Tetrahedron Vol 49, No 32, pp 7159-7168, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00

Photochemical Synthesis of Oxime Acetates Derivatives of 1-Carbaldehydobicyclo[n.1.0]alkanes by the Aza-di-π-methane Rearrangement.

Diego Armesto* and Ana Ramos

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

(*Received in UK* 29 *April* 1993; *accepted* 11 *June* 1993)

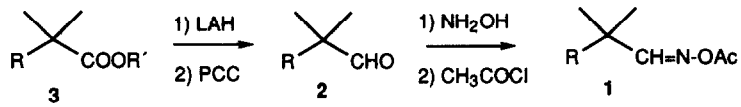
Abstract: *The first photochemical synthesis of some 1-carbaldehydobicyclo[n 1 0]alkane oxime acetates has been achieved by the aza-di-π-methane (ADPM) rearrangement of oxime acetates of 2-(cyclopent-1-enyl)- and 2-(cyclohex-1-enyl)-2-methylpropanals Further increase in ring-size affects adversely the reaction and the oxime acetate of 2-(cyclohept-1-enyl)-2-methylpropanal is unreactive by the ADPM path The low efficiency of rearrangement of 2-(cyclohex-1-enyl)-2-methylpropanal can be overcome by incorporation of a benzo substituent and this compound, 2-(2-[3,4-dihydronaphthalenyl])-2-methylpropanal, undergoes the ADPM rearrangement efficiently*

The aza-di-π-methane (ADPM) reaction has been shown[1] by us to be a more general photochemical reaction than the oxa-di-π-methane counterpart.[2] The ADPM rearrangement has considerable synthetic potential and one recent example of this is its application to the synthesis of compounds related to the pyrethrins.[3] Currently our efforts are aimed at synthetic approaches to naturally occurring bicyclic compounds such as the caranes and we report here our success in this area.

RESULTS AND DISCUSSION

The compounds required for this synthetic approach are the acetates of the aldoximes **1a-d**. These materials are obtained readily by conventional reaction of the corresponding aldehydes **2**. The route used by us to synthesise the aldehydes **2** involves conversion of the esters **3** by reduction and oxidation as shown in Scheme 1. The identity of all the compounds **1** and their precursors was established readily by conventional spectroscopic and microanalytical methods.

Previously we have shown[4] that the oxime acetate of an alkyl substituted compound **4** undergoes the ADPM rearrangement to the cyclopropane **5**, thus it was not unreasonable to expect that the cycloalkenylderivatives **1** would also be photochemically reactive and rearrange to the novel bicyclic derivatives **6** (Scheme 2).



3

2

1

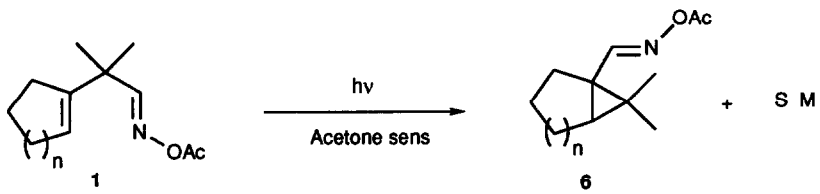
3a. R = cyclopent-1-enyl, R'= Me
3b: R = cyclohex-1-enyl; R'= Me
3c. R = cyclohept-1-enyl; R'= Me
3d· R = 2-(3,4-dihydronaphthalenyl); R'= Et

1a = 2a. R = cyclopent-1-enyl
1b = 2b: R = cyclohex-1-enyl
1c = 2c: R = cyclohept-1-enyl
1d = 2d: R = 2-(3,4-dihydronaphthalenyl)

Scheme 1

4

5



1

6

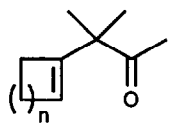
1a = 6a: n = 1	76%	20%
1b = 6b: n = 2	24%	12%
1c = 6c: n = 3		52%

Scheme 2

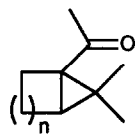
The irradiation of the oxime acetates **1** was carried out in a conventional immersion well apparatus using acetone-sensitization since our earlier experience had shown this to be an effective method for the generation of the triplet state of **4**, while lower energy sensitizers such as acetophenone led to oxetane formation.[4] Irradiation of the derivative **1a** results in smooth conversion into a single product, isolated by column chromatography, in 76% yield after 1 h irradiation. Starting material **1a** was recovered in 20% yield giving excellent mass balance for the reaction. The identity of this product was shown to be that of the bicyclo[3.1.0]hexane **6a** by the usual spectroscopic and analytical methods. Of particular value in this respect is the disappearance of the vinyl hydrogen (δ 5.5) of **1a** and the appearance of a cyclopropyl hydrogen at δ 2.5 in the product. Furthermore the ^{1}H NMR spectrum of **6a** exhibits two resonances at δ 1.2 and 1.1 for the cyclopropyl methyl groups. This structural assignment is supported by the ^{13}C NMR spectrum in which the resonance for the vinyl carbon has disappeared to be replaced by two quaternary carbons at δ 29.8 and δ 39.7. All of this is confirmation that the

structure of the product is **6a**. This product is proposed to arise by a triplet sensitized ADPM rearrangement involving the production of the alkene triplet state followed by bridging in accord with the mechanism proposed by us in earlier publications.[1]

