Steric and Electronic Effects on the Photochemical Reactivity of Oxime Acetates of β,γ-Unsaturated Aldehydes

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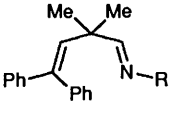
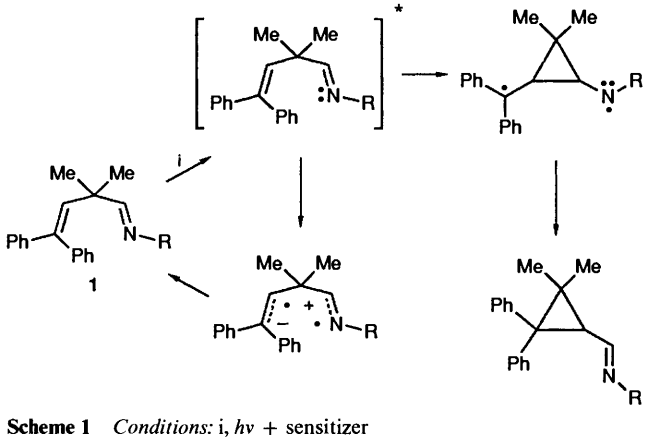
A general synthesis of 5-substituted *N*-acetoxy 3,3-dimethyl-1-azapenta-1,4-dienes starting from 2-(1,3-dithian-2-yl)-2-methylpropanal is described. The influence of 5-phenyl, 4-phenyl, 5-cyclohexyl, 5-*tert*-butoxycarbonyl and 5,5-dicyclohexyl substitution on the outcome of the photochemical reactions of the oxime acetates of β,γ-unsaturated aldehydes has been studied with a view to proving or disproving the operation of a deactivating *free rotor* in the aza-di-π-methane rearrangement. The results obtained show that if the radical formed at C-5 can be stabilized by conjugation with an aryl group or by certain types of disubstitution then the aza-di-π-methane rearrangement takes place successfully. In any other situation the reaction fails. These results clearly show that the *free rotor* effect is not responsible for the failure of C-5 monosubstituted 1-aza-1,4-dienes to undergo the aza-di-π-methane rearrangement.

The influence of substituents on the photochemical aza-di-π-methane reaction of 1-aza-1,4-dienes **1** yielding cyclopropanes has been studied in some detail.[1] In particular the substitution



1 R = Ar, $ArCH_2$, or Alkyl

on the nitrogen has been shown to be important for the optimization of chemical and quantum yields. The latter studies[2] indicated that it was important to have a group attached to the nitrogen which had the capability of raising the ionization potential of the nitrogen lone pair of electrons. From this it was postulated that the inefficiency observed earlier in the work was due to an energy-wasting electron-transfer step as shown in Scheme 1. This line of thinking led to the discovery



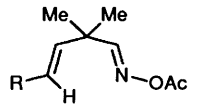
Scheme 1 *Conditions:* i, *hν* + sensitizer

that oxime acetate derivatives[3] and other stable derivatives such as a semicarbazone and a benzoylhydrazone[4] provided molecules which underwent the rearrangement efficiently. Further work was aimed at obtaining 1-aza-1,4-dienes with fewer substituents, which would permit the use of cyclization as a regiospecific path to the synthesis of cyclopropane derivatives. This study showed that the monosubstituted 1-aza-1,4-dienes **2** were unreactive in the aza-di-π-methane rearrangement[5] and only *E–Z* isomerization took place. However, the incorporation of a second substituent at position 5 gave dienes **3**, which were again photoreactive, yielding the corresponding cyclopropyl derivatives **4**. The failure of the monosubstituted compound to undergo the triplet-sensitized rearrangement, where the energy from the sensitizer is transferred to the alkene moiety, was interpreted as an example of triplet excited state deactivation by a free rotor. Others[6] have reported similar problems with the oxa-di-π-methane rearrangement under sensitized conditions. As in our example, the energy in that case was transferred to the alkene group. There are, of course, many examples in the di-π-methane reaction where the triplet state is deactivated by free-rotor effects.[7]

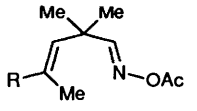
In order to obtain further evidence on substituent effects and particularly to assess the feasibility of free-rotor deactivation we have examined the photochemical behaviour of the oxime acetates of β,γ-unsaturated aldehydes **5–9** which can be considered as examples of 1-aza-1,4-dienes.

Results and Discussion

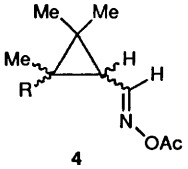
The diene **5** is conveniently obtained by oximation and acetylation of 2,2-dimethyl-4-phenylbut-3-enal. The identity of this diene **5** was established from conventional spectroscopic and accurate mass data. The dienes **6** and **7** are prepared by Reformatsky reaction of ethyl 2-bromo-2-methylpropanoate with cyclohexylethanal and acetophenone to afford compounds **12** and **13**, respectively. Dehydration to the corresponding alkenes, $LiAlH_4$ (LAH) reduction of the ester group to the alcohols, followed by oxidation with pyridinium chlorochromate (PCC) afforded the corresponding aldehydes, that were readily converted into the dienes **6** and **7** by oximation and acetylation. The diene **8** was synthesized using the route shown in Scheme 2. This route was also used for the synthesis of compounds **2** and **3**, the photochemistry of which has been reported previously.[5] The proof of identity of all of these compounds was carried out by conventional methods. Diene **9** is also readily synthesized from the cyclopropane **10** originally described and used by Zimmerman and his group.[8] Reaction of



2 **a**; R = CO_2Et
b; R = CN
c; R = CH_2OAc
d; R = CH_2OMe



3 **a**; R = CO_2Et
b; R = CN
c; R = CH_2OAc



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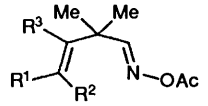
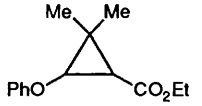


5 R^1 = Ph, R^2 = R^3 = H
6 R^1 = cyclohexyl, R^2 = R^3 = H
7 R^1 = R^2 = H, R^3 = Ph
8 R^1 = CO_2Bu^t, R^2 = R^3 = H
9 R^1 = R^2 = cyclohexyl, R^3 = H



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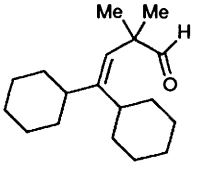

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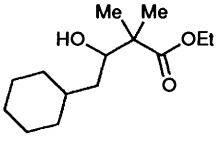

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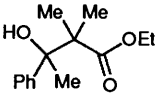

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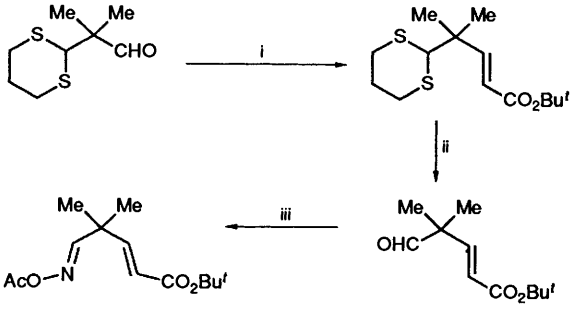
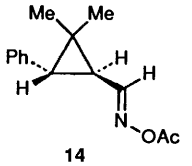
compound **10** with cyclohexylmagnesium bromide, followed by hydrolysis, affords the aldehyde **11** in good yield. Oximation and acetylation of this aldehyde readily gives the diene **9**. Again the authenticity of this product was readily verified by conventional means.



