Extension of the Aza-di-π-methane Reaction to Stable Derivatives. Photochemical Cyclization of β,γ-Unsaturated Oxime Acetates

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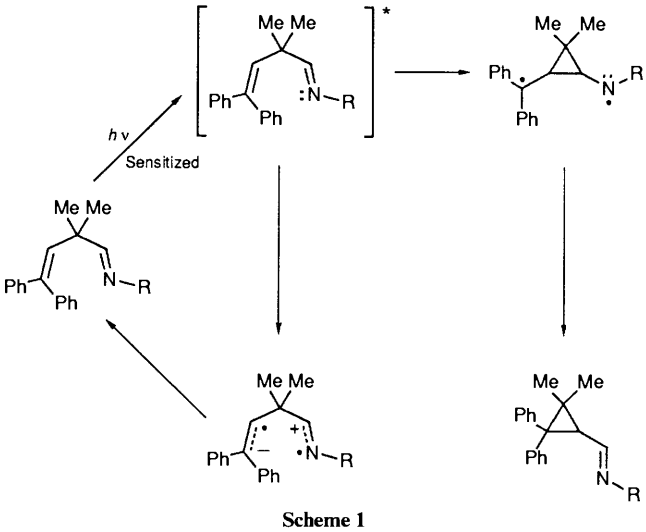
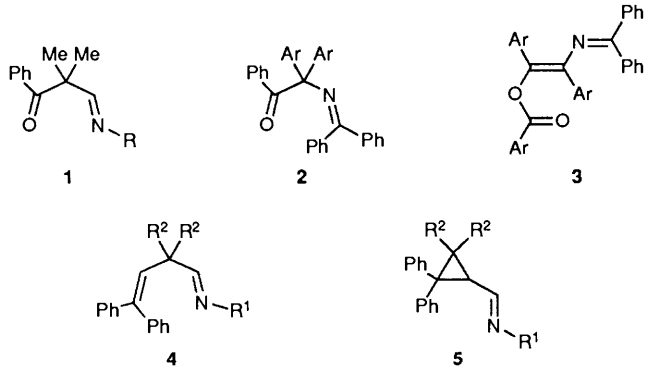
The successful sensitized photochemical conversion of oxime acetates of some β,γ-unsaturated aldehydes and of one ketone into cyclopropane derivatives by the aza-di-π-methane (ADPM) rearrangement has been carried out. Thus, for example, the acetophenone-sensitized irradiation of the oxime acetate of 2,2-dimethyl-4,4-diphenylbut-3-enal affords the oxime acetate of 2,2-dimethyl-3,3-diphenylcyclopropanecarboxaldehyde in 86% yield and with a quantum yield of 0.12. The first report of the successful ADPM rearrangement with all-alkyl substitution is described.

The photochemistry of molecules containing the imine group has been a subject of study for many years.[1,2] In recent years we have been interested in the effect of the incorporation of an imine group on the photochemical reactivity of organic molecules and we have observed the novel photoreactions of imines **1**,[3] **2**[4] and **3**.[5] It is clear from these results that the incorporation of a nitrogen into the system has a profound effect on the course of the reaction and the behaviour of these molecules is substantially different from the reactions of the all-carbon analogues. The discovery of the photochemical reaction in which imines from β,γ-unsaturated aldehydes **4** rearrange *via* the ADPM process to yield the cyclic imines **5** is of importance.[6,7] Our previous studies on the ADPM reaction had shown that the efficiency of the cyclization was dependent on the nature of the substituent on the nitrogen atom.[8,9] Thus with an electron withdrawing group in the *N*-aryl imines **4a** the quantum yield for product formation increased by a factor of four from the unsubstituted compound (**4a**; R^1 = Ph).[8] This change in reactivity was substantiated further in a study of *N*-benzylimines **4b**.[9] In both of these studies an excellent linear correlation was obtained between log Φ and the σ^+ substituent constants. Based on these results we interpreted the mechanism of the cyclization as that shown in Scheme 1. The route to product involves the conventional di-π-methane bridging mechanism. However, the alternative reaction mode of the excited state is intramolecular electron transfer from the imine nitrogen lone pair to the alkene moiety. This electron transfer process is energy wasting and results in decay back to starting material. Thus for the success of the ADPM rearrangement this electron transfer step has to be minimised.



Scheme 1

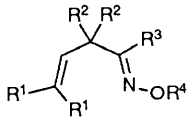


4a = **5a**; R^1 = Ar, R^2 = Me
4b = **5b**; R^1 = CH_2Ar, R^2 = Me

Attempts made by us[7] and others[10] to extend the reaction to more stable derivatives of aldehydes and ketones such as the oximes and oxime ethers failed. We reasoned that in these derivatives the oxime and oxime ether groups had low ionization potentials which would lead to facile electron transfer and low efficiency of cyclization, if any took place. Thus, the aim of the current research was to find a stable derivative of β,γ-unsaturated aldehydes or ketones which would complement the earlier study and provide a system which did not require special precautions to prevent hydrolysis. The present report details the use of oxime acetate derivatives, one example of which was published in preliminary form,[11] and the determination of quantum yields for two of the oxime acetates.