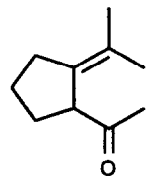
It is interesting to note that β,γ-unsaturated aldehydes do not undergo the oxa-di-π-methane rearrangement and only decarbonylate quantitatively.[5] It is noteworthy that the photochemical reactivity of the methyl ketones **7a-e** related to the aldehydes **2** has been studied.[6] This work established that the sensitized irradiation of the cyclopentyl system undergoes 1,3 acyl migration affording **9b** with a quantum yield of 0.17. In addition the oxa-di-π-methane process was also observed as a secondary reaction path with a quantum yield of 0.03, although no isolated yields were reported.



7a n = 1
7b: n = 2
7c. n = 3
7d· n = 4
7e n = 5



8a: n = 1
8b: n = 2

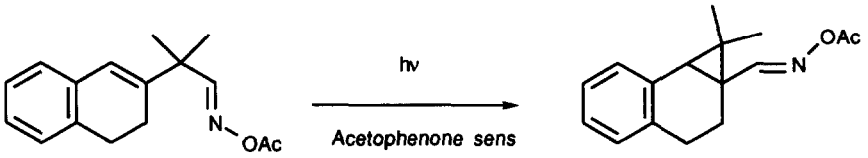


9b

This study by Engel and Schexnayder[6] also demonstrated that the C_6 and C_7 unsaturated ketones are unreactive by the oxa-di-π-methane process on triplet-sensitized irradiation. Direct excitation to the singlet state also afforded two products, coming now from hydrogen abstraction and (2+2)-cycloaddition. Our result in the irradiation of **1a** shows that the ADPM reaction is more efficient than the ODPM, and avoids secondary reactions such as 1,3 acyl migration. Because of the failure of the cyclohexenyl system **7c** to undergo the oxa-di-π-methane rearrangement it was of interest to study the behaviour of the oxime acetate derivative **1b**. Irradiation of **1b** under the same conditions as used for **1a** but for 2 h affords the bicyclo[4.1.0]heptane **6b**. Again the authenticity of this structure is proven readily. The yield of product in this example is much lower at 24% and the mass balance is poorer with only 12% of starting material recovered. This result strengthens the proposal that the ADPM rearrangement is much more general than the oxa-di-π-methane analogue. However, the poorer mass balance and yield of product from this cyclization compared to that obtained from the irradiation of **1a** would indicate that alternative reaction modes are also operational leading to the destruction of starting material. Consumption of the starting material was also observed on irradiation of the third compound of the series **1c**. No product arising from ADPM rearrangement was isolated in this case, instead a complex inseparable mixture of products was obtained. It is interesting to note that the yield of product arising by the aza-di-π-methane rearrangement of **1a-c** appears to be dependent upon the size of the cycloalkenyl component with decreasing efficiency as the ring size increases. Thus, the C_5 compound is efficient, the C_6 compound is less efficient and the C_7 compound fails to rearrange. A possible explanation of this could be that, as the ring size increases from C_5 to C_6 and C_7, the triplet state of the alkene has a greater chance of relaxation by twisting. Such behaviour is well established in, for example, the sensitized addition of alcohols to cycloalkenes.[7]

One route to test whether or not ring flexibility was responsible for deactivation of the excited state is by the

use of the dihydronaphthalene derivative **1d**. Another benefit from the use of this compound could be the enhanced stability of the ADPM bridged biradical intermediate by participation of the phenyl ring. Previously we have observed that in situations where there are groups on C-5 of the aza-1,4-diene system capable of stabilizing the intermediate biradical the efficiency of the ADPM reaction is greatly enhanced.[8] From experience we knew that compounds such as **1d** are likely to have a lower triplet energy than compounds **1a-c** and thus **1d** was irradiated using acetophenone as sensitizer. The irradiation of compound **1d** for 20 min using these conditions brought about facile conversion affording the tricyclic product **6d** in 90% yield (Scheme 3). Based on our previous studies it is likely that this enhanced efficiency is due to radical stabilization although the decrease in flexibility of the cyclohexenyl component could also be important. It is not impossible that the use of benzene stabilization of the bridged biradical could be applied to the synthesis of larger ring compounds.



1 d **6 d** (90%)

Scheme 3

The results obtained by us previously[1] and also in this study indicate that the failure of the oxa-di-π-methane rearrangement of β,γ-unsaturated aldehydes and some β,γ-unsaturated ketones can be overcome using the ADPM approach. Our examples of the aza-di-π-methane conversion of oxime acetates **1** into the bicyclic aldehyde derivatives **6** is the first photochemical synthesis of such compounds and opens a new synthetic approach to bicyclic naturally occurring compounds.

