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PHOTOCHEMISTRY OF β,γ-UNSATURATED OXIME ACETATES. AZA-DI-π-METHANE REACTIVITY OF FUNCTIONALISED ALL-ALIPHATIC SYSTEMS. A PHOTOCHEMICAL APPROACH TO PYRETHRIN-LIKE CYCLOPROPANE DERIVATIVES.

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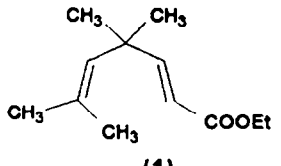
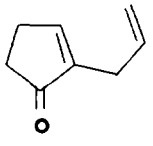
Summary: The acetone-sensitized irradiation of two series of oxime acetates has been studied. The first group, oxime acetates of 4-ethoxycarbonyl-, 4-cyano-, 4-methoxymethyl-, and 4-acetoxymethyl-2,2-dimethylbut-3-enal, undergoes *E-Z*-isomerization of the C=C bond. The second group of compounds, oxime acetates of 4-ethoxycarbonyl-, 4-cyano-, and 4-acetoxymethyl-2,2-dimethylpent-3-enal, rearranges by the aza-di-π-methane reaction to afford cyclopropane derivatives.

The cyclopropane moiety is one of the key structural features in the pyrethrin insecticides.[1] These insecticides are important in agriculture because of low mammalian toxicity and biodegradability making them ecologically valuable pesticides.[2] There are many methods for the synthesis of cyclopropane derivatives.[3] However, our interest has been focussed on the photochemical paths and among these the di-π-methane rearrangement of 1,4-dienes is a reasonable route for cyclopropane synthesis.[4] This reaction has been studied in great detail and is very general. However, the di-π-methane process is not applicable to molecules where the double bonds in the compound do not absorb above 220 nm. This situation would not permit direct irradiation and population of the excited singlet state, the condition under which most di-π-methane reactions take place in an acyclic 1,4-diene.[4] There are ways around this problem. One method available is the conjugation of one of the double bonds with a chromophore which will move the absorption into the accessible spectral region. This method has been used to effect in the ester (1)[5,6] and the enone (2)[7] which photochemically rearrange to (3) and (4) respectively.



(1)



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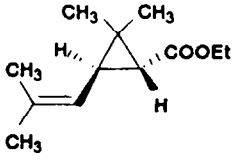

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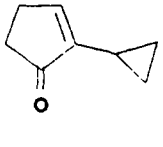
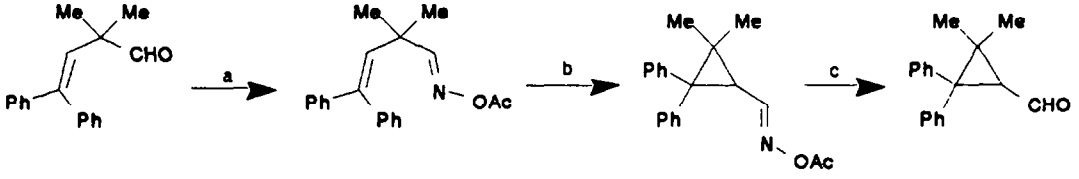


(4)

Another method available is the replacement of a double bond by a carbonyl group and molecules of this type can rearrange by the oxa-di-π-methane pathway.[8] While this can be a useful approach there are many exceptions to the generality of the reaction such as the failure of all but one aldehyde[9] to rearrange and often decarbonylation is the major photochemical reaction path.[8] On the other hand acyclic β,γ-unsaturated enones are rather unpredictable in their photochemical reactivity. Many such compounds undergo 1,3-acyl migrations on direct irradiation but many of them fail to undergo triplet state oxa-di-π-methane rearrangement.[8]