Scheme 2 *Reagents*: i, $(EtO)_2POCH_2CO_2Bu^t$; ii, HgO, BF_3·Et_2O; iii, NH_2OH·HCl; then pyridine, AcCl

Irradiation of the β,γ-unsaturated oxime acetates, 1-azadienes **5**–**9**, in this study was carried out by using triplet sensitization in accordance with our previous observations.[1,2] Under these conditions the 5-phenyl-substituted diene **5** is smoothly and efficiently converted into a single photoproduct in 71% isolated yield. This result has been the subject of a preliminary communication.[9] This product was identified as the cyclopropane **14** formed by an aza-di-π-methane rearrangement. The evidence from NMR spectroscopy indicates that the reaction is stereospecific and yields only the *trans*-isomer as illustrated. The success with this derivative **5** raised the question of whether electronic effects or steric effects were important in determining the success of the aza-di-π-methane rearrangement. Previously we had observed that the C-5 ester **2a** underwent only *E*–*Z*-isomerization under the reaction conditions.[5] Increasing the bulk of the ester function by the use of the *t*-butyl ester **8** did not change the outcome of the reaction and again only *E*–*Z*-isomerization took place. Irradiation of the bulky 5-cyclohexyl-substituted diene **6** also fails to yield products by way of the aza-di-π-methane path and again only *Z*–*E*-isomerization occurs on benzene sensitization. Surprisingly, even the 5,5-dicyclohexyl derivative is unreactive on sensitized irradiation.



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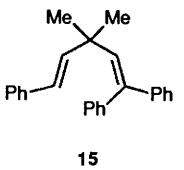

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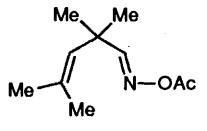

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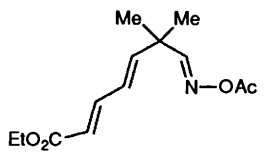

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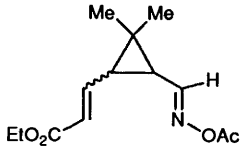

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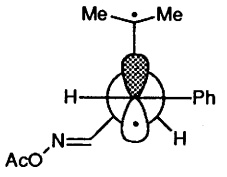

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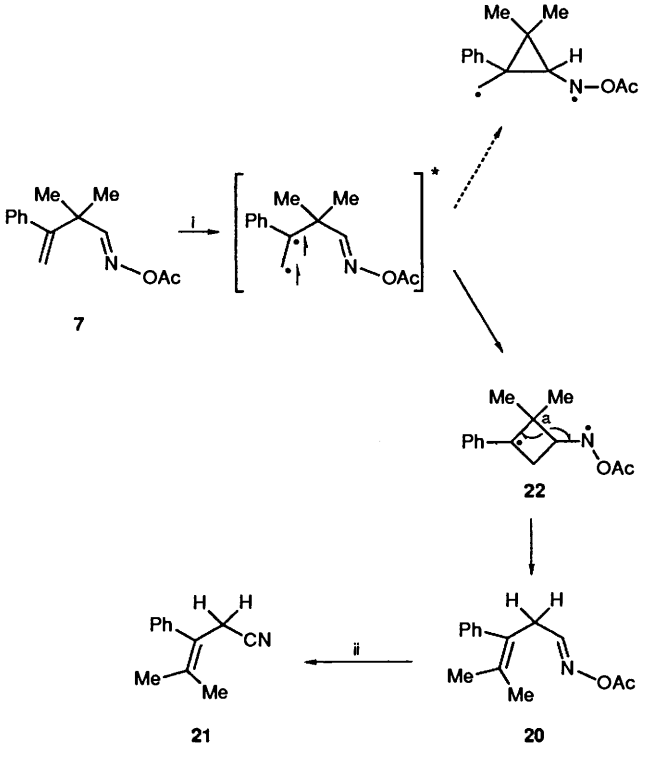
In view of our earlier observation that 1-aza-1,4-dienes with monosubstitution at C-5 did not undergo the aza-di-π-methane process and only isomerized around the C-4–C-5 bond the successful conversion of diene **5** into the cyclopropane **14** is surprising. In the latter, and the present examples, energy transfer from the sensitizer will take place, in the first instance, to the alkene moiety. Our original reasoning was that monosubstitution at C-5 would allow the alkene triplet state to deactivate *via* the free-rotor effect, previously observed to operate in the all-carbon di-π-methane systems.[7] It could be argued, since diene **5** undergoes the aza-di-π-methane cyclization efficiently, that the phenyl group on position 5 is larger than an ester group and this difference in bulk is sufficient to suppress the deactivating free-rotor effect. However, this argument does not stand up to comparison with results from the di-π-methane reaction of diene **15** where even with two phenyl groups on one of the terminal carbons and a phenyl group on the other, identical with that situation in our molecule, the triplet state is unreactive.[10] The argument of deactivation based on size alone also falls with the observation that the 5-cyclohexyl diene **6** is also unreactive to the aza-di-π-methane reaction on acetone sensitization. The use of benzene, a sensitizer of higher energy, also fails to effect rearrangement and only *E*–*Z*-isomerization around the C-4–C-5 bond results, showing that the failure of the aza-di-π-methane reaction is not due to lack of energy transfer. An alternative explanation has to be found for the above results. The most likely explanation is based on radical stability. For this, it is important that a stable cyclopropyl biradical be formed after bridging (Scheme 1) and that subtle stabilizing effects are in operation. Monosubstitution at C-5 is ineffective if the substituent group is ethoxycarbonyl, cyano or alkyl. However, if there is good conjugative stabilization of the radical[11] (as with the 5-phenyl group) then the aza-di-π-methane reaction is again operative. This argument is also sustained by our earlier observation that dienes **3** with disubstitution at C-5 also undergo the aza-di-π-

methane rearrangement successfully.[5] Again the literature substantiates the view that the radical-stabilizing effects of a methyl and an ethoxycarbonyl or cyano group are better than those of the ethoxycarbonyl or cyano group on its own.[12] In a previous study we demonstrated that it was possible to effect acetone-sensitized conversion of the tetramethyl derivative **16** to afford the corresponding cyclopropane derivative.[3] The unsuccessful attempted photoreaction of diene **9** also fits into this pattern of the control exercised by the stability of the radical at C-5. Literature evidence shows that the stabilization of radicals by alkyl groups relies heavily on the number of β-hydrogens.[13] On this argument alone the dicyclohexyl substituents will be a poorer stabilizer than will dimethyl substitution. The conclusion that the dimethyl-substituted radical is more stable than the dicyclohexyl-substituted radical is substantiated by bond dissociation data.[14] All the evidence gathered regarding the effects of substitution on the outcome of the aza-di-π-methane from this study point to the fact that those dienes which fail to undergo the rearrangement do so because of a poorly stable cyclopropyl biradical. Further support for this concept of radical stabilization comes from our report of the successful synthesis of the triene **17** and its efficient photochemical cyclization to the corresponding cyclopropane **18**.[15] The idea that deactivation was due to a free-rotor effect cannot be sustained.