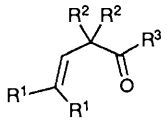
Results and Discussion

The oximes **6** and the corresponding acetates **7** were readily prepared from the aldehydes or ketones **8** by conventional methods in yields >70%. The identity of these compounds was readily proven by standard spectroscopic techniques. In our previous studies of the ADPM reaction acetophenone-sensitization had been shown to be effective[6] and these conditions were used for the irradiation of the oxime acetate **7a** in a conventional



6; R^4 = H
7; R^4 = COMe

6a = **7a**; R^1 = Ph, R^2 = Me, R^3 = H
6b = **7b**; R^1 = R^2 = Ph, R^3 = H
6c = **7c**; R^1 = Ph, R^2 = R^3 = Me
6d = **7d**; R^1 = Ph, R^2 = Me, R^3 = Ph
6e = **7e**; R^1 = R^2 = Me, R^3 = H
6f = **7f**; R^1 = R^2 = R^3 = Me



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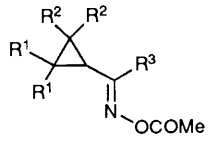

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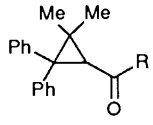
8a = **9a**; R^1 = Ph, R^2 = Me, R^3 = H
8b = **9b**; R^1 = R^2 = Ph, R^3 = H
8c = **9c**; R^1 = Ph, R^2 = R^3 = Me
8d; R^1 = R^3 = Ph, R^2 = Me
8e = **9e**; R^1 = R^2 = Me, R^3 = H
8f; R^1 = R^2 = R^3 = Me



10a; R = H
10b; R = Me

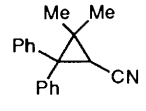
immersion well apparatus. After irradiation for 30 min the solvent was removed under reduced pressure at low temperature. The resultant mixture was separated by flash column chromatography to afford acetophenone, starting material (11%) and a new product in 86% yield. This compound had retained the acetate group and exhibited an absorption at 1765 cm^{-1}. The ^1H NMR spectrum showed that the absorption at δ 5.90 for the vinyl hydrogen of the starting material had disappeared indicating that a major change in the molecule had taken place and new absorptions had appeared in the δ 2–2.5 region. From previous studies[6–9] with the imines of aldehyde **8a** it was clear that this product was a cyclopropyl derivative, namely the oxime acetate **9a**. Final proof for the structure was obtained by hydrolysis in EtOH–$NaHSO_3$ where the aldehyde **10a** was obtained in good yield. The separation of the reaction mixture using column chromatography on silica gel is an improvement on the method described previously[11] in which the acetophenone was removed by distillation under reduced pressure. Using that method we observed the formation of the corresponding nitrile **11** produced by thermal elimination of acetic acid from the cyclopropyl oxime acetate. This thermal elimination was totally suppressed by the new procedure described herein.

The success of this ADPM reaction mode was further demonstrated by the photochemical conversion of the oxime acetates **7b** and **7c** into the corresponding cyclopropane derivatives **9b** and **9c** in 90% and 18% yield respectively. From these results it can be seen that the aldoxime acetates **7a** and **7b** are more reactive than the ketoxime acetate **7c** and this is further substantiated by the failure of oxime acetate **7d** to afford a cyclized product after 20 h irradiation.

Changing the substitution on the terminal carbon of the azadiene system to methyl groups in oxime acetate **7e** does not alter the reaction path and using acetophenone as sensitizer the cyclopropane **9e** was obtained in 12% yield. This, however, was not the major product of the reaction and a second product, obtained in 57% yield, was identified as the oxetane **12** formed by the addition of the acetophenone in its triplet state to the alkene moiety of the oxime acetate **7e**. The identity of the oxetane **12** was established by the usual spectroscopic techniques and microanalysis. The only regioisomer formed is in accord with the accepted mechanistic path for the formation of oxetanes.[12] Previously we have suggested[8] that the aza-di-π-methane process was brought about by the excitation of the alkene moiety. It was clear from the result with acetophenone and oxime acetate **7e** that there is an energy mismatch between the sensitizer and the alkene leading to the formation of the oxetane as the major product. This difficulty was overcome by using acetone as sensitizer whereby **7e** gave the cyclopropane **9e** in 32%. No oxetane was obtained from this reaction. The success of the ADPM rearrangement of this all-alkyl substituted oxime acetate **7e** is of considerable importance. A similar reaction has not been reported in the oxa-di-π-methane reaction[13] and there is only one example in the di-π-methane system reported by Baeckstrom[14] and by Bullivant and Pattenden.[15] The synthetic value of this cannot be stressed too much since the extension of this process to differently substituted oxime acetates will allow the ready synthesis of naturally occuring compounds or compounds of commercial value such as pyrethroid insecticides.[16] The other oxime acetate **7f** was unreactive under acetophenone sensitization and this is further conformation that the ketoxime acetates are less reactive in qualitative terms.