In the last few years we have described the aza-di-π-methane cyclization of imines[10] and oxime acetates[11] as a route to variously substituted cyclopropanes. The reaction is more general than the oxa-di-π-methane process and has the added advantage of overcoming the failure of most β,γ-unsaturated aldehydes to undergo this rearrangement.[8] Therefore the principal advantage of the aza-di-π-methane reaction is that it permits the photochemical transformation of these compounds *via* stable C=N derivatives into cyclopropyl compounds in an efficient manner using a cyclization which is regiospecific, as outlined in Scheme I.[11] As a result of our success we have sought to use the aza-di-π-methane rearrangement as a synthetic path to cyclopropanes related to pyrethroids.[1] To this end we have described already the application of our method to the synthesis of the oxime acetate of 2,2,3,3-tetramethylcyclopropanecarboxaldehyde.[12] This can be converted into the corresponding carboxylic acid which is the cyclopropane moiety in the pyrethroid *terallethrin*.[1]



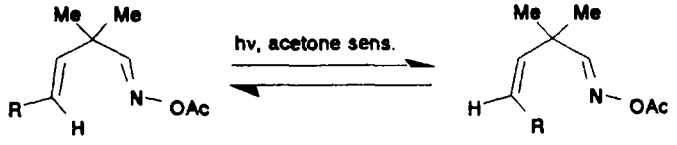
Reagent: (a) (1) $NH_2OH.HCl$; (2) MeCOCl, pyridine; (b) hν, $PhCOCH_3$ sens.; (c) H_2O-EtOH-HCl

Scheme I

So far our studies on the aza-di-π-methane rearrangement have always involved the use of 5,5-disubstitution on the 1-aza-1,4-diene.[10,11] Furthermore the cyclopropane derivatives obtained have only one functional group. However, many of the pyrethroids described in the literature have a greater variety of substituents on the cyclopropane ring and usually two functional groups are present.[1] The aim of this work was to study the reactivity of 1-aza-1,4-dienes with varying substitution at C-5 and to develop a photochemical path to cyclopropanes where two functional groups were included. The syntheses of the oxime acetates (**5**) and (**6**) on which this study is based have been reported elsewhere.[13]

The irradiation of the (*E*)-oxime acetate (**5a**) for 1 h, using acetone as sensitizer, yields exclusively a 2:1 mixture of the (*E*)- and (*Z*)-isomers (Scheme II) respectively as determined by ^1H n.m.r. spectroscopy of the photolysate. Longer irradiation of (**5a**) up to 7 h gives the same result indicating that this was the photostationary state composition. Direct irradiation of the oxime acetate

(**5a**) at 254 nm also brought about *E-Z*-isomerization affording a separable mixture of the isomers in a ratio of 1.25:1. A similar result was obtained from the acetone-sensitized irradiation of the (*E*)-oxime acetate (**5b**) where a 2.5:1 mixture of the (*E*)- and (*Z*)-isomers was formed. These isomers proved almost impossible to separate on column chromatography. However, a sample was obtained which was almost pure (*Z*)-isomer (**5b***Z*) and from this the identity of the compound was established conclusively.



(5*E*) (5*Z*)