A further feature of the successful cyclization of the diene **5** which merits comment is the fact that the reaction is apparently stereospecific and yields only the cyclopropane **14**. The stereospecificity of the cyclization presumably arises from the fact that cyclization within the biradical, shown as the Newman projection formula **19** will follow the route of minimum hindrance, which places the phenyl and the oxime acetate groups preferentially *trans* to one another.

Irradiation of the diene **7** provided a surprise. This diene was considered to be a good example for the putative free-rotor activity due to the absence of substituents on C-5. The incorporation of a phenyl at C-4 still ensures that triplet energy will be transferred to the alkene moiety and irradiation using



Scheme 5 *Conditions: hv* + sensitizer; ii, heat

acetophenone sensitization again brought about smooth and efficient conversion into a single photoproduct in 62% yield. Recovered starting material amounted to 37%. This novel product was readily identified as the oxime acetate of 4-methyl-3-phenylpent-3-enal, *i.e.* compound **20**. This compound is thermally unstable and on storage elimination of acetic acid affords the nitrile **21**. The identification of the photoproduct as compound **20** clearly shows that the diene **7** does not undergo the aza-di-π-methane process and that an alternative reaction mode is operative. This alternative path is outlined in Scheme 3, where energy transfer from the sensitizer affords, as always, the triplet alkene. Conventional bridging would yield a biradical in which there was minimal stabilization. The molecule, therefore, follows a path which forms a better biradical **22** by attack of the methylene radical at the oxime acetate carbon atom. This route yields the cyclobutane intermediate **22** which subsequently ring opens by rupture of bond 'a' to yield the diene **20**. Superficially this rearrangement can be considered as an example of a 1,3-migration of a C=N function in a β,γ-unsaturated system. 1,3-Migrations are common in β,γ-unsaturated enones where the acyl group migrates on direct irradiation involving the singlet state.[16] 1,3-Vinyl migrations in 1,4-dienes are uncommon although such a rearrangement has been reported to give a minor product on sensitized irradiation of 5-methyl-1,1,3,3-tetraphenylhexa-1,4-diene.[17] When the substitution on the all-carbon skeleton, as in 3,3-dimethyl-1,1,4-triphenylpenta-1,4-diene,[10] is similar to that on diene **7** direct irradiation brings about the formation of a cyclopropyl derivative, albeit inefficiently, *via* the di-π-methane rearrangement, while the triplet state undergoes a 1,3-vinyl migration in 48% yield. Nevertheless, as far as we are aware, the 1,3-migration of a C=N group in 1,4-diene **7** is completely novel and without precedent.

The results obtained from this study have increased our knowledge of the scope of the aza-di-π-rearrangement and provided further evidence for major differences between it and the di-π-methane process.[10,17] We have shown that the substitution pattern on the 1-aza-1,4-diene skeleton can be quite critical concerning the success or failure of the aza-di-π-methane process. It is now clear that monosubstitution by an alkyl, cyano, or alkoxycarbonyl group provides insufficient stability for the radical at the terminal carbon, C-5, of the alkene. However, if the monosubstituent at C-5 is a phenyl group the rearrangement is again highly efficient. Disubstitution supplied by two methyl groups or a methyl group in conjunction with an ethoxycarbonyl or cyano group is also effective in promoting the rearrangement, while disubstitution by cyclohexyl groups is ineffective. The reason for these subtle changes in the molecule leading to success or failure is entirely dependent upon the stability of the radical at that site. It seems unlikely that the failure of the cyclization is due to a free-rotor effect as proposed earlier.[5]

Experimental

M.p.s were determined on a Buchi 510D apparatus in open capillaries and are uncorrected. IR spectra were recorded as liquid films unless otherwise stated, on a Perkin-Elmer 257 spectrophotometer. NMR spectra were recorded in deuteriochloroform solution unless otherwise stated, on a Varian FT-80A spectrometer for ^1H and a Varian FT-300A spectrometer for ^{13}C spectra with chemical shifts (δ) expressed in ppm downfield from internal Me_4Si, and coupling constants J are given in Hz. UV–VIS spectra were recorded in methylene dichloride solution on a Perkin-Elmer 550 spectrometer. Mass spectra were determined on a Varian MAT-711 spectrometer.

Synthesis of Diene **5**. *The De-O-acetyl Compound.*—2,2-Dimethyl-4-phenylbut-3-enal, obtained in 90% yield *via* a syn-

thesis reported previously,[11] was converted into its oxime in the following manner. The aldehyde (1.8 g, 10 mmol), hydroxylamine hydrochloride (1.1 g, 15 mmol) and pyridine (1.2 cm^3, 15 mmol) were heated at reflux in ethanol (50 cm^3) for 1 h. Purification by column chromatography with hexane–diethyl ether (9:1) yielded the oxime of 2,2-dimethyl-4-phenylbut-3-enal as an oil (1.6 g, 85%); ν_{max}/cm^{-1} 3300; $\delta_H(CDCl_3)$ 8.0 (1 H, s, OH), 7.4–7.0 (5 H, m, ArH), 6.4 (1 H, d, *J* 16, vinyl H), 6.0 (1 H, d, *J* 16, vinyl H) and 1.4 (6 H, s, Me).

Acetylation of Oxime.—The oxime (474 mg, 2.5 mmol) and acetyl chloride (2 cm^3, 2.5 mmol) were treated at room temperature and the product was worked up conventionally. Chromatography on silica gel with hexane–diethyl ether (8:2) as eluent yielded the desired *diene* **5** (440 mg, 76%) as an oil; ν_{max}/cm^{-1} 1765 and 1625; $\delta_H(CDCl_3)$ 7.7 (1 H, s, CH=N), 7.5 (5 H, m, ArH), 6.4 (1 H, d, *J* 16, vinyl H), 6.2 (1 H, d, *J* 16, vinyl H), 2.1 (3 H, s, MeCO) and 1.4 (6 H, s, Me); $\delta_C(CDCl_3)$ 168.7 (C=O), 163.6 (C=N), 136.6–127.6 (Aryl C and C=C), 39.8 (quaternary C), 24.9 (Me) and 19.5 (MeCO); λ_{max}/nm 251 (ε 18 000 $dm^3\ mol^{-1}\ cm^{-1}$); *m/z* 231 (M^+, 10%), 177 (15), 171 (79), 163 (27), 156 (100), 143 (16), 135 (39), 129 (89), 121 (44), 115 (68), 103 (54), 91 (35) and 77 (56) (Found: M^+, 231.1259. $C_{14}H_{17}NO_2$ requires M, 231.1259).