EXPERIMENTAL

Melting points were determined on a Buchi 510D apparatus in open capillaries and are uncorrected. IR spectra were recorded on a Perkin-Elmer Lambda 3B spectrophotometer and band positions are reported in wavenumbers. NMR spectra were recorded on a Varian FT-300A spectrometer for proton and carbon 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 or ethanol solution using a Perkin Elmer 550 spectrometer. The mass spectra were run at the University of Strathclyde using an AEI (Kratos) MS 9 mass spectrometer fitted with a Mass Spectrometry Services Solid State Console and a GEC 905 computer.

Methyl 2-(*cycloalk*-1-*enyl*)-2-*methylpropanoates* **3a-c** were prepared by the literature procedure.[6]

Ethyl 2-(2-[3,4-*dihydronaphthalenyl*])-2-*methylpropanoate* **3d**. This was prepared by Reformatsky reaction of β-tetralone and ethyl α-bromoisobutyrate followed by dehydration of the resulting hydroxy ester with phosphorous pentoxide. The Reformatsky reaction was carried out following the method described by Rinehart and Perkins.[9] Thus β-tetralone (5 g, 34 mmol), ethyl α-bromoisobutyrate (20.2 g, 102 mmol) and zinc (6.7 g,

102 mmol) were allowed to react in dried benzene under reflux for three hours. Conventional work-up followed by vacuum distillation gave the corresponding hydroxy ester (8.42 g, 94%) as an oil, b.p. 115 °C/0.1 mmHg; ν_{max}(film)/cm^{-1} 3500 (OH) and 1700 (C=O); δ_H 1.31 (6 H, s, 2Me), 1.32 (3 H, t, *J* 7.2, Me), 1.8 (2 H, m, CH_2), 2.7 (2 H, m, CH_2), 3.1 (2 H, m, CH_2), 3.6 (1 H, s, OH), 4.2 (2 H, q, *J* 7.2, CH_2O) and 7.0-7.2 (4 H, m, aryl); δ_C 14.1, 20.8, 20.9 (3 Me), 25.7, 28.6, 36.7 ($3CH_2$), 49.7 (quaternary C), 60.9 (CH_2O), 73.5 (quaternary C-OH), 125.5-136.1 (aryl C) and 178.2 (C=O); *m/z* 262 (M^+, 6%), 244 (12), 171 (23), 147 (16), 146 (17), 129 (32), 117 (23), 116 (100), 104 (35) and 88 (51) (Found: M^+, 262.1562. $C_{16}H_{22}O_3$ requires M, 262.1569). Dehydration was carried out by refluxing β-hydroxy ester (8.42 g, 32 mmol) and P_2O_5 (5.5 g, 39 mmol) in benzene (100 ml). The reaction mixture was refluxed for 3 hr. The mixture was cooled to room temperature and filtered through alumina. Conventional work-up gave *propanoate* **3d** (7.2 g, 92%) as an oil which was used without further purification; ν_{max}(film)/cm^{-1} 1730 (C=O) and 1640 (C=C); δ_H 1.1 (3 H, t, *J* 7.2, Me), 1.3 (6 H, s, 2Me), 2.1 (2 H, m, CH_2), 2.7 (2 H, m, CH_2), 4.1 (2 H, q, *J* 7.2, CH_2O), 6.3 (1 H, s, vinyl) and 6.8-7.2 (4 H, m, aryl); δ_C 14.0 (Me), 23.9 (2Me), 25.0, 28.3 ($2CH_2$), 47.5 (quaternary C), 60.5 (CH_2O), 121.0 (vinyl), 126.0-134.7 (aryl), 143.6 (vinyl) and 179.3 (C=O); *m/z* 244 (M^+, 68%), 242 (28), 172 (60), 171 (100), 170 (58), 169 (73), 155 (43), 143 (32), 141 (48), 129 (69), 128 (57), and 127 (21) (Found: M^+, 244.1464. $C_{16}H_{20}O_2$ requires M, 244.1463).

General Method for the Synthesis of Alcohols from Propanoates **3a-d**.

A solution of the ester in dry diethyl ether (70 ml) was added slowly at 0 °C to a suspension of an equimolar amount of LAH in diethyl ether (50 ml). The resulting mixture was kept at room temperature until starting material had reacted completely. The residual LAH was decomposed by addition of acetone followed by aqueous NH_4Cl, and the ethereal layer was washed with brine. The extract was dried ($MgSO_4$), filtered and evaporated to dryness. The crude alcohol was obtained as an oil which was used without further purification.

2-(*Cyclopent*-1-*enyl*)-2-*methylpropanol*. From **3a** (3.2 g, 19.2 mmol) and LAH (731 mg, 19.2 mmol). This gave 2-(*cyclopent*-1-*enyl*)-2-*methylpropanol* (2.7 g, 99%); ν_{max}(film)/cm^{-1} 3400 (OH); δ_H 1.1 (6 H, s, 2Me), 1.4 (1 H, br s, OH), 1.9 (2 H, m, CH_2), 2.3 (4 H, m, $2CH_2$), 3.4 (2 H, s, CH_2O) and 5.5 (1 H, m, vinyl); δ_C 23.3 (CH_2), 23.7 (2Me), 31.3 (CH_2), 32.3 (CH_2), 38.3 (quaternary C), 69.9 (CH_2O), 124.9 and 149.1 (vinyl); *m/z* 140 (M^+, 50%), 125 (13), 110 (31), 109 (100), 108 (29), 93 (27), 81 (40) and 67 (70) (Found: M^+, 140.1195. $C_9H_{16}O$ requires M, 140.1201).