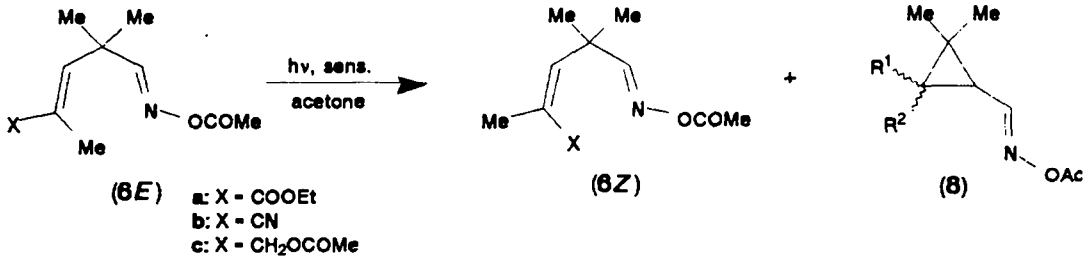
a: COOEt
b: CN
c: CH_2OCOMe
d: CH_2OMe

Scheme II

The failure of these two oxime acetates (**5a**) and (**5b**) to undergo cyclization was considered to be due either to a deactivation of the excited triplet state by a free rotor effect,[4] as has been observed frequently in the di-π-methane rearrangement, or to an alternative deactivation path *via* single electron transfer (S.E.T.) from the nitrogen lone pair to the alkene moiety. The latter would bring about the formation of an intermediate such as (**7**) that would allow the isomerization to take place before going back to the starting material. Previously we have postulated that such a process is responsible for the lack of the di-π-methane reactivity in β,γ-unsaturated oximes.[11] However, this electron transfer can be minimized or even suppressed by increasing the ionization potential of the nitrogen by forming the corresponding oxime acetate.[11] In the present cases the presence of an electron withdrawing group conjugated with the alkene molety could make the electron transfer process possible again. To establish the feasibility of this hypothesis the oxime acetates (**5c**) and (**5d**) where the electron withdrawing groups have been replaced by an acetoxymethyl or by a methoxymethyl group were studied. This should decrease the electron affinity of the C=C and therefore make the S.E.T. process more difficult. However, irradiation of (**5c***E*) and (**5d***E*) again brings about *E-Z*-isomerization exclusively. The ratio of isomers obtained in these cases were 3.5:1 for (**5c**) and 3.7:1 for (**5d**). These results clearly demonstrate that S.E.T. is not responsible for the absence of di-π-methane reactivity in these oxime acetates.

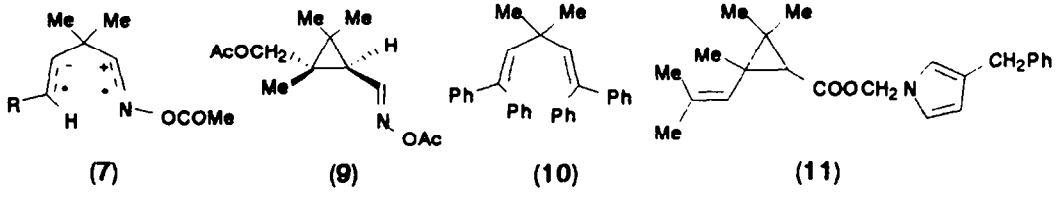
In order to determine if the free rotor effect was responsible for the suppression of the cyclization the photochemical reactivity of the series of oxime acetates (**6**) was studied. Irradiation of the (*E*)-oxime acetate (**6a**) by acetone-sensitization for 1.5 h also brings about *E-Z*-isomerization in a ratio 2.5:1 established by ^1H n.m.r. spectroscopy. In addition new products were detected. The mixture was separated by column chromatography and gave the *E-Z*-isomers (72% total yield) and the new products as an inseparable mixture (28%). Spectroscopic analysis and mass spectroscopy showed that this was a 1:1 mixture of compounds which were isomeric with

starting material. The ^1H n.m.r. of the mixture showed that the new compounds were the isomeric cyclopropanes (**8a**) (Scheme III). The principal features of this spectrum are the vinyl H as doublets at δ 8.0 and δ 7.5 and the solitary ring proton at δ 2.6 and δ 1.8 again as doublets with a coupling constant of 9Hz. The structures are confirmed by the ^{13}C n.m.r. spectrum. The (*E*)-oxime acetate (**6b**) behaves in a similar manner. Acetone-sensitized irradiation yields a photolysate composed of a 1.3:1 mixture of *E*-*Z*-isomers and a 54% yield of a mixture of cyclopropanes (**8b**) in a ratio of 4.4:1. Under similar conditions the (*E*)-oxime acetate (**6c**) affords *E*-*Z*-isomers (ratio of 2:1) and the cyclopropanes (**8c**, ratio of 1.3:1). In this instance an NOE experiment showed that the principal isomer had the *trans*-arrangement as shown in (**9**). Irradiation of the *Z*-isomer (**6c***Z*) was also carried out and afforded the same result that was obtained from the corresponding (*E*)-isomer.