Synthesis of Oxime Acetate **6**. *Ethyl* 4-*Cyclohexyl*-3-*hydroxy*-2,2-*dimethylbutanoate* **12**.—The procedure followed for the modified Reformatsky reaction has been described previously.[18] 2-Cyclohexylethanal (9.2 g, 73 mmol), ethyl α-bromoisobutyrate[19] (42.7 g, 219 mmol) and zinc (14.3 g, 219 mmol) were allowed to react in dry benzene (100 cm^3). After conventional work-up the crude butanoate **12** (15.6 g) was obtained as an oil; ν_{max}/cm^{-1} 3550 and 1740; $\delta_H(CDCl_3)$ 4.4 (1 H, OH), 4.2 (2 H, q, CH_2O), 3.6 (1 H, m, CH) and 2.0–1.0 (22 H, m, CH_2, cyclohexyl H and Me).

Ethyl 4-*Cyclohexyl*-2,2-*dimethylbut*-3-*enoate*.—The ester **12** (15.6 g, 64 mmol), obtained from the above synthesis, was dissolved in dry pyridine (27 cm^3). Phosphoryl trichloride (21.5 g, 140 mmol) was added dropwise at such a rate that the temperature did not exceed 50 °C. The mixture was then kept at 90–100 °C for 5 h, then was cooled, poured onto ice, and extracted with diethyl ether. The extracts were washed successively with HCl (dil.), aq. $NaHCO_3$, and water, dried ($MgSO_4$), filtered, and evaporated to dryness. Distillation of the crude material gave the title but-3-enoate (10.5 g, 73%), b.p. 75–80 °C/0.5 mmHg; ν_{max}/cm^{-1} 1750 and 1660; $\delta_H(CDCl_3)$ 5.3 (2 H, m, vinyl H), 4.1 (2 H, q, CH_2) and 1.9–1.0 (20 H, m, cyclohexyl H and Me).

4-*Cyclohexyl*-2,2-*Dimethylbut*-3-*en*-1-*ol*.—The above but-3-enoate (10 g, 44 mmol) was dissolved in dry diethyl ether (25 cm^3) and the solution was added dropwise to a stirred suspension of LAH (1.35 g, 36 mmol) in dry diethyl ether (100 cm^3) under nitrogen. The resulting mixture was heated at reflux for 1.5 h. The residual LAH was decomposed by the addition of ethyl acetate followed by water. The metal hydroxides were dissolved in HCl and the organic material was dissolved in diethyl ether. This solution was then extracted, and washed successively with aq. $NaHSO_4$ and brine until neutral. The extract was dried ($MgSO_4$), filtered, and evaporated to dryness. The crude material was distilled to yield the desired 4-cyclohexyl-2,2-dimethylbut-3-en-1-ol (5.3 g, 66%), b.p. 70–75 °C/0.4 mmHg; ν_{max}/cm^{-1} 3350 and 1650; $\delta_H(CDCl_3)$ 5.2 (2 H, m, vinyl H), 3.0 (2 H, s, CH_2O) and 2.0–1.0 (18 H, m, OH, cyclohexyl H and Me); $\delta_C(CDCl_3)$ 135.8 and 133.6 (C=C), 71.3 (CH_2OH), 40.7 (C), and 33.2, 26.0, 25.9 and 23.8 (cyclohexyl C and Me).

4-*Cyclohexyl*-2,2-*dimethylbut*-3-*enal*.—The above alcohol (3 g, 16 mmol) and PCC (5.6 g, 24.7 mmol) were allowed to react in methylene dichloride at room temperature for 24 h. Conventional work-up gave the 4-cyclohexyl-2,2-dimethylbut-3-enal (1.92 g, 65%) as an oil; ν_{max}/cm^{-1} 1710; $\delta_H(CDCl_3)$ 8.4 (1 H, s, CHO), 5.2 (2 H, m, vinyl H) and 2.0–1.0 (17 H, m, cyclohexyl H and Me).

Oxime of 4-*Cyclohexyl*-2,2-*dimethylbut*-3-*enal*.—The above aldehyde (1.92 g, 10 mmol), hydroxylamine hydrochloride (1.04 g, 15 mmol) and pyridine (1.2 g, 15 mmol) were heated at reflux in ethanol (50 cm^3) for 1.5 h. After work-up, chromatography of the crude product with hexane–diethyl ether (8:2) as eluent gave the oxime (1.4 g, 69%) as an oil; ν_{max}/cm^{-1} 3350; $\delta_H(CDCl_3)$ 8.8 (1 H, s, OH), 7.3 (1 H, s, CH=N), 5.4 (2 H, m, vinyl H) and 1.8–1.0 (17 H, m, cyclohexyl H and Me); $\delta_C(CDCl_3)$ 157 (C=N), 134 and 132.7 (C=C), 40 (C) and 30.4–21.0 (cyclohexyl C and Me).

Diene **6**.—The oxime (1.4 g, 7 mmol), acetyl chloride (0.88 g, 11 mmol) and pyridine (3 cm^3) were allowed to react at room temperature. Conventional work-up, followed by chromatography with hexane-ethyl acetate (8:2), gave *diene* **6** (1.2 g, 67%) as an oil; ν_{max}/cm^{-1} 1790; $\delta_H(CDCl_3)$ 7.2 (1 H, s, CH=N), 5.2 (2 H, m, vinyl H), 2.1 (3 H, s, Me) and 1.9–1.0 (17 H, m, cyclohexyl H and Me); $\delta_C(CDCl_3)$ 169.0 (C=O), 164.0 (C=N), 135.6 and 131.8 (C=C), 40.4 (C) and 32.6–19.3 (cyclohexyl C and Me); λ_{max}/nm 231 (8400); *m/z* 237 (M^+, 17%), 195 (24), 178 (63), 162 (42), 150 (51), 135 (36), 121 (23), 112 (59), 107 (33), 96 (59), 81 (49), 77 (32) and 169 (100) (Found: M^+, 237.17288. $C_{14}H_{23}NO_2$ requires M, 237.1729).

Synthesis of Oxime Acetate **7**. *Ethyl* 2,2-*Dimethyl*-3-*hydroxy*-3-*phenylbutanoate* **13**.—Ethyl α-bromoisobutyrate[19] (11.4 g, 58 mmol), acetophenone (2.3 g, 19 mmol) and zinc (3.8 g, 58 mmol) were allowed to react in dried benzene (50 cm^3). After conventional work-up the crude hydroxybutanoate **13** (7.1 g) was obtained as an oil; ν_{max}/cm^{-1} 3470 and 1720; $\delta_H(CDCl_3)$ 7.3 (5 H, m, ArH), 4.6 (1 H, s, OH), 4.2 (2 H, q, CH_2O), 1.7 (3 H, s, Me), 1.4 (3 H, t, Me) and 1.3 (6 H, s, Me).

