 12. The procedure used for the synthesis of 2-(3,4-dihydro-2-naphthyl)-2-methylpropanal was followed in this case. Thus, from pyridinium chlorochromate (1.45 g, 6.8 mmol) and the above alcohol (0.9 g, 4.5 mmol), the *aldehyde* **12** (0.87 g, 98%) was obtained as an oil which was used in the next step without further purification; ν_{max}/cm^{-1} 2800, 2700, 1730 (CO) and 1630 (C=C); δ_H(250 MHz) 1.2 (6 H, s, 2 Me), 5.0 (1 H, s, CH_2=C), 5.4 (1 H, s, CH_2=C), 6.5 (1 H, d, *J* 16, CH=C), 6.6 (1 H, d, *J* 16, CH=C), 7.0–7.3 (5 H, m, aryl H) and 9.4 (1 H, s, CHO); δ_C(62 MHz) 21.4, 21.5 (Me), 31.7 (quaternary C), 114.2, 125.4, 126.6, 127.6, 128.0, 128.3, 128.7, 129.1, 130.9 (aryl and vinyl C) and 203.4 (CHO).

(*E*)-2,2-Dimethyl-3-methylidene-5-phenylpent-4-enal oxime. A procedure similar to that used for the synthesis of **7b** was followed in this case. Thus, the aldehyde **12** (0.9 g, 4.5 mmol), hydroxylamine hydrochloride (0.38 g, 5.4 mmol) and pyridine (0.56 cm^3, 5.4 mmol), after flash chromatography using hexane–ether (95:5) as eluent, gave the *title compound* (0.85 g, 88%) as an oil; ν_{max}/cm^{-1} 3300 (OH) and 1630 (C=N); $\lambda_{max}(CH_2Cl_2)$/nm 281 (13 320); δ_H(250 MHz) 1.3 (6 H, s, 2 Me), 5.0 (1 H, s, CH_2=C), 5.5 (1 H, s, CH_2=C), 6.6 (1 H, d, *J* 16, CH=C), 6.8 (1 H, d, *J* 16, CH=C), 7.2–7.5 (6 H, m, aryl H and CH=N) and 8.1 (1 H, br s, OH); δ_C(62 MHz) 25.2 (2 Me), 41.5 (quaternary C), 110.7, 126.6, 127.7, 127.8, 128.7, 130.6 (aryl and vinyl C) and 157.7 (C=N); *m/z* 215 (M^+, 25%), 200 (100), 182 (24), 129 (55), 115 (10) and 77 (11) (Found: M^+, 215.130 32. $C_{14}H_{17}NO$ requires *M*, 215.131 02).

The oxime acetate 13. The procedure used for the synthesis of **7a** was followed in this case. Thus, the above oxime (0.78 g, 3.6 mmol) and acetyl chloride (0.31 cm^3, 4.3 mmol) gave, after flash chromatography using hexane–ether (9:1) as eluent, the *oxime acetate* **13** (0.62 g, 67%) as an oil; ν_{max}/cm^{-1} 1770 (CO) and 1630 (C=N); $\lambda_{max}(CH_2Cl_2)$/nm 281 (15 600); δ_H(300 MHz) 1.3 (6 H, s, 2 Me), 2.1 (3 H, s, COMe), 4.9 (1 H, s, CH_2=C), 5.3 (1 H, s, CH_2=C), 6.6 (1 H, d, *J* 16, CH=C), 6.8 (1 H, d, *J* 16, CH=C), 7.2–7.4 (5 H, m, aryl H) and 7.6 (1 H, s, CH=N); δ_C(62 MHz) 19.7 (COMe), 24.4 (2 Me), 42.7 (quaternary C), 115.3, 126.7, 127.8, 127.9, 128.5, 128.8, 128.9, 131.7, 136.8, 147.7 (aryl and vinyl C), 163.9 (C=N) and 168.9 (CO).