These results substantiate our original proposal that the use of oxime acetate derivatives will suppress the adverse electron transfer from nitrogen to the alkene and permit the ADPM rearrangement of these derivatives of β,γ-unsaturated aldehydes. Steric factors do influence the reactivity as is seen by the sluggish behaviour of the ketoxime acetates. The photochemistry of the carbonyl compounds (**8a–d, f**) has been studied[13] before and the usual reactivity found on sensitized irradiation is 1,3-acyl migration or decarbonylation. We have demonstrated that decarbonylation is also the fate of acetone-sensitized irradiation of **8e** when the diene **14** is obtained in 32% yield.

Further confirmation of the value of using oxime acetate derivatives was obtained from quantum yield measurements. These were measured for the photocyclization of the acetates **7a**



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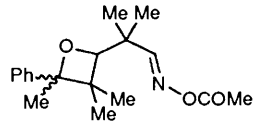

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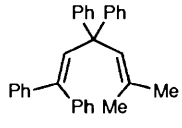

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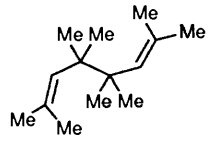

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and **7b** and are made on conversions ranging from 4.9 to 24.7% with four determinations for each compound. The results were plotted and extrapolated to zero time to give the optimum quantum yield in each case and details are recorded in the Experimental section. The results from the quantitative work show that the quantum efficiency for the formation of **9a** from the oxime acetate **7a** by acetophenone sensitization is 0.12 which is 13 fold better than the quantum yield for the cyclization of the imine (**4a**; Ar = Ph) to the corresponding cyclopropane **5a**.[8] The ADPM reaction can, in fact, be extremely efficient as shown by the cyclization of oxime acetate **7b** which yields the corresponding cyclopropane **9b** with a quantum yield of 0.82. The high efficiency of this reaction could be due to the diphenyl substitution of the central carbon. Zimmerman *et al.*[17] have also observed similar changes in the di-π-methane reaction of **13** where the quantum yield of cyclization was measured as 0.42 for the sensitized reaction. These results show that in some cases the aza-di-π-methane reaction is more efficient than the di-π-methane counterpart.

The reason for the low reactivity of the ketoxime acetate **7c** yielding the cyclopropane **9c** and the failure of the derivative **7f** to rearrange is unclear. However, Zimmerman *et al.*[18] have shown that substituents on the C-2 and C-4 positions of the 1,4-diene system suppress the di-π-methane rearrangement. This is interpreted as a steric effect. In our examples steric factors could also be responsible for the lowering of the efficiency of the ADPM rearrangement. Steric factors may be responsible for the failure of the cyclization of derivative **7d**. In this case, however, an alternative deactivating mechanism involving the interaction of the phenyl group on C-1 with the C=N of the oxime acetate resulting in a decrease in the ionization potential of the oxime acetate group could be operative. Under these conditions the adverse electron transfer, discussed earlier, would become operative and suppress the cyclization.

This study has shown that the ADPM rearrangement can be carried out using the stable oxime acetate derivative of unsaturated ketones and aldehydes. In addition to the stability of the derivatives another advantage is that the efficiency of the transformation to the cyclopropane derivatives is greatly enhanced and in some cases is greater than the efficiency reported for the di-π-methane rearrangement. The demonstration that the ADPM reaction can be carried out on substrates with only alkyl substituents increases greatly the synthetic potential of this rearrangement. It is interesting to note that the ADPM rearrangement provides a method to overcome the failure of β,γ-unsaturated aldehydes and some ketones to undergo the oxa-di-π-methane process[13] by the simple method of converting them into the corresponding stable oxime acetates followed by sensitized irradiation and hydrolysis of the resultant cyclopropane derivative.

Experimental

M.p.s were determined on a Buchi 510D apparatus in open capillaries and are uncorrected. IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer and band positions are reported in wavenumbers. NMR spectra were recorded on a Varian T-60A, Bruker WM-250 or a Bruker 300 spectrometer with chemical shifts δ expressed in ppm downfield from internal Me_4Si and coupling constants *J* are given in Hz. UV–visible spectra were recorded in methylene dichloride solution using a Perkin-Elmer 550 spectrometer. The mass spectra were run by Dr. P. Bladon at the University of Strathclyde, Glasgow, UK, using an AEI (Kratos) MS 9 mass spectrometer fitted with a Mass Spectrometry Services Solid State Console and a GEC 905 computer.

Standard Procedure for Synthesis of Oximes.—The oximes were prepared by refluxing the corresponding carbonyl compound with equimolecular amounts of hydroxylamine hydrochloride and pyridine (1 cm^3) in ethanol (30 cm^3) for 1.5 h for aldehydes and for 2.5 h for ketones. After conventional work up the oximes were isolated and purified by chromatography on silica gel and/or crystallization.

2,2-*Dimethyl*-4,4-*diphenylbut*-3-*enal oxime* **6a**. From **8a**[19] as previously described.[7] The ^{13}C NMR spectrum of **6a** showed the following signals: $\delta_C(CDCl_3)$ 27.4, 39.2, 127.0, 127.1, 127.3, 127.9, 128.1, 130.1, 134.7, 139.3, 141.9, 142.9 and 157.2.