Ethyl 2,2-*Dimethyl*-3-*phenylbut*-3-*enoate*.—The above ester (7.1 g, 31 mmol) was heated at reflux with $KHSO_4$ (15.6 g, 0.115 mol) for 3 h. The mixture was cooled and poured into water, then extracted with diethyl ether, and the extracts washed with brine until neutral before being dried ($MgSO_4$), filtered, and evaporated to dryness. The crude product was purified by chromatography with hexane–diethyl ether (9:1) as eluent. The butenoate (1.95 g, 47%) was obtained as an oil; ν_{max}/cm^{-1} 1740 and 1630; $\delta_H(CDCl_3)$ 7.2 (5 H, m, ArH), 5.3 (1 H, s, vinyl H), 5.1 (1 H, s, vinyl H), 4.0 (2 H, q, CH_2O), 1.4 (6 H, s, Me) and 1.2 (3 H, t, Me).

2,2-*Dimethyl*-3-*phenylbut*-3-*en*-1-*ol*.—The ester (1.90 g, 8.7 mmol) from the above preparation was dissolved in dry diethyl ether (6 cm^3) and the solution was added dropwise to a stirred suspension of LAH (0.26 g, 6.9 mmol) in dry diethyl ether (30 cm^3) under nitrogen. The resulting mixture was heated at reflux for 1.5 h. The residual LAH was decomposed by the addition of ethyl acetate followed by water. The metal hydroxides were dissolved in HCl and the organic material was dissolved in diethyl ether. The ethereal layer was then washed successively with aq. $NaHSO_4$ and brine until neutral. The extract was dried ($MgSO_4$), filtered, and evaporated to dryness to afford the desired alcohol (1.4 g, 91%), which was used without further purification; ν_{max}/cm^{-1} 3450, 1730 and 1630; $\delta_H(CDCl_3)$ 7.2 (5 H, m, ArH), 5.2 (1 H, s, vinyl H), 5.0 (1 H, s, vinyl H), 2.4 (2 H, s, CH_2OH) and 1.2 (6 H, s, Me).

2,2-Dimethyl-3-phenylbut-3-enal.—The above alcohol (1.4 g, 8 mmol) and PCC (3.1 g, 14 mmol) were allowed to react in methylene dichloride at room temperature for 24 h. Conventional work-up gave 2,2-dimethyl-3-phenylbut-3-enal (1.1 g, 79%) as an oil; ν_{max}/cm^{-1} 3400, 1740 and 1620; $\delta_H(CDCl_3)$ 9.4 (1 H, s, CHO), 7.3 (5 H, m, ArH), 5.4 (2 H, s, vinyl H) and 1.4 (6 H, s, Me).

Oxime of 2,2-Dimethyl-3-phenylbut-3-enal.—The above aldehyde (1.05 g, 6 mmol), hydroxylamine hydrochloride (629 mg, 9.05 mmol) and pyridine (0.73 g, 9.05 mmol) were heated at reflux in ethanol (15 cm^3) for 1.5 h. After work-up, chromatography of the crude product with hexane–diethyl ether (9:1) as eluent gave the oxime (590 mg, 52%) as an oil; ν_{max}/cm^{-1} 3300; $\delta_H(CDCl_3)$ 8.3 (1 H, s, OH), 7.4 (1 H, s, CH=N), 7.1 (5 H, m, ArH), 5.2 (1 H, s, vinyl H), 4.9 (1 H, s, vinyl H) and 1.4 (6 H, s, Me); $\delta_C(CDCl_3)$ 153 (C=N), 141.6, 127.8, 127.7, 127.6, 126.8 and 114.3 (arom. C and C=C), 47.7 (C) and 25.7 (Me).

Diene **7**.—The oxime (551 mg, 2.9 mmol), acetyl chloride (2.3 cm^3, 2.9 mmol) and pyridine (3 cm^3) were allowed to react at room temperature. Conventional work-up, followed by chromatography with hexane–diethyl ether (8:2), gave the *diene* **7** (485 mg, 72%) as an oil; ν_{max}/cm^{-1} 1760 and 1690; $\delta_H(CDCl_3)$ 7.4 (1 H, s, CH=N), 7.2 (5 H, m, ArH), 5.3 (1 H, s, vinyl H), 5.1 (1 H, s, vinyl H), 2.1 (3 H, s, MeCO) and 1.4 (6 H, s, Me); $\delta_C(CDCl_3)$ 168.9 (C=O), 164.3 (C=N), 153.8, 141.1, 128.5, 127.8, 127.1 and 115.6 (Ar-C and C=C), 42.8 (C), 25.1 (Me) and 19.6 (*Me*CO); λ_{max}/nm 229 (5600); *m/z* 231 (M^+, 2%), 216 (16), 174 (78), 171 (43), 156 (16), 129 (25), 103 (100), 91 (19) and 77 (34) (Found: M^+, 231.1246. $C_{14}H_{17}NO_2$ requires M, 231.1259).

Synthesis of Diene **8**.—A solution of 2-(1,3-dithian-2-yl)-2-methylpropanal[20] (3 g, 15.7 mmol) in dry tetrahydrofuran (THF) (50 cm^3) was added slowly dropwise, at −78 °C and under nitrogen to a solution of *t*-butyl (diethoxyphosphoryl)-acetate* (4 g, 15.7 mmol) and lithium diisopropylamide (LDA) [prepared *in situ* from reaction of butyllithium (16 mmol) and diisopropylamine (16 mmol) in THF (25 cm^3) under nitrogen]. After 2 h at −78 °C and 24 h at room temperature, the reaction was quenched by addition of saturated aq. ammonium chloride. Conventional work-up, followed by chromatography on silica gel, gave the desired alkene, *t*-butyl (*E*)-4-(1,3-dithian-2-yl)-4-methylpent-2-enoate (2.42 g, 54%). Deprotection by the method of Vedejs and Fuchs[21] yielded the aldehyde which after oximation and acetylation, afforded *diene* **8** (470 mg, 60%) as an oil; ν_{max}/cm^{-1} 1770, 1725, 1660 and 1640; $\delta_H(CDCl_3)$ 7.6 (1 H, s, CH=N), 6.8 (1 H, d, *J* 17, vinyl H), 5.7 (1 H, d, *J* 17, vinyl H), 2.1 (3 H, s, MeCO), 1.4 (9 H, m, Bu^t) and 1.3 (3 H, s, Me); $\delta_C(CDCl_3)$ and 167.8 and 164.8 (C=O), 162.0 (C=N), 149.0 (C=C), 122.0 (C=C), 39.3 (C), 27.6 and 24.0 (Me), 19.0 (*Me*CO) and 14.0 (Me); λ_{max}/nm (232 (1000); *m/z* 240 ($M^+ - 15$, 1%), 112 (22), 109 (35), 96 (48), 87 (14), 71 (19) and 57 (100) [Found: ($M^+ - 15$), 240.1231. $C_{12}H_{18}NO_4$ requires *m/z*, 240.1236].

This same general procedure was used to synthesize the following 1-aza-1,4-dienes.