Synthesis of the Oxime Acetate 14

Methyl 2-(1-hydroxy-4,4-dimethylcyclohex-2-enyl)-2-methylpropanoate. The procedure used for the synthesis of **10** was followed in this case. Thus, isopropylcyclohexylamine (6.6 cm^3, 40 mmol), butyllithium (solution 1.6 mol dm^{-3} in hexane; 25 cm^3, 40 mmol), 4,4-dimethylcyclohex-2-enone (5 g, 40 mmol) and methyl isobutyrate (4.11 g, 40 mmol) gave, after flash chromatography of the crude product using hexane–ether (9:1) as eluent, the *title compound* (9.08 g, 100%) as an oil; ν_{max}/cm^{-1} 3520 (OH) and 1720 (CO); δ_H(250 MHz) 0.95 (3 H, s, Me), 1.06 (3 H, s, Me), 1.20 (3 H, s, Me), 1.26 (3 H, s, Me), 1.5 (2 H, m, CH_2), 1.8 (2 H, m, CH_2), 3.4 (1 H, br s, OH), 3.7 (3 H, s, OMe), 5.5 (1 H, dd, *J* 10.2, 1.7, CH=C) and 5.6 (1 H, dd, *J* 10.2, 1.5, CH=C); δ_C(62 MHz) 21.05, 21.06, 26.4, 28.2 (Me), 30.6 (CH_2), 31.7 (quaternary C), 33.0 (CH_2), 49.2 (quaternary C), 52.1 (OMe), 72.3 (COH), 125.3, 142.3 (vinyl C) and 178.7 (CO); *m/z* 226 (M^+, 3%), 125 (100), 107 (14), 102 (34), 96 (10) and 70 (10) (Found: M^+, 226.1579. $C_{13}H_{22}O_3$ requires *M*, 226.1563).

Methyl 2-(4,4-dimethylcyclohexa-1,5-dienyl)-2-methylpropanoate. The procedure used for the synthesis of **11** was followed in this case. Thus, methyl 2-(1-hydroxy-4,4-dimethylcyclohex-2-enyl)-2-methylpropanoate (8.9 g, 39 mmol) and P_2O_5 (10 g, 70 mmol) in methylene dichloride (100 cm^3) gave, after flash chromatography of the crude using hexane–ether (95:5) as eluent, the desired *ester* (6 g, 74%) as an oil; ν_{max}/cm^{-1} 1740 (CO); δ_H(300 MHz) 0.9 (6 H, s, 2 Me), 1.2 (6 H, s, 2 Me), 2.0 (2 H, d, *J* 4.5, CH_2), 3.6 (3 H, s, OMe), 5.5 (2 H, m, 2 CH=C) and 5.7 (1 H, dd, *J* 10, 1.5, CH=C); δ_C(62 MHz) 24.4 (2 Me), 27.6 (2 Me), 30.7 (quaternary C), 37.8 (CH_2), 45.8

(quaternary C), 52.1 (OMe), 118.1, 122.1, 137.5, 138.8 (vinyl C) and 177.3 (CO); *m/z* 208 ($M^+ - 2$, 21%), 147 (100), 119 (13) and 107 (12) (Found: $M^+ - 2$, 206.1310. $C_{13}H_{18}O_2$ requires *M*, 206.1302).

2-(4,4-Dimethylcyclohexa-1,5-dienyl)-2-methylpropanol. The procedure used for the synthesis of 2-(3,4-dihydro-1-naphthyl)-2-methylpropanol was followed in this case. Thus, lithium aluminium hydride (1.04 g, 27 mmol) and the preceding propanoate (5.72 g, 27 mmol) gave, after flash chromatography of the crude product using hexane–ether (8:2) as eluent, the *title compound* (3.9 g, 79%) as an oil; ν_{max}/cm^{-1} 3350 (OH); δ_H(300 MHz) 0.90 (6 H, s, 2 Me), 0.98 (6 H, s, 2 Me), 1.2 (1 H, br s, OH), 2.0 (2 H, d, *J* 4.5, CH_2), 3.3 (2 H, s, CH_2OH), 5.5 (2 H, m, 2 CH=C) and 5.8 (1 H, dd, *J* 9.8, 1.6, CH=C); δ_C(62 MHz) 23.5 (2 Me), 27.7 (2 Me), 30.5 (quaternary C), 38.0 (CH_2), 39.3 (quaternary C), 70.3 (CH_2OH), 120.1, 121.2, 138.0 and 139.3 (vinyl C); *m/z* 178 ($M^+ - 2$, 14%), 147 (100), 124 (21), 107 (16) and 91 (10) (Found: $M^+ - 2$, 178.1356. $C_{12}H_{18}O$ requires *M*, 178.1353).