2,2,4,4-*Tetraphenylbut*-3-*enal oxime* **6b**. From **8b**[17] (710 mg, 1.9 mmol). This gave **6b** (610 mg, 83%) as white crystals, m.p. 174–175 °C (from EtOH); ν_{max}(Nujol)/cm^{-1} 3300, 1600 and 1580; $\delta_H(CDCl_3)$ 6.8 (1 H, s, vinyl), 6.9–7.3 (20 H, m, ArH), 7.4 (1 H, s, HC=N) and 7.8 (1 H, s, NOH); $\delta_C(CDCl_3)$ 56.1, 126.7, 127.0, 127.2, 127.4, 127.9, 128.1, 129.0, 129.8, 133.5, 143.5, 144.3 and 155.7; *m/z* 389 (M^+, 12%), 373 (27), 372 (100), 345 (18), 344 (55), 267 (32), 191 (33), 167 (76), 165 (48) and 51 (31) (Found: M^+, 389.1802. $C_{28}H_{23}NO$ requires M^+, 389.1780).

3,3-*Dimethyl*-5,5-*diphenylpent*-4-*en*-2-*one oxime* **6c**. From ketone **8c**[19] (2.18 g, 8.3 mmol). This gave **6c** (2.02 g, 88%) as white crystals, m.p. 86–88 °C (from hexane); ν_{max}(KBr)/cm^{-1} 3350 and 1620; $\delta_H(CDCl_3)$ 1.2 (6 H, s, CMe_2), 1.7 (3 H, s, CH_3), 6.0 (1 H, s, vinyl) and 7.1–7.3 (11 H, m, ArH and NOH); $\delta_C(CDCl_3)$ 11.8, 27.4, 43.2, 127.0, 127.0, 127.1, 127.6, 127.9, 130.0, 135.2, 141.9, 143.6 and 162.5; *m/z* 279 (M^+, 38%), 264 (19), 263 (19), 262 (100), 167 (14), 91 (11), 77 (7) and 51 (12) (Found: M^+, 279.1595. $C_{19}H_{21}NO$ requires M^+, 279.1623).

2,2-*Dimethyl*-1,4,4-*triphenylbut*-3-*en*-1-*one oxime* **6d**. From ketone **8d**[20] (1 g, 3 mmol). This gave **6d** (848 mg, 81%) as a white crystalline solid, m.p. 134–136 °C (from EtOH); ν_{max}(KBr)/cm^{-1} 3230, 1595 and 1570; $\delta_H(CDCl_3)$ 1.1 (6 H, s, CMe_2), 6.1 (1 H, s, vinyl) and 6.9–7.4 (16 H, m, ArH and NOH); $\delta_C(CDCl_3)$ 27.7, 43.6, 126.9, 127.0, 127.0, 127.7, 127.9, 128.0, 128.0, 128.1, 129.9, 133.6, 134.4, 139.8, 141.7, 143.3 and 170.0; *m/z* 341 (M^+, 100%), 324 (96), 221 (9), 205 (12), 197 (10), 191 (10), 167 (31), 143 (16), 131 (97), 103 (25), 91 (55), 77 (30) and 51 (13) (Found: M^+, 341.1779. $C_{24}H_{23}NO$ requires M^+, 341.1774).

2,2,4-*Trimethylpent*-3-*enal oxime* **6e**. From **8e**[21] (2.7 g, 21 mmol). This gave **6e** (2.51 g, 85%) as white crystals, m.p. 43–45 °C (from hexane); ν_{max}(KBr)/cm^{-1} 3300, 1640 and 1600; $\delta_H(CDCl_3)$ 1.2 (6 H, s, CMe_2), 1.6 (3 H, d, *J* 2, *Me*–C=C), 1.7 (3 H, d, *J* 2, MeC=C), 5.1 (1 H, m, vinyl), 7.4 (1 H, s, HC=N) and 8.1 (1 H, br s, NOH); $\delta_C(CDCl_3)$ 18.6, 27.1, 37.6, 129.8, 134.7 and 158.6; *m/z* 141 (M^+, 4%), 127 (100), 109 (14), 97 (72), 71 (6), 59 (15), 43 (37) and 41 (17) (Found: M^+, 141.1153. $C_8H_{15}NO$ requires M^+, 141.1150).

3,3,5-*Trimethylhex*-4-*en*-2-*one oxime* **6f**. From **8f**[22] (1.51 g, 11 mmol). This gave **6f** (1.27 g, 76%) as a white crystalline solid, m.p. 59–61 °C (from EtOH–H_2O); ν_{max}(Nujol)/cm^{-1} 3290 and 1660; $\delta_H(CDCl_3)$ 1.2 (6 H, s, CMe_2), 1.6 (3 H, d, *J* 2, *Me*C=C), 1.7 (3 H, d, *J* 2, MeC=C), 1.8 (3 H, s, MeC=N), 5.1 (1 H, br m, vinyl) and 7.1 (1 H, br s, NOH); $\delta_C(CDCl_3)$ 11.6, 17.6, 26.7, 27.2, 41.5, 130.5, 134.0 and 163.5; *m/z* 155 (M^+, 19%), 140 (100), 138 (20), 122 (11), 96 (19), 69 (11), 55 (33), 42 (18) and 41 (28) (Found: M^+, 155.1338. $C_9H_{17}NO$ requires M^+, 155.1310).