Synthesis of Diene **2a**.—2-(1,3-Dithian-2-yl)-2-methylpropanal (4 g, 21 mmol) and ethyl (diethoxyphosphonyl)acetate (4.17 cm^3, 21 mmol) gave ethyl (*E*)-4-(1,3-dithian-2-yl)-4-methylpent-2-enoate (4.7 g, 86%) as a viscous oil. Deprotection, oximation and acetylation afforded *diene* **2a** (900 mg, 98%), as an oil; ν_{max}/cm^{-1} 1760, 1720, 1650 and 1630; $\delta_H(CDCl_3)$ 7.5 (1 H, s, CH=N), 6.8 (1 H, d, *J* 16, vinyl H), 5.7 (1 H, d, *J* 16, vinyl H), 4.1 (2 H, q, CH_2), 2.1 (3 H, s, MeCO) and 1.3 (9 H, m, Me); $\delta_C(CDCl_3)$ 170 (*C*OMe), 162.0 (*C*O_2Et), 156.0 (C=N), 151.0 (C=C), 120.0 (C=C), 60.7 (CH_2O), 39.8 (C), 24.5 and 24.4 (2 × Me), 19.0 (*Me*CO) and 14.0 (Me); λ_{max}/nm 232 (1230); *m/z* 227 (M^+, 1%), 185 (99), 170 (20), 142 (100), 122 (65), 117 (36), 114 (28), 112 (48), 99 (13), 96 (30), 94 (17) and 89 (12) (Found: M^+, 227.1153. $C_{11}H_{17}NO_4$ requires M, 227.1157).

Synthesis of Diene **2b**.—2-(1,3-Dithian-2-yl)-2-methylpropanal (4 g, 21 mmol) and diethyl cyanomethylphosphonate[22] (2.98 cm^3, 18 mmol) gave (*E*)-4-(1,3-dithian-2-yl)-4-methylpent-2-enonitrile (3.8 g, 99%), m.p. 70–72 °C (from hexane). Deprotection, oximation, and acetylation afforded *diene* **2b** (600 mg, 66%) as an oil; ν_{max}/cm^{-1} 2220, 1760, 1630 and 1620; $\delta_H(CDCl_3)$ 7.6 (1 H, s, CH=N), 6.8 (1 H, s, *J* 17, vinyl H), 5.4 (1 H, d, *J* 17, vinyl H), 2.1 (3 H, s, MeCO) and 1.4 (6 H, s, Me); $\delta_C(CDCl_3)$ 168.0 (C=O), 161.1 (C=N), 157.4 (C=C), 116.5 (CN), 99.2 (C=C), 40.5 (C), 23.9 (Me) and 19.2 (*Me*CO); λ_{max}/nm 228 (1110); *m/z* 166 ($M^+ - 14$, 1%), 138 (100), 100 (11), 95 (50) and 67 (13) [Found: ($M^+ - 14$), 166.0858. $C_9H_{12}NO_2$ requires *m/z*, 166.0865].

Synthesis of Diene **2c**.—Ethyl (*E*)-4-(1,3-dithian-2-yl)-4-methylpent-2-enoate (2.2 g, 8.4 mmol) and diisobutylaluminium hydride (DIBAL) (13.5 cm^3, 21.8 mmol) gave (*E*)-4-(1,3-dithian-2-yl)-4-methylpent-2-enol (1.6 g, 87%) as an oil. Acetylation of this gave a product, which was deprotected and converted into the oxime acetate to yield the *diene* **2c** (550 mg, 75%) as an oil; ν_{max}/cm^{-1} 1770, 1730 and 1620; $\delta_H(CDCl_3)$ 7.6 (1 H, s, CH=N), 5.7 (2 H, m, vinyl H), 4.6 (2 H, d, CH_2), 2.1 (3 H, s, MeCO), 2.0 (3 H, s, MeCO), and 1.3 (6 H, s, 2 Me); $\delta_C(CDCl_3)$ 170.9 and 168.9 (C=O), 139.1 (C=C), 123.6 (C=C), 64.6 (CH_2O), 39.5 (C), 24.8 (Me) and 20.9 and 19.5 (*Me*CO); λ_{max}/nm 232 (361); *m/z* 227 (M^+, 5%), 152 (42), 125 (15), 110 37), 98 (16), 82 (42), 67 (16) and 43 (100) (Found: M^+, 227.1158. $C_{11}H_{17}NO_4$ requires M, 227.1157).

Synthesis of Diene **2d**.—Methylation of (*E*)-4-(1,3-dithian-2-yl)-4-methylpent-2-enol gave (*E*)-4-(1,3-dithian-2-yl)-1-methoxy-4-methylpent-2-ene, which was deprotected and converted into the oxime acetate to yield the *diene* **2d** (280 mg, 70%) as an oil; ν_{max}/cm^{-1} 1760 and 1630; $\delta_H(CDCl_3)$ 7.6 (1 H, s, CH=N), 5.7 (2 H, m, vinyl H), 3.9 (2 H, d, CH_2), 3.3 (3 H, s, MeO), 2.1 (3 H, s, MeCO) and 1.3 (6 H, s, Me); $\delta_C(CDCl_3)$ 168.5 (C=O), 163.5 (C=N), 137.4 (C=C), 125.8 (C=C), 72.5 (CH_2O), 57.8 (MeO), 39.2 (C), 24.9 (Me) and 19.3 (*Me*CO); λ_{max}/nm 230 (303); *m/z* 198 ($M^+ - 1$, 4%), 184 (18), 157 (50), 142 (30), 126 (18), 114 (23), 112 (100), 97 (17), 82 (91), 79 (17), 71 (61), 67 (47) and 55 (49) [Found: ($M^+ - 1$), 198.113. $C_{10}H_{16}NO_3$ requires *m/z*, 198.1126].

Synthesis of Diene **3a**.—2-(1,3-Dithian-2-yl)-2-methylpropanal (3 g, 15 mmol) and ethyl 2-(diethoxyphosphonyl)propanoate (3.73 cm^3, 17 mmol) yielded (*Z*)- (1.65 g, 38%) and (*E*)-(1.95 g, 46%) ethyl 4-(1,3-dithian-2-yl)-2,4-dimethylpent-2-enoate as oils. Deprotection, oximation, and acetylation of the *E*-isomer afforded *diene* **3a** (1.0 g, 83%) as an oil; ν_{max}/cm^{-1} 1760, 1705, 1640 and 1625; $\delta_H(CDCl_3)$ 7.8 (1 H, s, CH=N), 6.8 (1 H, s, vinyl H), 4.2 (2 H, q, CH_2Me), 2.1 (3 H, s, MeCO), 1.9 (3 H, s, MeC=C), 1.4 (6 H, s, Me) and 1.3 (3 H, t, CH_2*Me*); $\delta_C(CDCl_3)$ 168.3 (*C*OMe), 167.7 (*C*O_2Et), 163.3 (C=N), 144.2 (C=C), 130.5 (C=C), 60.8 (CH_2O), 38.8 (C), 25.9 (Me), 19.4 (*Me*CO), 14.2 (*Me*C=C) and 13.3 (Me); λ_{max}/nm 229 (4140); *m/z* 241 (M^+, 3%), 199 (82), 184 (29), 153 (78), 136 (27), 126 (96), 108 (46), 83 (16), 70 (32) and 43 (100) (Found: M^+, 241.131. $C_{12}H_{19}NO_4$ requires M, 241.1314).