2-(4,4-Dimethylcyclohexa-1,5-dienyl)-2-methylpropanal. The procedure used for the synthesis of 2-(3,4-dihydro-2-naphthyl)-2-methylpropanal was followed in this case. Thus, pyridinium chlorochromate (6.54 g, 30 mmol) and the above alcohol (3.62 g, 20 mmol) gave the *title compound* (1.12 g, 31%) as an oil which was used in the next step without further purification; ν_{max}/cm^{-1} 2820, 2720, 1720 (CO) and 1650 (C=C); δ_H(250 MHz) 1.0 (6 H, s, 2 Me), 1.2 (6 H, s, 2 Me), 2.0 (2 H, d, *J* 4.5, CH_2), 5.60 (2 H, m, 2 CH=C), 5.68 (1 H, dd, *J* 10, 1.4, CH=C) and 9.3 (1 H, s, CHO); δ_C(62 MHz) 20.5, 27.5 (Me), 30.6 (quaternary C), 38.1 (CH_2), 49.9 (quaternary C), 121.3, 121.4, 134.6, 139.5 (vinyl C) and 203.4 (CHO).

2-(4,4-Dimethylcyclohexa-1,5-dienyl)-2-methylpropanal oxime. The procedure used for the synthesis of **7b** was followed in this case. Thus, the preceding aldehyde (1.04 g, 5.8 mmol), hydroxylamine hydrochloride (0.48 g, 6.96 mmol) and pyridine (0.7 cm^3, 6.96 mmol) gave, after flash chromatography using hexane–ethyl acetate (95:5) as eluent, the *title compound* (0.84 g, 74%) as an oil; ν_{max}/cm^{-1} 3340 (OH) and 1650 (C=N); δ_H(250 MHz) 0.9 (6 H, s, 2 Me), 1.2 (6 H, s, 2 Me), 2.0 (2 H, d, *J* 4.5, CH_2), 5.4 (1 H, m, CH=C), 5.5 (1 H, d, *J* 9.8, CH=C), 5.7 (1 H, dd, *J* 9.8, 1.7, CH=C), 7.2 (1 H, s, CH=N) and 8.6 (1 H, br s, OH); δ_C(75 MHz) 24.1 (2 Me), 27.4 (2 Me), 30.4 (quaternary C), 37.8 (CH_2), 40.0 (quaternary C), 118.5, 121.6, 137.7, 138.6 (vinyl C) and 157.6 (C=N); *m/z* 193 (M^+, 24%), 178 (100), 107 (10), 91 (14) and 86 (24) (Found: M^+, 193.1467. $C_{12}H_{19}NO$ requires *M*, 193.1462).

The oxime acetate 14. The procedure used for the synthesis of **7a** was followed in this case. Thus, the above oxime (0.82 g, 4.2 mmol) and acetyl chloride (0.36 cm^3, 5.04 mmol) gave, after flash chromatography using hexane–ether (9:1) as eluent, the *oxime acetate* **14** (0.89 g, 89%) as an oil; ν_{max}/cm^{-1} 1770 (CO) and 1620 (C=N); $\lambda_{max}(CH_2Cl_2)$/nm 258 (2300); δ_H(250 MHz) 0.9 (6 H, s, 2 Me), 1.2 (6 H, s, 2 Me), 2.06 (2 H, d, *J* 4.3, CH_2), 2.09 (3 H, s, COMe), 5.4 (1 H, m, CH=C), 5.5 (1 H, d, *J* 9.8, CH=C), 5.7 (1 H, dd, *J* 9.8, 1.7, CH=C) and 7.4 (1 H, s, CH=N); δ_C(62 MHz) 19.7 (COMe), 23.9 (2 Me), 27.6 (2 Me), 30.6 (quaternary C), 38.0 (CH_2), 41.0 (quaternary C), 119.5, 121.3, 137.1, 139.3 (vinyl C), 164.2 (C=N) and 169.0 (CO); *m/z* 235 (M^+, 13%), 220 (17), 208 (28), 192 (55), 178 (100), 160 (42), 153 (32), 119 (33), 107 (84), 95 (54) and 79 (46) (Found: M^+, 235.1585. $C_{14}H_{21}NO_2$ requires *M*, 235.1567).