Standard Method for the Synthesis of Oxime Acetates.—Acetyl chloride was added dropwise to a solution of the oxime in pyridine (2 cm^3) at 0 °C. The mixture was stirred for 1 h at room temperature, poured into sulphuric acid (10%) and extracted with diethyl ether. The organic layer was washed with a saturated solution of $NaHCO_3$ and water, and dried over $MgSO_4$. The desiccant was filtered off and the solvent removed by evaporation under reduced pressure. The product was purified by either crystallization or column

chromatography on silica gel using hexane–diethyl ether (9:1) as eluent.

1-*Acetoxy*-3,3-*dimethyl*-5,5-*diphenyl*-1-*azapenta*-1,4-*diene* **7a**. From **6a** (1.10 g, 4 mmol). This gave **7a** (1.21 g, 95%) as white crystals, m.p. 82–84 °C (from hexane); ν_{max}(KBr)/cm^{-1} 1760 and 1625; δ_H($CDCl_3$) 1.3 (6 H, s, CMe_2) 1.9 (3 H, s, MeCOO), 5.9 (1 H, s, vinyl) and 7.0–7.3 (11 H, m, ArH and HC=N); δ_C($CDCl_3$) 19.6, 27.3, 39.9, 127.0, 127.4, 128.2, 128.9, 129.1, 130.3, 130.5, 139.0, 141.9, 142.4, 163.4 and 168.7; λ_{max}(CH_2Cl_2)/nm 248 (ε 12 300 dm^3 mol^{-1} cm^{-1}); *m/z* 307 (M^+, 10%), 248 (100), 232 (28), 205 (21), 165 (11), 129 (8), 91 (19), 77 (6) and 51 (8) (Found: M^+, 307.1572. $C_{20}H_{21}NO_2$ requires M^+, 307.1577).

1-*Acetoxy*-3,3,5,5-*tetraphenyl*-1-*azapenta*-1,4-*diene* **7b**. From **6b** (700 mg, 1.8 mmol). This gave **7b** (600 mg, 77%) as white crystals, m.p. 116–117 °C (from EtOH); ν_{max}(KBr)/cm^{-1} 1750; δ_H($CDCl_3$) 2.0 (3 H, s, MeCOO), 6.8 (1 H, s, vinyl), 7.0–7.3 (20 H, m, ArH) and 7.6 (1 H, s, HC=N); δ_C($CDCl_3$) 19.6, 56.6, 127.1, 127.4, 127.6, 128.0, 128.2, 128.2, 129.1, 129.9, 132.4, 138.9, 142.8, 142.9, 162.3 and 169.0; λ_{max}(CH_2Cl_2)/nm 235 (ε 13 700 dm^3 mol^{-1} cm^{-1}) and 251 (14 800); *m/z* 431 (M^+, 0.5%) 373 (57), 372 (98), 371 (100), 344 (60), 294 (33), 293 (28), 267 (30), 265 (26), 216 (28), 191 (19), 178 (40), 167 (84), 152 (16) and 43 (22) (Found: M^+, 431.1885. $C_{30}H_{25}NO_2$ requires M^+, 431.1885).

1-*Acetoxy*-2,3,3-*trimethyl*-5,5-*diphenyl*-1-*azapenta*-1,4-*diene* **7c**. From **6c** (1.93 g, 7 mmol). This gave **7c** (1.7 g, 77%) as a colourless oil after flash chromatography; ν_{max}(KBr)/cm^{-1} 1760 and 1630; δ_H($CDCl_3$) 1.3 (6 H, s, CMe_2), 1.7 (3 H, s, CH_3C=N), 2.1 (3 H, s, MeCOO), 6.0 (1 H, s, vinyl) and 7.0–7.7 (10 H, m, ArH); δ_C($CDCl_3$) 13.7, 19.4, 27.3, 43.5, 126.8, 126.9, 127.3, 127.7, 129.8, 134.0, 138.3, 142.1, 142.9, 168.5 and 169.2; λ_{max}(CH_2Cl_2)/nm 227 (ε 34 800 dm^3 mol^{-1} cm^{-1}), 253 (28 700) and 257 (24 700); *m/z* 321 (M^+, 13%), 264 (12), 263 (54), 262 (100), 220 (60), 205 (30), 194 (33), 179 (13), 167 (30), 143 (17), 105 (12), 91 (29) and 77 (14) (Found: M^+, 321.1750. $C_{21}H_{23}NO_2$ requires M^+, 321.1729).