2-(*Cyclohex*-1-*enyl*)-2-*methylpropanol*.[10] From **3b** (7.3 g, 40 mmol) and LAH (1.5 g, 40 mmol). This gave 2-(*cyclohex*-1-*enyl*)-2-*methylpropanol* (6.25 g, 100%); ν_{max}(film)/cm^{-1} 3400 (OH); δ_H 0.9 (6 H, s, 2Me), 1.4-2.2 (9 H, m, $4CH_2$ and OH), 3.2 (2 H, s, CH_2O) and 5.4 (1 H, m, vinyl).

2-(*Cyclohept*-1-*enyl*)-2-*methylpropanol*. From **3c** (4.2 g, 21.3 mmol) and LAH (0.81 g, 21.3 mmol). This gave 2-(*cyclohept*-1-*enyl*)-2-*methylpropanol* (3.4 g, 96%); ν_{max}(film)/cm^{-1} 3360 (OH); δ_H 1.0 (6 H, s, 2Me), 1.3 (1 H, t, *J* 6.0, OH), 1.4 (4 H, m, $2CH_2$), 1.8 (2 H, m, CH_2), 2.1 (4 H, m, $2CH_2$), 3.4 (2 H, d, CH_2O) and 5.8 (1 H, t, *J* 6.8, vinyl); δ_C 23.3 (2Me), 26.9, 27.0, 28.0, 28.2, 32.9 ($5CH_2$), 41.8 (quaternary C), 60.1 (CH_2O), 127.6 and 148.1 (vinyl); *m/z* 168 (M^+, 27%), 153 (27), 137 (87), 111 (64), 95 (86), 93 (45), 81 (100), 79 (61) and 77 (33) (Found: M^+, 168.1515. $C_{11}H_{20}O$ requires M, 168.1514).

2-(2-[3,4-*dihydronaphthalenyl*])-2-*methylpropanol*. From **3d** (4 g, 16.4 mmol) and LAH (0.62 g, 16.4 mmol). This gave 2-(2-[3,4-*dihydronaphthalenyl*])-2-*methylpropanol* (3.1 g, 94%); ν_{max}(film)/cm^{-1} 3400 (OH) and 1640 (C=C); δ_H 1.2 (6 H, s, 2Me), 2.3 (2 H, m, CH_2), 2.8 (2 H, m, CH_2), 3.5 (1 H, s, OH), 6.4 (1 H, s, vinyl) and 7.0-7.2 (4 H, m, aryl); δ_C 23.1 (2Me), 23.3, 28.3 ($2CH_2$), 41.0 (quaternary C), 69.6 (CH_2O), 122.8 (vinyl), 125.8-134.5 (aryl) and 145.2 (vinyl); *m/z* 202 (M^+, 21%), 171 (100), 143 (13), 141 (16), 129 (33), 128 (22) and 115 (18) (Found: M^+, 202.1352. $C_{14}H_{18}O$ requires M, 202.1358).

General Method for the Synthesis of Aldehydes **2a-d**.

The above alcohols and PCC were allowed to react in methylene dichloride at room temperature for 24 h. The crude reaction mixture was filtered through silica gel and the solvent evaporated to give the corresponding aldehyde as an oil which was used in the next step without further purification.

2-(*Cyclopent*-1-*enyl*)-2-*methylpropanal* **2a**. From 2-(*cyclopent*-1-*enyl*)-2- *methylpropanol* (0.9 g, 6.4 mmol) and PCC (2.1 g, 9.6 mmol). This gave **2a** (0.77 g, 87%); ν_{max}(film)/cm^{-1} 2800, 2700 and 1710; δ_H 1.2 (6 H, s, 2Me), 1.3-2.3 (6 H, m, $3CH_2$), 5.6 (1 H, m vinyl), 9.3 (1 H, s, CHO); δ_C 20.5 (2Me), 23.0, 31.7, 32.3 ($3CH_2$), 48.4 (quaternary C), 127.0 (vinyl), 144.0 (vinyl) and 202.4 (C=O).

2-(*Cyclohex*-1-*enyl*)-2-*methylpropanal* **2b**.[10] From 2-(*cyclohex*-1-*enyl*)-2-*methylpropanol* (4g, 26.2 mmol) and PCC (8.5 g, 39 mmol). This gave **2b** (3.3 g, 85%); ν_{max}(film)/cm^{-1} 2800, 2690 and 1720; δ_H 1.1 (6 H, s, 2Me), 1.2-2.1 (8 H, m, $4CH_2$), 5.6 (1 H, m, vinyl) and 9.2 (1 H, s, CHO); δ_C 20.2 (2Me), 22.0, 22.9, 25.1, 25.6 ($4CH_2$), 51.5 (quaternary C), 124.6 (vinyl), 136.8 (vinyl) and 203.3 (C=O).