Synthesis of the oxime acetate 18

3-Hydroxy-2,2-dimethyl-3-phenylcyclohexanone 16. Phenyllithium (2 mol dm^{-3} solution in cyclohexane–ether; 10.64 cm^3, 21.2 mmol) was added dropwise to a solution of 2,2-dimethylcyclohexane-1,3-dione[9] (2 g, 14.2 mmol) in anhydrous ether (100 cm^3), at room temperature under argon. After 5 h at room temperature, the reaction mixture was quenched by addition of saturated aqueous NH_4Cl (70 cm^3). Conventional work-up gave an oil (3.1 g) which was treated with hexane and filtered, to afford the dialcohol **15** as a solid (543 mg, (13%), mp > 270 °C; ν_{max}(KBr)/cm^{-1} 3170 (OH); δ_H(300 MHz) 0.7 (3 H, s, Me), 0.8 (3 H, s, Me), 1.6 (2 H, br s, 2 OH), 2.0 (2 H, m, CH_2), 2.3 (4 H, m, 2 CH_2) and 7.2–7.6 (10 H, m, aryl H); δ_C(75 MHz) 17.5 (2 Me), 25.0, 34.7 (3 CH_2), 44.5 (quaternary C), 80.7 (2 COH) and 126.6–145.2 (aryl C) (Found: C, 80.7; H, 8.1. $C_{20}H_{24}O_2$ requires C, 81.09; H, 8.10%). The filtrate was concentrated under reduced pressure and flash chromatography of the resultant residue with hexane–ether (9:1) as eluent, gave the *title compound* as a viscous oil (948 mg, 31%); ν_{max}/cm^{-1} 3460 (OH) and 1700 (CO); δ_H(300 MHz) 1.03 (3 H, s, Me), 1.08 (3 H, s, Me), 1.6 (2 H, m, CH_2), 1.7 (1 H, br s, OH), 2.2 (2 H, m, 4-H), 2.4 (2 H, m, 6-H) and 7.1–7.5 (5 H, m, aryl H); δ_C(75 MHz) 17.7, 17.9 (2 Me), 36.9, 39.8, 40.9 (3 CH_2), 65.5 (quaternary C), 77.6 (COH), 125.5, 125.6, 125.8, 126.4, 126.5, 127.4 (aryl C) and 210.0 (CO); *m/z* 218 (M^+, 5%), 175 (100), 165 (15), 147 (77), 105 (90), 97 (31) and 77 (56) (Found: M^+, 218.1303. $C_{14}H_{18}O_2$ requires *M*, 218.1307).

2,2-Dimethyl-3-phenylcyclohex-3-enone 17. The alcohol **16** (440 mg, 2 mmol), dry benzene (25 cm^3) and P_2O_5 (340 mg, 2.4 mmol) were refluxed for 3 h, after which the crude reaction mixture was filtered through silica gel and the filtrate purified by flash chromatography with hexane as eluent, to give **17** as an oil (353 mg, 88%). This was used in the next step without further purification; ν_{max}/cm^{-1} 1710 (CO); $\lambda_{max}(CH_2Cl_2)$/nm 249 (9000); δ_H(300 MHz) 0.97 (3 H, s, Me), 1.00 (3 H, s, Me), 2.3 (2 H, m, CH_2C=C), 2.6 (2 H, m, CH_2CO), 5.9 (1 H, t, *J* 7.5, CH=C) and 7.1–7.3 (5 H, m, aryl H); δ_C(75 MHz) 18.0 (2 Me), 24.0 (CH_2C=C), 40.1 (CH_2CO), 40.6 (quaternary C), 125.8, 126.8, 127.8, 127.9, 129.0, 129.6, 139.7, 142.5 (aryl and vinyl C) and 213.5 (CO).