1-*Acetoxy*-3,3-*dimethyl*-2,5,5-*triphenyl*-1-*azapenta*-1,4-*diene* **7d**. From **6d** (600 mg, 1.76 mmol). This gave **7d** (531 mg, 79%) as white crystals, m.p. 109–111 °C (from EtOH); ν_{max}(KBr)/cm^{-1} 1710 and 1610; δ_H($CDCl_3$) 1.2 (6 H, s, $C(Me_2)$, 1.9 (3 H, s, MeCOO), 6.1 (1 H, s, vinyl) and 6.9–7.5 (15 H, m, ArH); δ_C($CDCl_3$) 19.4, 27.3, 44.3, 126.8, 126.9, 127.0, 127.5, 127.6, 127.9, 128.2, 129.6, 133.0, 139.3, 142.4, 143.1, 168.9 and 172.4; λ_{max}(CH_2Cl_2)/nm 253 (ε 13 600 dm^3 mol^{-1} cm^{-1}) and 237 (12 600); *m/z* 383 (M^+, 1%), 324 (67), 282 (12), 221 (8), 205 (11), 165 (10), 143 (16), 131 (100), 105 (11), 103 (38), 91 (46), 77 (12) and 43 (30) (Found: M^+, 383.1885. $C_{26}H_{25}NO_2$ requires M^+, 383.1879).

1-*Acetoxy*-3,3,5-*trimethyl*-1-*azahexa*-1,4-*diene* **7e**. from **6e** (1 g, 7 mmol). This gave **7e** (947 mg, 73%) as a colourless liquid after flash chromatography; ν_{max}(liq. film)/cm^{-1} 1770 and 1625; δ_H($CDCl_3$) 1.3 (6 H, s, CMe_2), 1.6 (3 H, d, *J* 2, CH_3C=C), 1.7 (3 H, d, *J* 2, MeC=C), 2.2 (3 H, s, MeCOO), 5.1 (1 H, m, vinyl) and 7.6 (1 H, s, HC=N); δ_C($CDCl_3$) 13.7, 19.3, 26.7, 28.4, 73.9, 128.7, 135.4, 164.9 and 168.6; λ_{max}(CH_2Cl_2)/nm 228 (ε 10 300 dm^3 mol^{-1} cm^{-1}); *m/z* 182 (M^+, 3%), 126 (59), 108 (28), 97 (100), 71 (10), 55 (32), 43 (44) and 41 (29) (Found: M^+, 183.1259. $C_{10}H_{17}NO_2$ requires M^+, 183.1255).

1-*Acetoxy*-2,3,3,5-*tetramethyl*-1-*azahexa*-1,4-*diene* **7f**. From **6f** (1.23 g, 8 mmol). This gave **7f** (1.10 g, 71%) after flash chromatography as a colourless oil; ν_{max}(KBr)/cm^{-1} 1760 and 1630; δ_H($CDCl_3$) 1.3 (6 H, s, CMe_2), 1.6 (3 H, d, *J* 2, MeC=C), 1.7 (3 H, d, *J* 2, MeC=C), 1.9 (3 H, s, MeCOO), 2.1 (3 H, s, MeC=N) and 5.1 (1 H, m, vinyl); δ_C($CDCl_3$) 13.3, 17.4, 19.4, 26.3, 26.9, 42.0, 129.5, 134.6, 168.9 and 171.9; λ_{max}(CH_2Cl_2)/nm 228 (ε 8500 dm^3 mol^{-1} cm^{-1}); *m/z* 197 (M^+, 8%), 182 (53), 140 (100), 138 (40), 97 (19), 96 (33), 51 (14), 43 (32) and 41 (6) (Found: M^+, 197.1386 $C_{11}H_{19}NO_2$ requires M^+, 197.1416).

Preparative Photolysis of Oxime Acetates **7a–f**.—Preparative 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 oxime acetates in the solvent indicated in each case were purged for 1 h with deoxygenated nitrogen and irradiated under a positive pressure of nitrogen. After completion of the irradiation the solvent was removed under reduced pressure, and the products were separated by chromatography on silica gel using mixtures of hexane–diethyl ether as eluent.