2-(*Cyclohept*-1-*enyl*)-2-*methylpropanal* **2c**. From 2-(*cyclohept*-1-*enyl*)-2-*methylpropanol* (2.2 g, 13 mmol) and PCC (4.2 g, 19 mmol). This gave **2c** (1.75 g, 82%); ν_{max}(film)/cm^{-1} 2800, 2690 and 1720; δ_H 1.1 (6 H, s, 2Me), 1.2-2.2 (10 H, m, $5CH_2$), 5.8 (1 H, t, *J* 6.8, vinyl) and 9.3 (1 H, s, CHO); δ_C 20.1 (2Me), 26.4, 26.8, 28.2, 29.4, 32.6 ($5CH_2$), 58.3 (quaternary C), 128.8 (vinyl), 136.8 (vinyl) and 203.8 (C=O).

2-(2-[3,4-*dihydronaphthalenyl*])-2-*methylpropanal* **2d**. From 2-(2-[3,4-*dihydronaphthalenyl*])-2-*methylpropanol* (2.3 g, 11.4 mmol) and PCC (4.9 g, 22.5 mmol). This gave **2d** (1.6 g, 69%); ν_{max}(film)/cm^{-1} 2790, 2700, 1730 and 1640; δ_H 1.3 (6 H, s, 2Me), 2.2 (2 H, m, CH_2), 2.8 (2 H, m, CH_2), 6.4 (1 H, s, vinyl), 7.0-7.2 (4 H, m, aryl) and 10.8 (1 H, s, CHO); δ_C 20.0 (2Me), 24.1, 28.1 ($2CH_2$), 51.7 (quaternary C), 124.5 (vinyl), 126.2-140.2 (aryl), 145.0 (vinyl) and 202.3 (C=O).

General Method for the Synthesis of Oximes from Aldehydes **2a-d**.

The oximes were prepared by refluxing the corresponding aldehyde with hydroxylamine hydrochloride and pyridine in ethanol (100 cc) for 2-3 h. The aldehyde/hydroxylamine/pyridine ratio was 1:1.2:1.2 for all the experiments. After conventional work-up, the oximes were isolated and purified by chromatography on silica gel with hexane-diethyl ether (9:1).

2-(*Cyclopent*-1-*enyl*)-2-*methylpropanal oxime*. From **2a** (1.7 g, 12.5 mmol). This gave 2-(*cyclopent*-1-*enyl*)-2-*methylpropanal oxime* (1.3 g, 69%) as an oil; ν_{max}(film)/cm^{-1} 3350, 1640 and 1610; δ_H 1.2 (6 H, s, 2Me), 1.2-2.2 (6 H, m, $3CH_2$), 5.4 (1 H, m, vinyl), 7.3 (1 H, s, CH=N) and 8.3 (1 H, br s, OH); δ_C 23.3 (2Me), 24.5, 31.6, 32.0 ($3CH_2$), 38.7 (quaternary C), 124.2 (vinyl), 148.3 (vinyl) and 157.3 (C=N); *m/z* 153 (M^+, 36%), 138 (100), 136 (51), 120 (25), 109 (19), 91 (37) and 67 (66) (Found: M^+, 153.1142. $C_9H_{15}NO$ requires M, 153.1154).

2-(*Cyclohex*-1-*enyl*)-2-*methylpropanal oxime*. From **2b** (5 g, 33 mmol). This gave 2-(*cyclohex*-1-*enyl*)-2-*methylpropanal oxime* (3.6 g, 65%) as an oil; ν_{max}(film)/cm^{-1} 3300 and 1640; δ_H 1.2 (6 H, s, 2Me), 1.2-2.1 (8 H, m, $4CH_2$), 5.5 (1 H, m, vinyl), 7.3 (1 H, s, CH=N) and 9.0 (1 H, br s, OH); δ_C 22.1, 23.0 ($2CH_2$), 24.0 (2Me), 24.7, 25.3 ($2CH_2$), 41.7 (quaternary C), 121.4 (vinyl), 140.6 (vinyl) and 157.8 (C=N); *m/z* 167 (M^+, 6%), 152 (94), 107 (27), 91 (21), 81 (100) and 79 (47) (Found: M^+, 167.1302. $C_{10}H_{17}NO$ requires M, 167.1310).

2-(*Cyclohept*-1-*enyl*)-2-*methylpropanal oxime*. From **2c** (2.5 g, 15 mmol). This gave 2-(*cyclohept*-1-*enyl*)-2-*methylpropanal oxime* (2.31 g, 85%) as an oil; ν_{max}(film)/cm^{-1} 3300 and 1640; δ_H 1.2 (6 H, s, 2Me), 1.4-2.2 (10 H, m, $5CH_2$), 5.7 (1 H, t, *J* 6.8, vinyl), 7.3 (1 H, s, CH=N) and 9.0 (1 H, br s, OH); δ_C 24.0 (2Me), 26.7, 27.0, 28.1, 29.3, 32.8 ($5CH_2$), 42.9 (quaternary C), 126.0 (vinyl), 147.8 (vinyl) and 157.5 (C=N); *m/z* 181 (M^+, 11%), 167 (18), 166 (100), 95 (26) and 67 (20) (Found: M^+, 181.1460. $C_{11}H_{19}NO$ requires M, 181.1466).