* *t*-Butyl (diethoxyphosphonyl)acetate was synthesized by refluxing of triethyl phosphite (10 g, 51 mmol) and *t*-butyl bromoacetate (8.5 g, 51 mmol) for 72 h. The crude product was purified by distillation (b.p. 152 °C, 12 mmHg) to yield an oil (6 g, 50%).

Synthesis of Diene **3b**.—2-(1,3-Dithian-2-yl)-2-methylpropanal (3 g, 15 mmol) and 2-diethoxyphosphonyl)propanonitrile * (3.0 g, 1.5 mmol) yielded (*Z*)-(0.25 g, 7%; as an oil) and (*E*)-[2.45 g, 72%; as crystals, m.p. 92–94 °C (from hexane)] 4-(1,3-dithian-2-yl)-2,4-dimethylpent-2-enonitrile. Deprotection, oximation, and acetylation of the *E*-isomer afforded *diene* **3b** (550 mg, 72%) as an oil; ν_{max}/cm^{-1} 1710 and 1620; δ_H($CDCl_3$) 7.7 (1 H, s, CH=N), 6.4 (1 H, s, vinyl H), 2.1 (3 H, s, MeCO), 1.9 (3 H, s, MeC=C) and 1.4 (6 H, s, Me); δ_C($CDCl_3$) 168.3 (C=O), 162.3 (C=N), 150.4 (C=C), 120.25 (C=C), 112.6 (CN), 39.6 (C), 25.7 (Me), 19.5 (*Me*CO) and 16.2 (*Me*C=C); λ_{max}/nm 229 (1600); *m/z* 179 (M^+ − 15, 1%), 152 (100), 135 (12), 122 (26), 119 (25), 107 (19), 92 (12) and 70 (12) [Found: (M^+ − 15), 179.082. $C_9H_{11}N_2O_2$ requires *m/z*, 179.0820].

Synthesis of Diene **3c**.—(*E*)-Ethyl 4-(1,3-dithian-2-yl)-2,4-dimethylpent-2-enoate (1.0 g, 3.6 mmol) and DIBAL (5.8 cm^3, 8.6 mmol) gave (*E*)-4-(1,3-dithian-2-yl)-2,4-dimethylpent-2-enol (0.6 g, 84%) as an oil. This was acetylated, deprotected, and converted into the oxime acetate to afford the *diene* **3c** (800 mg, 74%) as an oil; ν_{max}/cm^{-1} 1770, 1730 and 1620; δ_H($CDCl_3$) 7.7 (1 H, s, CH=N), 5.5 (1 H, s, vinyl H), 4.4 (2 H, s, CH_2O), 2.2 (3 H, s, MeCO), 2.1 (3 H, s, MeCO), 1.7 (3 H, s, MeC=C) and 1.3 (6 H, s, Me); δ_C($CDCl_3$) 170.6 and 168.7 (C=O), 164.4 (C=N), 133.7 (C=C), 132.7 (C=C), 62.5 (CH_2O), 38.2 (C), 26.4 (Me), 20.9 and 19.6 (*Me*CO) and 14.7 (*Me*C=C); λ_{max}/nm 230 (438); *m/z* 241 (M^+, 5%), 226 (17), 181 (16), 139 (14), 124 (38), 112 (72), 96 (18), 79 (16) and 43 (100) (Found: M^+, 241.131. $C_{12}H_{19}NO_4$ requires M, 241.1314).

Synthesis of Diene **9**.—2-[Dicyclohexyl(hydroxy)methyl]-1,1-*dimethyl*-3-*phenoxycyclopropane*. This was obtained from ethyl 2,2-dimethyl-3-phenoxycyclopropane-1-carboxylate[10] (2 g, 8.5 mmol) and cyclohexylmagnesium bromide (5.5 g, 34 mmol), by following the procedure previously described by Hiers.[23] After conventional work-up, followed by column chromatography with hexane–diethyl ether (95:5), 2-[dicyclohexyl (hydroxy)methyl]-1,1-dimethyl-3-phenoxycyclopropane was obtained as an oil; ν_{max}/cm^{-1} 3570; δ_H($CDCl_3$) 7.0 (5 H, m, ArH), 3.4 (1 H, d, CH), 3.0 (1 H, d, CH) and 2.0–1.0 (29 H, m, cyclohexyl H, OH and Me).

4,4-*Dicyclohexyl*-2,2-*dimethylbut*-3-*enal* **11**.—This compound was synthesized by treatment of 2-[dicyclohexyl(hydroxy)-methyl]-1,1-dimethyl-3-phenoxycyclopropane with a mixture of acetone–HCl–water (4:2:1) for 2 h at room temperature, as was described previously by Julia and Baiclarge.[24] The desired butenal **11** (1 g, 84%) was obtained as an oil, which was used in the following step without further purification ν_{max}/cm^{-1} 2810, 2710 and 1740; δ_H($CDCl_3$) 8.4 (1 H, s, CHO), 4.9 (1 H, s, CH) and 2.1–1.0 (28 H, m, cyclohexyl H and Me).

Oxime of 4,4-*Dicyclohexyl*-2,2-*dimethylbut*-3-*enal*.—The above aldehyde **11** (1 g, 3.8 mmol), hydroxylamine hydrochloride (500 mg, 8 mmol) and pyridine (0.9 g, 8 mmol) were heated at reflux in ethanol (25 cm^3) for 3 h. After work-up, chromatography of the crude product with hexane–diethyl ether (8:2) as eluent gave the oxime (890 mg, 84%) as an oil; ν_{max}/cm^{-1} 3360 and 1610; δ_H($CDCl_3$) 8.2 (1 H, s, OH), 7.4 (1 H, s, CH=N), 5.0 (1 H, s, vinyl H) and 1.8–1.1 (28 H, m, cyclohexyl H and Me).

Diene **9**.—The above oxime (850 mg, 3 mmol), acetyl chloride (3.5 cm^3, 5 mmol) and pyridine (1 cm^3, 12 mmol) were allowed to react at room temperature. Conventional work-up, followed by chromatography with hexane–diethyl ether (8:2), gave the *diene* **9** (596 mg, 62%), m.p. 70–74 °C (from EtOH); ν_{max}(KBr)/cm^{-1} 1770 and 1620; δ_H($CDCl_3$) 7.6 (1 H, s, CH=N), 5.1 (1 H, s, vinyl H), 2.1 (3 H, s, MeCO) and 1.8–1.1 (28 H, m, cyclohexyl H and Me); λ_{max}/nm 231 (2200); *m/z* 319 (M^+, 0.1%), 234 (31), 189 (17), 161 (100), 150 (13), 141 (46), 113 (41), 95 (69), 83 (15) and 43 (24) (Found: C, 74.7; H, 10.5; N, 4.9. $C_{20}H_{33}NO_2$ requires C, 75.17; H, 10.43; N, 4.38%).