2,2-Dimethyl-3-phenylcyclohex-3-enone oxime. The procedure used for the synthesis of **7b** was followed in this case. Thus, the ketone **17** (870 mg, 4.35 mmol), hydroxylamine hydrochloride (0.36 g, 5.2 mmol) and pyridine (0.52 cm^3, 5.2 mmol) gave, after flash chromatography using hexane–ether (9:1) as eluent, the *title compound* (900 mg, 96%) as an inseparable 3.5:1 mixture of *E*:*Z* isomers; ν_{max}/cm^{-1} 3240 (OH); δ_H(300 MHz) 0.99 (minor isomer), 1.00 (major isomer), 1.01 (minor isomer), 1.03 (major isomer) (6 H, 4 s, 2 Me), 2.36–2.41 (4 H, m, 2 CH_2), 6.1 (1 H, m, CH=C), 7.2–7.3 (5 H, m, aryl H) and 9.0 (1 H, br s, OH); δ_C(75 MHz) 18.7 (minor isomer), 19.7 (major isomer) (Me), 26.1, 26.5, 26.6 (CH_2), 30.0 (minor isomer), 33.4 (major isomer) (quaternary C), 126.7, 126.8, 127.0, 127.7, 128.0, 128.3, 128.4, 129.7, 139.7, 142.2, 142.4 (aryl and vinyl C), 164.40 (minor isomer) and 164.43 (major isomer) (C=N).

The oxime acetate 18. The procedure used for the synthesis of **7a** was followed in this case. Thus, the oxime (900 mg, 4.2 mmol) synthesized above and acetyl chloride (0.36 cm^3, 5.0 mmol) gave, after flash chromatography using hexane–ether (5:5) as eluent, the oily *oxime acetate* **18** (870 mg, 81%) as an inseparable 3.5:1 mixture of *E*:*Z* isomers; ν_{max}/cm^{-1} 1710 (CO) and 1630 (C=N); $\lambda(CH_2Cl_2)$/nm 251 (10 000) and 280 (2000); δ_H(300 MHz) 1.00 (minor isomer), 1.03 (minor isomer), 1.07 (major isomer), 1.09 (major isomer) (6 H, 4 s, 2 Me), 2.0 (major isomer), 2.1 (minor isomer) (3 H, 2 s, COMe), 2.3–2.4 (4 H, m, CH_2), 6.1 (1 H, m, CH=C) and 7.1–7.4 (5 H, m, aryl H); δ_C(75 MHz) 18.8, 19.4, 19.5, 19.6 (Me), 26.5, 27.6, 27.7 (CH_2), 30.6, 33.9 (quaternary C), 125.9, 126.8, 126.9, 127.0, 127.1, 127.7, 127.9, 128.0, 128.1, 128.4, 128.5, 129.5, 139.5, 142.0, 143.0 (aryl

and vinyl C), 168.6, 168.8 (C=N) and 171.9 (CO); *m/z* 257 (M^+, 20%), 200 (21), 197 (73), 182 (36), 170 (74), 155 (100), 141 (65), 129 (84), 115 (40), 91 (10) and 77 (12) (Found: M^+, 257.1412, $C_{16}H_{19}NO_2$ requires *M*, 257.1416).