2-(2-[3,4-*dihydronaphthalenyl*])-2-*methylpropanal oxime*. From **3d** (1.42 g, 7 mmol). This gave 2-(2-[3,4-*dihydronaphthalenyl*])-2-*methylpropanal oxime* as a colourless crystalline solid (1.36 g, 89%) from hexane, m.p. 100-101°C; ν_{max}(KBr)/cm^{-1} 3250; δ_H 1.3 (6 H, s, 2Me), 2.3 (2 H, m, CH_2), 2.8 (2 H, m, CH_2), 6.3 (1 H, s, vinyl), 7.0-7.2 (4 H, m, aryl), 7.4 (1 H, s, CH=N) and 8.5 (1 H, br s, OH); δ_C 23.9 (2Me), 24.1, 28.3 ($2CH_2$), 41.9 (quaternary C), 122.0 (vinyl), 126.1-134.6 (aryl), 144.4 (vinyl) and 157.0 (C=N); *m/z* 215 (M^+, 39%), 198 (100), 181 (84), 155 (30), 141 (42), 129 (74) and 115 (37) (Found: C, 78.0; H, 7.8; N, 6.3. $C_{14}H_{17}NO$ requires C, 78.10; H, 7.96; N, 6.51%).

General Method for the Synthesis of Oxime Acetates **1a-d**.

Acetyl chloride was added to a solution of the oxime in pyridine (2-5 ml) at 0°C. The oxime/acetyl chloride ratio was 1:1.2 for all the experiments. The mixture was stirred for 2 h at room temperature and then diethyl ether was added. The pyridine was removed by washing successively with dilute HCl (10% aqueous), saturated solution of $NaHCO_3$ and brine. The solution was dried ($MgSO_4$), filtered, and evaporated to dryness. The product was purified by column chromatography on silica gel with hexane-diethyl ether (9:1).

1-*Acetoxy*-1-*aza*-3-(*cyclopent*-1-*enyl*)-3-*methylbut*-1-*ene* **1a**. From 2-(*cyclopent*-1-*enyl*)-2-*methylpropanal oxime* (1.3 g, 8.6 mmol). This gave **1a** (0.95 g, 57%) as an oil; ν_{max}(film)/cm^{-1} 1760 and 1620; δ_H 1.3 (6 H, s, 2Me), 1.8 (2 H, m, CH_2), 2.1 (3 H, s, MeCO), 2.3 (4 H, m, $2CH_2$), 5.5 (1 H, m, vinyl) and 7.6 (1 H, s,

CH=N); δ_C 19.5 (MeCO), 23.2 (CH_2), 24.0 (2Me), 31.5, 32.3 ($2CH_2$), 39.4 (quaternary C), 125.1 (vinyl), 147.2 (vinyl), 163.9 (C=N) and 168.8 (C=O); *m/z* 195 (M^+, 2%), 108 (73), 93 (100), 79 (24) (Found: M^+, 195.1224. $C_{11}H_{17}NO_2$ requires M, 195.1259); $\lambda_{max}(CH_2Cl_2)$/nm 229 (ε 2108 $dm^3\ l^{-1}\ cm^{-1}$).

1-*Acetoxy*-1-*aza*-3-(*cyclohex*-1-*enyl*)-3-*methylbut*-1-*ene* **1b**. From 2-(*cyclohex*-1-*enyl*)-2-*methylpropanal oxime* (0.55 g, 3.3 mmol). This gave **1b** (0.4 g, 58%) as an oil; ν_{max}(film)/cm^{-1} 1770 and 1620; δ_H 1.3 (6 H, s, 2Me), 1.4-2.1 (8 H, m, $4CH_2$), 2.2 (3 H, s, MeCO), 5.6 (1 H, m, vinyl) and 7.5 (1 H, s, CH=N); δ_C 19.6 (MeCO), 22.2 ($2CH_2$), 23.7 (2Me), 24.8, 25.5 ($2CH_2$), 42.6 (quaternary C), 122.5 (vinyl), 139.9 (vinyl), 164.7 (C=N) and 169.0 (C=O); *m/z* 209 (M^+, 1%), 153 (17), 152 (100), 149 (12), 134 (26), 123 (22), 107 (36), 81 (84) and 79 (44) (Found: M^+, 209.1411. $C_{12}H_{19}NO_2$ requires M, 209.1416); $\lambda_{max}(CH_2Cl_2)$/nm 226 (ε 3156 $dm^3\ l^{-1}\ cm^{-1}$).