Scheme III

The success of the acetone-sensitized irradiative cyclization of the C-5 disubstituted oxime acetates (**6**) lends support to the free rotor deactivation path in the mono-substituted series (**5**). However, it is surprising that the introduction of a methyl group should have such a profound effect. In many of the di-π-methane rearrangements the free rotor effect is still present even with diphenyl substitution on the terminal carbon as in (**10**).[4]



Even although the studies with mono-substitution at C-5 in the 1-aza-1,4-diene system (**5**) were unsuccessful the cyclization of the C-5 disubstituted derivatives (**6**) has opened a new photochemical route to cyclopropanes with two functional groups. The cyclopropanes synthesized by this route could be readily converted into derivatives which have already been demonstrated to have insecticidal activity such as (**11**).[1] The research described above also provides further information on the scope and reactivity of 1-aza-1,4-dienes in the aza-di-π-methane rearrangement.

Experimental

Melting points were determined on a Buchi 510D apparatus in open capillaries and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 256 spectrophotometer and band positions are reported in wavenumbers. NMR spectra were recorded on a Varian T-60A and a Bruker WM-250 spectrometer for protons and on a Bruker WP 60FT for carbon with chemical shifts (δ) expressed in ppm downfield from internal Me_4Si. UV spectra were recorded in methylene chloride solutions using a Perkin-Elmer 550 spectrometer. The mass spectra were run by Dr. P. Bladon 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. All the photolyses were carried out in an immersion-well apparatus with a Pyrex filter and a 400 watt medium pressure Hg arc lamp. Solutions of the oxime acetates in anhydrous acetone (350 ml) 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. Thin layer chromatography was carried out on Merck DC-Plastikfolien Kieselgel 60 F_{254}.

Irradiation of oxime acetate (**5a**). Compound (**5a**) (300 mg, 1.32 mmol) was irradiated for periods from 1 h to 7 h. The ^1H n.m.r. of the crude photolysate showed in all cases a mixture of the (*Z*)- and (*E*)-isomers in a ratio (1:2). In a typical experiment, after 1 h irradiation, chromatography of the crude photolysate using diethyl ether-hexane (5:95) afforded: pure (*Z*)-isomer (**5a**) (72 mg, 24%), a mixture of the (*Z*)- and (*E*)-isomers (51 mg, 17%) (ratio 1:2.5) and pure (*E*)-isomer (136 mg, 45%). The (*Z*)-oxime acetate (**5a**) was obtained as an oil; $\nu_{max.}$ (liq. film) 1 770, 1 715, 1 630 cm^{-1}; δ_H ($CDCl_3$) 8.0 (1H, s, CH=N), 6.1 (1H, d, *J* 14 Hz, C*H*=CHCO$_2$Et), 5.8 (1H, d, *J* 14 Hz, CH=C*H*CO$_2$Et), 4.2 (2H, q, CH_2), 2.1 (3H, s, CH_3CO), 1.5 (6H, s, $2CH_3$), 1.3 (3H, t, CH_2CH_3); δ_C ($CDCl_3$) 168.8 (*C*OCH$_3$), 164.1 (*C*OOEt), 156.0 (C=N), 150.5 (*C*H=CHCO$_2$Et), 121.1 (CH=*C*HCO$_2$Et), 60.5 (CH_2O), 39.0 (quaternary carbon), 24.7 ($2CH_3$), 29.6 (CH_3CO), 14.1 (CH_2CH_3); *m/z* 227 (*M*$^+$, 1%), 185 (70), 168 (35), 140 (91), 122 (92), 117 (30), 112 (46), 96 (34), 67 (20), and 43 (100). (Found: *M*$^+$, 227.1158. $C_{11}H_{17}NO_4$ requires *M*$^+$, 227.1157).

Irradiation of oxime acetate (**5b**). Compound (**5b**) (300 mg, 1.66 mmol) was irradiated for 105 min. Chromatography of the crude photolysate using ethyl acetate-hexane (5:95) afforded a mixture of the (*Z*)- and (*E*)-isomers (200 mg, 67%) (ratio 1:2.5). After several chromatographies of this mixture of isomers, a pure fraction (25 mg) of the (*Z*)-oxime acetate (**5b**) was obtained as an oil; $\nu_{max.}$ (liq. film) 2 220, 1 750, 1 650 cm^{-1}; δ_H ($CDCl_3$) 7.8 (1H, s, CH=N), 6.6 (1H, d, *J* 10 Hz, C*H*=CHCN), 5.5 (1H, d, *J* 10 Hz, CH=C*H*CN), 2.1 (3H, s, CH_3CO), 1.5 (6H, s, $2CH_3$); δ_C ($CDCl_3$) 168.0 (C=O), 161.4 (C=N), 156.0 (*C*H=CHCN), 116.0 (C=N), 98.5 (CH=*C*H CN), 40.5 (quaternary carbon), 24.9 ($2CH_3$), 19.1 (CH_3CO); *m/z* 166 (*M*$^+$-14, 1%), 138 (100), 110 (11), 95 (51), and 67 (14). (Found: *M*$^+$-14, 166.0857. $C_9H_{12}N_2O_2$ requires *M*$^+$-14, 166.0868).