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 hr 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 oxime acetate 4a.[1] The *E*-oxime acetate (200 mg, 0.84 mmol) and acetophenone (2 g) were irradiated in benzene for 3 h. After removal of the solvent and the sensitizer, flash chromatography of the residue using hexane–ether (9:1) as eluent gave 4-methyl-3-phenylpent-3-enonitrile **6**[1] (40 mg, 27%) and the oxime acetate **4a** (110 mg, 55%) as a 1:2 mixture of *Z*:*E* isomers. These were not separated. However, the NMR details of the *Z*-isomer can be obtained by difference, and are as follows: (*Z*)-oxime acetate δ_H(300 MHz) 1.6 (3 H, s, Me), 1.8 (3 H, s, Me), 2.1 (3 H, s, COMe), 3.5 (2 H, d, *J* 5.0, CH_2), 7.0 (1 H, t, *J* 5.0, CH=N) and 7.1–7.3 (5 H, m, aryl H). Further elution with ethanol afforded highly polar polymeric material (20 mg).

Acetophenone-sensitized irradiation of the oxime acetate 7a. This compound (300 mg, 1.2 mmol) and acetophenone (1.4 g) were irradiated in benzene for 30 min. After removal of the solvent and the sensitizer, chromatography of the residue using hexane–ether (95:5) as eluent gave **8a** as a colourless crystalline solid (240 mg, 80%), mp 63–65 °C (from hexane); ν_{max}(KBr)/cm^{-1} 1770 (CO) and 1630 (C=C); δ_H(300 MHz) 1.4 (1 H, m, cyclohexyl), 1.9 (6 H, s, 2 Me), 2.1 (3 H, s, MeCO), 2.3 (1 H, m, cyclohexyl), 2.5 (1 H, m, cyclohexyl), 2.6 (1 H, m, cyclohexyl), 4.0 (1 H, m, cyclohexyl), 7.1–7.2 (4 H, m, aryl H) and 7.3 (1 H, d, *J* 8.7, CH=N); δ_C(75 MHz) 19.3 (COMe), 20.7, 23.2 (Me), 28.3, 28.5 (CH_2), 38.4 (CH), 125.2, 126.5, 126.6, 129.6, 133.5, 135.6, 140.4 (aryl and vinyl C), 159.7 (C=N) and 168.5 (CO).

***m*-Methoxyacetophenone-sensitized irradiation of the oxime acetate 13.** The *E*,*E*-oxime acetate **13** (300 mg, 1.16 mmol) and *m*-methoxyacetophenone (4 g) were irradiated in methylene dichloride for 90 min. After removal of the solvent and the sensitizer, flash chromatography of the residue using hexane–ether (95:5) as eluent gave the oxime acetate **13** (240 mg, 80%) as a 1:1 mixture of *Z*:*E* isomers arising from the C=C bond. These were not separated. However, the NMR details of the *Z*-isomer can be obtained by difference and are as follows: (4*Z*)-3-methylene-2,2-dimethyl-5-phenylpent-4-enal oxime acetate: δ_H(250 MHz) 1.35 (6 H, s, Me), 2.1 (3 H, s, MeCO), 5.0 (1 H, s, CH_2=C), 5.1 (1 H, s, CH_2=C), 6.0 (1 H, d, *J* 12.4, CH), 6.4 (1 H, d, *J* 12.4, CH), 7.1–7.3 (5 H, m, aryl H) and 7.6 (1 H, s, CH=N); δ_C(62 MHz) 19.7 (COMe), 24.7 (2 Me), 42.3 (quaternary C), 111.7, 127.0, 127.2, 127.8, 128.2, 128.7, 128.9, 131.1, 137.0, 149.6 (aryl and vinyl C), 164.4 (C=N) and 169.0 (CO). Further elution afforded highly polar polymeric material (40 mg). Irradiation for 5 h afforded similar results.

Acetophenone-sensitized irradiation of the oxime acetate 14. This compound (214 mg, 0.91 mmol) and acetophenone (4 g) were irradiated in methylene dichloride for 30 min, after which removal of the solvent and the sensitizer followed by flash chromatography using hexane–ether (9:1), gave unchanged **14** (89 mg, 42%). Further elution with methylene dichloride gave a mixture of polymeric materials (90 mg). Irradiation of compound **14** (287 mg, 1.22 mmol) and acetophenone (4 g) for longer periods (3 h), exclusively afforded, after flash chromatography using hexane–ether (99:1), a complex mixture of decomposition products with no recovery of starting material.