Irradiation of **7a**. (*a*) Acetophenone as sensitizer. Compound **7a** (400 mg, 1.3 mmol) and acetophenone (2 g) in benzene (330 cm^3) were irradiated for 30 min. Chromatography of the crude photolysate using hexane–diethyl ether (9:1) afforded: acetophenone (1.96 g), starting material (46 mg, 11%) and *cyclopropane* **9a** (344 mg, 86%), m.p. 130–132 °C (from hexane); ν_{max}(KBr)/cm^{-1} 1765 and 1610; δ_H($CDCl_3$) 1.1 (3 H, s, Me), 1.3 (3 H, s, Me), 2.1 (3 H, s, MeCOO), 2.5 (1 H, d, *J* 10, CH) and 6.9–7.4 (11 H, m, ArH and HC=N); δ_C($CDCl_3$) 19.4, 20.7, 25.3, 29.7, 33.2, 48.2, 126.5, 126.7, 128.5, 128.7, 130.5, 140.3, 143.6, 159.7 and 168.5; *m/z* 307 (M^+, 2%), 265 (14), 248 (100), 232 (48), 220 (27), 206 (33), 191 (18), 165 (59), 154 (21), 91 (17), 60 (20) and 43 (47) (Found: M^+, 307.1572. $C_{20}H_{21}NO_2$ requires M^+, 307.1577); when acetophenone was removed from the crude photolysate by distillation *nitrile* **11** was obtained in 11% yield, m.p. 124–125 °C (from hexane); ν_{max}(KBr)/cm^{-1} 2230; δ_H($CDCl_3$) 1.1 (3 H, s, Me), 1.4 (3 H, s, Me), 2.1 (1 H, s, CH) and 7.2–7.5 (10 H, m, ArH); δ_C($CDCl_3$) 21.8, 22.1, 24.1, 29.8, 47.7, 119.2, 127.0, 127.3, 128.6, 128.8, 128.9, 129.8, 139.1 and 141.9; *m/z* 247 (M^+, 77%) 232 (94), 220 (38), 205 (11), 165 (100), 154 (47), 128 (5), 91 (10), 77 (12) and 51 (14) (Found: M^+, 247.1361. $C_{18}H_{17}N$ requires M^+, 247.1357) and the *cyclopropane* **9a** in 79% yield.

(*b*) *Acetone as sensitizer*. Compound **7a** (500 mg, 1.6 mmol) in anhydrous acetone (280 cm^3) was irradiated for 3 h. Flash chromatography of the crude photolysate afforded starting material (225 mg, 45%) and *cyclopropane* **9a** (175 mg, 35%).

Irradiation of **7b**. Compound **7b** (294 mg, 0.68 mmol), and acetophenone, (2 g) in benzene (350 cm^3) were irradiated for 30 min. Chromatography of the crude photolysate using hexane–diethyl ether (9:1) afforded acetophenone (1.9 g), starting material (20 mg, 7%) and *cyclopropane* **9b** (264 mg, 90%), m.p. 161–162 °C (from EtOH); ν_{max}(KBr)/cm^{-1} 1645 and 1590; δ_H($CDCl_3$) 2.1 (3 H, s, Me), 3.9 (1 H, d, *J* 10, CH) and 6.9–7.5 (21 H, m, ArH and HC=N); δ_C($CDCl_3$) 19.5, 31.9, 48.9, 126.2, 126.8, 127.9, 128.4, 129.2, 131.6, 139.5, 142.4, 160.6 and 168.5; *m/z* 431 (M^+, 1%), 430 (4), 373 (72), 372 (100), 371 (81), 370 (75), 345 (79), 344 (97), 294 (52), 167 (82), 166 (73), 165 (90), 77 (47) and 43 (64) (Found: M^+, 431.1882. $C_{30}H_{25}NO_2$ requires M^+, 431.1885).

Irradiation of **7c**. Compound **7c** (670 mg, 2.1 mmol) and acetophenone (2 g) in benzene (280 cm^3) were irradiated for 20 h. Chromatography of the crude photolysate using hexane–diethyl ether (95:5) afforded starting material (380 mg, 57%) and *cyclopropane* **9c** (121 mg, 18%), m.p. 153–154 °C (from hexane); ν_{max}(KBr)/cm^{-1} 1720 and 1620; δ_H($CDCl_3$) 1.1 (3 H, s, Me), 1.5 (3 H, s, Me), 1.9 (3 H, s, MeCN), 2.0 (3 H, s, MeCOO), 2.4 (1 H, s, CH) and 7.1–7.4 (10 H, m, ArH); δ_C($CDCl_3$) 14.9, 18.1, 20.4, 26.6, 29.5, 38.5, 48.1, 125.7, 128.0, 128.4, 130.0, 130.4, 140.2, 144.4, 163.4 and 170.4; *m/z* 321 (M^+, 2%), 279 (12), 263 (62), 262 (100), 220 (33), 205 (59), 165 (21), 91 (20) and 77 (12) (Found: M^+, 321.1759. $C_{21}H_{23}NO_2$ requires M^+, 321.1729).

Irradiation of **7d**. Compound **7d** (352 mg, 0.92 mmol) and acetophenone (2.1 g) in benzene (330 cm^3) were irradiated for 20 h. After removing the acetophenone by distillation under reduced pressure only starting material was recovered. No evidence of any reaction was found.

Irradiation of **7e**. (*a*) Acetophenone as sensitizer. Compound

Table 1 Summary of quantum yield data for the conversion of 1-acetoxy-3,3-dimethyl-5,5-diphenyl-1-azapenta-1,4-diene **7a** into cyclopropane **9a**

Run	Acetate (mmol)	Light input (mE)	Conversion (%)	Photoproduct (10^{-2} mmol)	Quantum[a] yield
1	0.1925	0.0799	4.9	0.954	0.120
2	0.1987	0.1569	9.8	1.95	0.124
3	0.1835	0.2425	13.9	2.55	0.105
4	0.2040	0.4475	24.7	5.04	0.113

[a] Optimum quantum yield = 0.12.