Irradiation of oxime acetate (**5c**). Compound (**5c**) (300 mg, 1.5 mmol) was irradiated for 120 min. The ^{1}H n.m.r. of the crude photolysate showed the presence of a mixture of the (*Z*)- and (*E*)-isomers in a ratio (1:3.7). Chromatography of the crude reaction mixture using ethyl acetate-hexane (5:95) afforded a mixture of the (*Z*)- and (*E*)-isomers (108 mg, 36%) (ratio 1:1.6) and pure (*E*)-isomer (**5c**) (85 mg, 28%). The first fraction was rechromatographed using ethyl acetate-hexane (2:98) and afforded 30 mg of pure (*Z*)-oxime acetate (**5c**) as an oil; $\nu_{max.}$ (liq. film) 1 760, 1 740, 1 620 cm^{-1}; δ_H ($CDCl_3$) 7.7 (1H, s, CH=N), 5.5 (2H, m, vinyl-H), 4.0 (2H, d, CH_2), 3.3 (3H, s, CH_3O), 2.1 (3H, s, CH_3CO), 1.3 (6H, s, $2CH_3$); δ_C ($CDCl_3$) 168.6 (C=O), 164.0 (C=N), 136.3 (*C*H=CHCH$_2$), 129.2 (CH=*C*H CH$_2$), 67.9 (CH_2), 58.0 (CH_3O), 39.0 (quaternary carbon), 25.8 ($2CH_3$), 19.4 (2*C* H_3CO); *m/z* 198 (*M*$^+$-1, 8%), 156 (21), 123 (15), 112 (56), 97 (40), 83 (44), 73 (59), 57 (74), and 43 (100). (Found: *M*$^+$-1, 198.11302. $C_{10}H_{16}NO_3$ requires *M*$^+$-1, 198.11302).

Irradiation of oxime acetate (**5d**). Compound (**5d**) (300 mg, 1.32 mmol) was irradiated for periods from 1 h to 7 h. The ^{1}H n.m.r. of the crude photolysate showed in all cases a mixture of the (*Z*)- and (*E*)-isomers in a ratio (1:3.5). In a typical experiment, after 90 min. irradiation, chromatography of the crude photolysate using diethyl ether-hexane (5:95) afforded: pure (*Z*)-isomer (**5d**) (48 mg, 16%), a mixture of the (*Z*)- and (*E*)-isomers (20 mg, 7%) (ratio 1:1) and pure (*E*)-isomer (**5d**) (180 mg, 60%). The (*Z*)-oxime acetate (**5d**) was obtained as an oil; $\nu_{max.}$ (liq. film) 1 760, 1 730, 1 620 cm^{-1}; δ_H ($CDCl_3$) 7.8 (1H, s, CH=N), 5.6 (2H, m, vinyl-H), 4.7 (2H, d, CH_2), 2.1 and 2.0 (3H, s, 2CH_3CO), 1.3 (6H, s, $2CH_3$); δ_C ($CDCl_3$) 170.9 and 168.7 (C=O), 163.7 (C=N), 137.5 (*C* H=CHCH$_2$), 126.6 (CH=*C*HCH$_2$), 60.3 (CH_2), 39.1 (quaternary carbon), 26.6 ($2CH_3$), 21.0 and 19.0 (2*C*H_3CO); *m/z* 185 (*M*$^+$-42, 2%), 152 (27), 110 (22), 98 (22), 83 (25), 67 (13), and 43 (100). (Found: *M*$^+$-42, 185.1052. $C_9H_5NO_3$ requires *M*$^+$-42, 185.1052).