1-*Acetoxy*-1-*aza*-3-(*cyclohept*-1-*enyl*)-3-*methylbut*-1-*ene* **1c**. From 2-(*cyclohept* 1-*enyl*)-2-*methylpropanal oxime* (0.66 g, 3.8 mmol). This gave **1c** (0.53 g, 64%) as an oil; ν_{max}(film)/cm^{-1} 1770 and 1620; δ_H 1.3 (6 H, s, 2Me), 1.4 (4 H, m, $2CH_2$), 1.7 (2 H, m, CH_2), 2.1 (4 H, m, $2CH_2$), 2.2 (3 H, s, MeCO), 5.7 (1 H, t, *J* 6.8, vinyl) and 7.5 (1 H, s, CH=N); δ_C 20.0 (MeCO), 23.5 (2Me), 26.5, 26.9, 28.1, 29.1, 32.7 ($5CH_2$), 44.0 (quaternary C), 126.8 (vinyl), 146.8 (vinyl), 164.3 (C=N) and 168.8 (C=O); *m/z* 223 (M^+, 9%), 208 (51), 166 (100), 148 (33) and 95 (39) (Found: M^+, 223.1578. $C_{13}H_{21}NO_2$ requires M, 223.1572); $\lambda_{max}(CH_2Cl_2)$/nm 227 (ε 4377 $dm^3\ l^{-1}\ cm^{-1}$).

1-*Acetoxy*-1-*aza*-3-(2-[3,4-*dihydronaphthalenyl*])-3-*methylbut*-1-*ene* **1d**. From 2-(2-[3,4-*dihydronaphthalenyl*])-2-*methylpropanal oxime* (0.6 g, 2.8 mmol). This gave **1d** (0.45 g, 63%) as an oil; ν_{max}(film)/cm^{-1} 1770 and 1620; δ_H 1.4 (6 H, s, 2Me), 2.2 (3 H, s, MeCO), 2.3 (2 H, m, CH_2), 2.8 (2 H, m, CH_2), 6.4 (1 H, s, vinyl), 7.0-7.2 (4 H, m, aryl) and 7.6 (1 H, s, CH=N); δ_C 19.5 (MeCO), 23.5 (2Me), 24.0, 28.2 ($2CH_2$), 42.5 (quaternary C), 122.7 (vinyl), 126.2-134.6 (aryl), 143.1 (vinyl), 163.5 (C=N) and 168.7 (C=O); *m/z* 255 (M^+-2, 0.7), 197 (70), 182 (100), 180 (27), 171 (11), 170 (31), 155 (81) and 129 (59) (Found: (M^+-2), 255.1261. $C_{16}H_{17}NO_2$ requires 255.1259) ; λ_{max}(EtOH)/nm 268 (ε 13866 $dm^3\ l^{-1}\ cm^{-1}$).

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 in anhydrous benzene (400 ml) using acetophenone as sensitizer were purged with argon for 1 h and irradiated under a positive pressure of argon for the times shown. After completion of the irradiation the solvent and sensitizer were removed under reduced pressure and the products were separated by column chromatography on silica gel.

Irradiation of Oxime Acetate **1a**.– This compound (406 mg, 2.1 mmol) was irradiated in acetone (400 ml) for 1 h. After removal of the solvent, chromatography using hexane-diethyl ether (9:1) gave the following; (i) recovered starting material **1a** (79 mg, 20%); (ii) the 1-*carbaldehydo*-6,6-*dimethylbicyclo*[3.1.0]*hexane oxime acetate* **6a** as an oil (315 mg, 76%); ν_{max}(film)/cm^{-1} 1770 and 1610; δ_H 1.1 (3 H, s, Me), 1.2 (3 H, s, Me), 1.5-2.0 (6 H, m, $3CH_2$), 2.1 (3 H, s, MeCO), 2.5 (1 H, m, cyclopropyl H) and 7.7 (1 H, s, CH=N); δ_C 16.8 (Me), 19.4 (MeCO), 24.1 (Me), 25.0, 25.7, 27.0 ($3CH_2$), 29.8 (quaternary C), 39.7 (quaternary C), 41.4

(CH), 163.1 (C=N) and 168.6 (C=O); *m/z* 195 (M^+, 2%), 153 (95), 120 (63), 108 (41), 93 (100) and 79 (35) (Found: M^+, 195.1249. $C_{11}H_{17}NO_2$ requires M, 195.1259).

Irradiation of Oxime Acetate **1b**.- This compound (377 mg, 1.8 mmol) was irradiated in acetone (400 ml) for 2 h. After removal of the solvent, chromatography using hexane-diethyl ether (9:1) gave the following: (i) recovered starting material **1b** (43 mg, 12%); (ii) the 1-*carbaldehydo*-7,7-*dimethylbicyclo*[4.1.0]*heptane oxime acetate* **6b** as an oil (90 mg, 24%); δ_H 1.1 (3 H, s, Me), 1.2 (3 H, s, Me), 1.2-1.6 (8 H, m, $4CH_2$), 2.1 (3 H, s, MeCO), 2.5 (1 H, m, cyclopropyl H) and 7.5 (1 H, s, CH=N); δ_C 17.6 (Me), 18.7 (MeCO), 20.1 (Me), 21.1, 21.5, 24.6 ($3CH_2$), 25.7 (quaternary C), 27.4 (quaternary C), 29.0 (CH), 165.7 (C=N) and 168.8 (C=O); *m/z* 194 (M^+-15, 4%), 167 (28), 152 (33), 150 (25), 149 (43), 134 (42), 108 (54), 107 (100), 79 (58) (Found: (M^+-15), 194.1167. $C_{11}H_{16}NO_2$ requires M, 194.1181). Shorter irradiation time (30 min) resulted in the formation of **6b** (12%) and 50% recovered starting material.