Table 2 Summary of quantum yield data for the conversion of 1-acetoxy-3,3,-5,5-tetraphenyl-1-azapenta-1,4-diene **7b** into cyclopropane **9b**

Run	Acetate (mmol)	Light input (mE)	Conversion (%)	Photoproduct (10^{-2} mmol)	Quantum[a] yield
1	0.1258	0.0176	10.1	1.27	0.722
2	0.1445	0.0247	13.5	1.95	0.790
3	0.1394	0.0396	20.7	2.89	0.730
4	0.1459	0.0500	22.3	3.26	0.650

[a] Optimum quantum yield = 0.82.

7e (370 mg, 2 mmol) and acetophenone (1.8 g) in benzene (280 cm^3) were irradiated for 2 h. The acetophenone was removed by distillation under reduced pressure at room temperature. Chromatography of the crude photolysate afforded starting material (100 mg, 27%), *cyclopropane* **9e** (40 mg, 12%) as a colourless oil; ν_{max}(liq. film)/cm^{-1} 1760 and 1610; $\delta_H(CDCl_3)$ 1.3 (6 H, s, CMe_2), 1.4 (6 H, s, CMe_2), 1.6 (1 H, d, *J* 10, CH), 2.3 (3 H, s, $MeCO_2$) and 7.6 (1 H, d, *J* 10, CH=N); $\delta_C(CDCl_3)$ 14.3, 17.0, 18.4, 22.2, 27.8, 32.3, 159.0 and 167.6; and the *oxetane* **12** (210 mg, 57%) as a colourless oil; ν_{max}(liq. film)/cm^{-1} 1760 and 1630; $\delta_H(CDCl_3)$ 0.7 (3 H, s, Me), 1.1 (3 H, s, Me), 1.2 (6 H, s, CMe_2), 1.6 (3 H, s, Me), 2.0 (3 H, s, Me), 4.1 (1 H, s, CH) and 6.9–7.1 (1 H, s, CH=N); $\delta_C(CDCl_3)$ 19.3, 21.8, 23.6, 24.6, 25.7, 40.3, 45.4, 87.5, 90.7, 123.5, 126.2, 127.7, 144.6, 163.0 and 168.5; *m/z* 243 (M^+ – AcOH, 1%), 184 (34), 183 (89), 169 (35), 168 (94), 146 (93), 122 (94), 121 (99), 108 (77), 96 (86), 77 (69) and 43 (100).

(*b*) *Acetone as sensitizer.* A solution of **7e** (460 mg, 2.5 mmol) in acetone (330 cm^3) was irradiated for 4 h. After removing the solvent, the crude photolysate was chromatographed using hexane–diethyl ether (9:1) yielding starting material (193 mg, 42%) and cyclopropane **9e** (147 mg, 32%).

Irradiation of **7f**. Compound **7f** (400 mg, 2 mmol) in acetone (280 cm^3) was irradiated for 20 h. After removing the solvent only unchanged **7f** was recovered. No evidence of any reaction was found.

Photolysis of **8e**. Aldehyde **8e** (509 mg, 4 mmol) in acetone (330 cm^3) was irradiated for 2 h. After the removal of the acetone by distillation (Vigreux column) the crude photolysate was chromatographed (pentane as eluent) affording starting material (53 mg, 10%) and diene **14** (124 mg, 32%) which was identified by comparison of spectroscopic data.[23]

General Procedure for Hydrolysis of Oxime Acetates.[24]—Sodium hydrogen sulphite (5 cm^3, 45%) was added to a solution of the oxime acetate in EtOH (15 cm^3) and the mixture was heated at reflux for variable times. The crude reaction mixture was extracted with diethyl ether, and the organic layer was washed with HCl (10%), $NaHCO_3$ (10%) and water, and dried over $MgSO_4$. The desiccant was filtered off, and the solvent evaporated under reduced pressure. The reaction products were separated by flash chromatography on silica gel.

Hydrolysis of **9a**. Compound **9a** (100 mg, 0.32 mmol) was refluxed for 2.5 h affording *nitrile* **11** (12 mg, 15%), *aldehyde* **10a** (41 mg, 52%) and starting material (31 mg, 31%).

Hydrolysis of **9c**. Compound **9c** (100 mg, 0.31 mmol) was refluxed for 15 h affording *ketone* **10b** (47 mg, 57%) and starting material (39 mg, 39%).

Quantum Yield Measurements.—Quantum yield determinations were carried out using a 200 W high pressure Hg arc lamp in conjunction with a Bausch and Lomb model 33-86-07 grating monochromator. Irradiations were carried out at 365 nm in benzene using acetophenone (2 g) as sensitizer. Potassium ferrioxalate actinometry[25] was used to measure light output in all the experiments. The conversion into products was determined using ^{1}H NMR (300 MHz) of the crude photolysate with anisole as the internal standard. Solutions of the compound in anhydrous benzene (31.5 cm^3) were irradiated in a cylindrical quartz cell to 4.9–24.7% conversion under an atmosphere of nitrogen. The solutions were purged with nitrogen for 30 min prior to irradiations. The results obtained are tabulated (Tables 1 and 2) below.

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