Phenanthrene-sensitized irradiation of the oxime acetate 14. This compound (290 mg, 1.23 mmol) and phenanthrene (2.2 g) were irradiated in methylene dichloride for 3 h after which removal of the solvent, followed by flash chromatography using hexane as eluent to remove phenanthrene, gave with methylene dichloride as eluent unchanged **14** (110 mg, 47%); finally, elution with ethyl acetate afforded polymeric material (90 mg).

Acetophenone-sensitized irradiation of the oxime acetate 18. This compound (300 mg, 1.16 mmol) and acetophenone (5 g) were irradiated in benzene for 2 h, after which removal of the solvent and the sensitizer followed by flash chromatography using hexane–ether (8:2), gave unchanged **18** (260 mg, 87%) and highly polar polymeric material (60 mg). Further irradiation for periods up to 10 h afforded a complex mixture of decomposition products with no recovery of starting material.

Acetone-sensitized irradiation of the oxime acetate 18. This compound (320 mg, 1.2 mmol) and acetone (420 cm^3) were irradiated for 4 h, after which removal of the solvent followed by flash chromatography using hexane–ether (95:5) as eluent, gave unchanged **18** (202 mg, 63%) and highly polar polymeric material (120 mg). Further irradiations for periods up to 10 h afforded a complex mixture of decomposition products and no recovery of starting material.

Acetophenone-sensitized irradiation of the oxime 7b. This compound (220 mg, 1.02 mmol) and acetophenone (2 g) were irradiated in methylene dichloride for 15 min, after which removal of the solvent and the sensitizer, followed by flash chromatography using hexane–ether (95:5) as eluent, gave a 1.4:1 mixture of *E*:*Z* isomers of the oxime **8b** as a white solid (186 mg, 86%), mp 97–99 °C (from hexane); ν_{max}(KBr)/cm^{-1} 3200 (OH); δ_H(250 MHz) 1.5 (1 H, m, cyclohexyl H), 1.85 (*Z* isomer), 1.88 (*E* isomer), 1.90 (*E* isomer), 1.92 (*Z* isomer) (6 H, 4 s, 2 Me), 2.1–2.7 (3 H, m, cyclohexyl H), 3.8 (*E* isomer), 4.5 (*Z* isomer) (1 H, m, CH), 6.4 (0.4 H, d, *J* 7.5, CH=N of *Z* isomer) and 7.2 (4.6 H, m, aryl H and CH=N of *E* isomer); δ_C(62 MHz) 20.9, 21.2, 23.3 (Me), 28.7, 28.8, 29.0 (CH_2), 38.7 (CH), 125.3, 125.4, 126.4, 126.8, 126.9, 127.8, 130.0, 132.1, 136.3, 140.6 (aryl and vinyl C) and 153.8 (C=N) (Found: C, 78.1; H, 7.8, N, 6.2. $C_{14}H_{17}NO$ requires C, 78.10; H, 7.96; N, 6.50%).

Acetophenone-sensitized irradiation of the oxime 1b. This compound (185 mg, 0.98 mmol) and acetophenone (2 g) were irradiated in methylene dichloride for 30 min, after which removal of the solvent and the sensitizer, followed by flash chromatography using hexane–ether as eluent, gave the oxime **1b** (60 mg, 32%) and **4b** (15 mg, 8%) as an oily 1:1 mixture of *Z*:*E* isomers; ν_{max}(KBr)/cm^{-1} 3200 (OH); δ_H(300 MHz) 1.53 (1.5 H, s, Me × 1/2), 1.55 (1.5 H, s, Me × 1/2), 1.77 (1.5 H, s, Me × 1/2), 1.78 (1.5 H, s, Me × 1/2), 3.2 (1 H, d, *J* 6.0, CH_2 × 1/2), 3.4 (1 H, d, *J* 4.8, CH_2 × 1/2), 6.6 (0.5 H, t, *J* 4.8, CH=N of *Z* isomer), 7.0–7.2 (5.5 H, m, aryl and CH=N of *E* isomer) and 7.9 (1 H, br s, OH). The oxime was characterized further by conversion into the corresponding acetate.[1]

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