Irradiation of Oxime Acetate **1c**.- This compound (507 mg, 2.3 mmol) was irradiated in acetone (400 ml) for 1h. After removal of the solvent, chromatography using hexane-diethyl ether (9:1) gave 267 mg (52%) of starting material and a complex mixture of unidentified products.

Irradiation of Oxime Acetate **1d**.– This compound (305 mg, 1.2 mmol) was irradiated in benzene (400 ml) with acetophenone (5 ml) for 20 min. After removal of the solvent and the sensitizer, chromatography using hexane-diethyl ether (9:1) gave 4,5-*benzo*-1-*carbaldehydo*-7,7-*dimethylbicyclo*-[4.1.0]-*hept*-4-*ene oxime acetate* **6d** (275 mg, 90%) as an oil; ν_{max}(film)/cm^{-1} 1770 and 1610; δ_H 0.9 (3 H, s, Me), 1.4 (3 H, s, Me), 2.2 (3 H, s, MeCO), 2.5 (2 H, m, CH_2), 2.73 (2 H, m, CH_2), 2.74 (1 H, s, cyclopropyl H), 7.0-7.2 (4 H, m, aryl) and 7.7 (1 H, s, CH=N); δ_C 18.4 (Me), 19.5 (MeCO), 22.0 (Me), 23.6, 28.3 ($2CH_2$), 29.8 (quaternary C), 32.3 (quaternary C), 33.3 (CH), 126.0-138.0 (aryl), 163.3 (C=N) and 168.7 (C=O); *m/z* 257 (M^+, 5%), 215 (13), 198 (100), 197 (49), 182 (54), 155 (37), 129 (39) and 115 (24) (Found: M^+, 257.1407. $C_{16}H_{19}NO_2$ requires M, 257.1416).

ACKNOWLEDGEMENTS

We are grateful to Dr. William M. Horspool, University of Dundee, Scotland for fruitful discussions. We also thank the Dirección General de Investigación Científica y Técnica (Grant No. PB 91/0396) and NATO (Grant 870734/92) for financial assistance.

REFERENCES

1. (a) Armesto, D.; Martin, J. A. F.; Perez-Ossorio, R.; Horspool, W. M. *Tetrahedron Lett.* **1982**, *23*, 2149. (b) Armesto, D.; Horspool, W. M.; Fernandez-Martin, J. A.; Perez-Ossorio, R. *J. Chem. Res.* **1986**, (*S*), 46; (*M*), 631. (c) Armesto, D.; Horspool, W. M.; Langa, F.; Perez-Ossorio, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1039. (d) Armesto, D.; Horspool, W. M.; Langa, F. *J. Chem. Soc., Perkin Trans. 2* **1989**, 903. (e) Armesto, D.; Langa, F.; Fernandez-Martin, J. A.; Perez-Ossorio, R.; Horspool, W. M. *J. Chem. Soc., Perkin Trans. 1* **1987**, 743. (f) Armesto, D.; Horspool, W. M.; Langa, F. *J. Chem. Soc., Chem. Commun.* **1987**, 1874. (g) Armesto, D.; Horspool, W. M.; Langa, F.; Ramos, A. *J. Chem. Soc., Perkin Trans. 1* **1991**, 223. (h) Armesto, D.; Horspool, W. M.; Mancheño, M. J.; Ortiz, M. J. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2348. (i) Armesto, D.; Horspool, W. M.; Mancheño, M. J.; Ortiz, M. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2325.
2. Demuth, M. *Org. Photochem.*; Padwa, A. Eds.; Marcel Dekker, **1991**, *11*, 37.
3. (a) Armesto, D.; Horspool, W. M.; Gallego, M. G. *Tetrahedron* **1990**, *46*, 6185. (b) Armesto, D.; Horspool, W. M.; Gallego, M. G. *Tetrahedron Lett.* **1990**, *31*, 2475. (c) Armesto, D.; Horspool, W. M.; Gallego, M. G.; Bermejo, F. Patent **PCT APPLICATION ES92/00017 (Publication No. 92/16499)**. Priority Spain 13/3/91.
4. Armesto, D.; Horspool, W. M.; Langa, F.; Ramos, A. *J. Chem. Soc., Perkin Trans. 1* **1991**, 223.
5. Houk, K. N. *Chem. Rev.* **1976**, *76*, 1.
6. Engel, P. S.; Schexnayder, M. A. *J. Am. Chem. Soc.* **1975**, *97*, 145.
7. Kropp, P. J. *Org. Photochem.*; Padwa, A. Eds.; Marcel Dekker, **1979**, *4*, 1.
8. Armesto, D.; Horspool, W. M.; Gallego, M. G.; Agarrabeitia, A. R. *J. Chem. Soc., Perkin Trans. 1* **1992**, 163.
9. Rinehart, K. L.; Perkins, E. G. *Organic Synthesis* **1957**, *37*, 37.
10. Eilbracht, P.; Acker, M.; Hüttmann, G.; Winkels, I. *Chem. Ber* **1989**, *122*, 159.