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 in acetone or acetophenone in anhydrous benzene were purged with oxygen-free nitrogen for 1 h and irradiated under a positive pressure of nitrogen for the times shown. After completion of the irradiation the solvent and sensitizer were removed under reduced pressure and the products were separated by chromatography.

Irradiation of Diene **5**.—The diene (311 mg, 1.3 mmol) and acetophenone (2 g) were irradiated in benzene (270 cm^3) for 1 h. After removal of the solvent, chromatography with hexane–diethyl ether (9:1) gave the *cyclopropane* **14** (222 mg, 71%) as crystals, m.p. 99–100 °C (from EtOH); ν_{max}(KBr)/cm^{-1} 1750, 1620 and 1210; δ_H($CDCl_3$) 7.5 (1 H, d, J_a 8.8, CH=N), 7.4 (5 H, m, ArH), 2.4 (1 H, d, J_b 5.5, CH), 2.16 (1 H, q, J_b 5.5, J_a 8.8, CH), 2.15 (3 H, s, MeCO), 1.3 (3 H, s, Me) and 0.9 (3 H, s, Me); δ_C($CDCl_3$) 168.4 (C=O), 159.9 (C=N), 136.7–126.4 (aryl C), 37.4 (C), 28.6 (CH) and 27.3 (CH) and 22.6, 21.4 and 19.2 (Me); *m/z* 231 (M^+, 4%), 189 (85), 172 (100), 156 (75), 143 (15), 129 (81), 115 (64), 91 (49) and 77 (28) (Found: C, 72.6; H, 7.4; N, 5.9. $C_{14}H_{17}NO_2$ requires C, 72.72; H, 7.36; N, 6.06%).

Irradiation of Diene **6**.—The diene (370 mg, 1.5 mmol) was irradiated in acetone (280 cm^3) for 2 h. After removal of the solvent, chromatography with hexane–diethyl ether (8:2) gave the following: (i) Recovered diene **6** (180 mg, 45%); (ii) 4-cyclohexyl-2,2-dimethylbut-3-enal (119 mg, 39%); and (iii) unidentified polar products (70 mg).

Irradiation in benzene (280 cm^3). This gave (i) recovered diene **6** (178 mg, 48%); (ii) a mixture of *Z*- and *E*-isomer of diene **6** (90 mg, 24%) (ratio 1:1); *Z*-isomer; ν_{max}/cm^{-1} 1740 and 1640; δ_H($CDCl_3$) 7.4 (1 H, s, CH=N), 5.2 (2 H, m, vinyl H), 1.9 (3 H, s, MeCO) and 1.7–0.9 (17 H, m, cyclohexyl H and Me); and (iii) unidentified polar products (50 mg).

Irradiation of Diene **7**.—The diene (308 mg, 1.3 mmol) and acetophenone (2 g) were irradiated in benzene (370 cm^3) for 1 h. After removal of the solvent, chromatography with hexane–diethyl ether (9:1) gave the following: (i) recovered starting material **7** (114 mg, 37%); (ii) 4-*methyl*-3-*phenylpent*-3-*enal oxime acetate* **20** (190 mg, 61.7%) as an oil; ν_{max}/cm^{-1} 1780 and 1640; δ_H($CDCl_3$) 7.5 (1 H, t, *J* 7, CH=N), 7.3–7.1 (5 H, m, ArH), 3.4 (2 H, d, *J* 7, CH_2), 2.1 (3 H, s, MeCO), 1.9 (3 H, s, Me) and 1.6 (3 H, s, Me); δ_C($CDCl_3$) 168.5 (C=O), 156.6 (C=N), 142–126.4 (aryl C and C=C), 34.5 (CH_2), 22.2 and 20.2 (Me) and 19.3 (*Me*CO); *m/z* 231 (M^+, 4%), 144 (55), 129 (100), 121 (66), 115 (38), 105 (51), 91 (59) and 77 (54) (Found: M^+, 231.1246. $C_{14}H_{17}NO_2$ requires M, 231.1259).

4-*Methyl*-3-*phenylpent*-3-*enonitrile* **21**.—4-Methyl-3-phenylpent-3-enal oxime acetate **20** underwent thermal elimination of acetic acid at room temperature to afford 4-*methyl*-3-*phenylpent*-3-*enonitrile* **21** as an oil; ν_{max}/cm^{-1} 2240 and 1640; δ_H($CDCl_3$) 7.4–7.2 (5 H, m, ArH), 3.3 (2 H, s, CH_2), 1.9 (3 H, s,

* 2-(Diethoxyphosphonyl)propanonitrile was synthesized as follows: 2-bromopropanonitrile (5 g, 37 mmol) and triethyl phosphite (6.4 g, 37 mmol) were refluxed together at 150 °C for 5 h. 2-(Diethoxyphosphonyl)propanonitrile was purified by distillation, b.p. 128–130 °C (3 mmHg) to yield an oil (3 g, 42%).

Me) and 1.6 (3 H, s, Me); $\delta_C(CDCl_3)$ 140.9–123.7 (aryl C and C=C), 117.7 (CN), 22.1 (CH_2) and 22.6 and 20.5 (Me); *m/z* 171 (M^+, 85%), 156 (25), 144 (60), 129 (100), 115 (55), 102 (21), 91 (65) and 77 (38) (Found: M^+, 171.1032. $C_{12}H_{13}N$ requires M, 171.1048).

Irradiation of Diene **8**.—The diene (260 mg, 1.1 mmol) was irradiated in acetone (280 cm^3) for 1.5 h. After removal of the solvent, chromatography with hexane–ethyl acetate (9:1) gave the following: (i) recovered starting material **8** (160 mg, 62%); (ii) *Z*-isomer of diene **8** (60 mg, 23%); ν_{max}/cm^{-1} 1770, 1660, 1640 and 1630; $\delta_H(CDCl_3)$ 8.0 (1 H, s, CH=N), 5.9 (1 H, d, *J* 11, vinyl H), 5.7 (1 H, d, *J* 11, vinyl H), 2.1 (3 H, s, MeCO and 1.4 (15 H, m, Me); $\delta_C(CDCl_3)$ 165.3 and 165.1 (CO_2), 148.3 (C=C), 122.8 (C=C), 38.8 (C), 27.8 and 26.7 (Me) and 19.5 (*Me*CO); *m/z* 213 ($M^+ - 42$, 3%), 199 (20), 182 (13), 157 (27), 139 (49), 122 (53), 112 (28), 109 (66), 96 (54), 81 (28), 71 (33), 69 (37) and 57 (100) [Found: ($M^+ - 42$), 213.1335. $C_{11}H_{19}NO_3$ requires *m/z* 213.1279]; and (iii) unidentified polar products (80 mg).

Irradiation of Diene **9**.—The diene (256 mg, 0.8 mmol) was irradiated in acetone (280 cm^3) for 1 h. After removal of the solvent, chromatography with hexane–diethyl ether (9:1) gave unaltered starting material **9** (230 mg, 90% recovery).

Further irradiation of compound **9** for periods of between 6 and 20 h afforded only the starting material, in addition to unidentified polar products.

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