Irradiation of oxime acetate (**6a**). Compound (**6a**) (300 mg, 1.24 mmol) was irradiated for 90 min. Chromatography of the crude photolysate using ethyl acetate-hexane (1:9) afforded a mixture of the (*Z*)- and (*E*)-isomers (192 mg, 64%) (ratio 4:1), pure (*E*)-isomer (**6a**) (20 mg, 7%) and a mixture of the cyclopropanes (**6a**) (84 mg, 28%). The first fraction was rechromatographed using ethyl acetate-hexane (5:95) and afforded 40 mg of pure (*Z*)-oxime acetate (**6a**) as an oil; $\nu_{max.}$ (liq. film) 1 760, 1 710, 1 650, 1 620 cm^{-1}; δ_H ($CDCl_3$) 7.8 (1H, s, CH=N), 5.7 (1H, s, vinyl-H), 4.2 (2H, q, C*H*$_2$CH$_3$), 2.1 (3H, s, CH_3CO), 1.9 (3H, s, CH_3C=C), 1.4 (6H, s, $2CH_3$), 1.3 (3H, t, CH_2CH_3); δ_C ($CDCl_3$) 168.6 and 168.0 (C=O), 164.1 (C=N), 140.2 (*C*H=C), 130.0 (CH=*C*), 60.8 (CH_2), 38.9 (quaternary carbon), 26.8 ($2CH_3$), 21.8 (*C*H_3CO), 19.5 (*C*H_3C=C), 13.9 (CH_3); *m/z* 199 (M$^+$-42, 3%), 172 (45), 154 (52), 131 (17), 126 (60), 103 (45), 98 (74), 85 (54), 74 (82), 70 (100), 56 (92), and 43 (72). (Found: *M*$^+$-42, 199.1208. $C_{10}H_{17}NO_3$ requires *M*$^+$-42, 199.1208). *Cyclopropanes* (**8a**) were obtained as an oily, inseparable mixture of diastereoisomers (**a** and **b**) (ratio 1:1); $\nu_{max.}$ (liq. film) 1 760, 1 715, 1 610 cm^{-1}; δ_H ($CDCl_3$) 8.0 (isomer **a**) and 7.5 (isomer **b**) (1H, d, *J* 9 Hz, CH=N), 4.2 (2H, q, C*H*$_2$CH$_3$), 2.6 (isomer **b**) and 1.8 (isomer **a**) (1H, d, *J* 9 Hz, ring CH), 2.14 and 2.12 (3H, s, CH_3CO), 1.4 (3H, s, CH_3), 1.2 (9H, m, $3CH_3$); δ_C ($CDCl_3$) 172.0 and 169.0 (C=O), 158.8 and 156.8 (C=N), 61.1 (CH_2), 36.9, 36.1, 35.5, 30.9, 29.9, 29.6 (ring C), 22.2 ($2CH_3$ on C-3), 19.4, 18.3, 17.6, 17.2, (CH_3 on C-2 and *C*H_3CO), 14.3 (*C*H_3CH_2); *m/z* 241 (*M*$^+$, 1%), 199 (27), 181 (64),

153 (68), 136 (92), 126 (86), 112 (61), 108 (100), 94 (30), 81 (75), 66 (22), 59 (60), and 43 (26). (Found: M^+, 241.1294. $C_{12}H_{19}NO_4$ requires M^+, 241.1314).

Irradiation of oxime acetate (**6b**). Compound (**6b**) (220 mg, 1.13 mmol) was irradiated for 45 min. Chromatography of the crude photolysate using ethyl acetate-hexane (1:9) afforded a mixture of the (*Z*)- and (*E*)-isomers (**6b**) (100 mg, 45%) (ratio 1:1.3) and a mixture of the cyclopropanes (**8b**) (119 mg, 54%). The first fraction was rechromatographed using ethyl acetate-hexane (5:95) and afforded 30 mg of pure (*Z*)-oxime acetate (**6b**) as an oil; $\nu_{max.}$ (liq. film) 2 200 cm^{-1}; δ_H ($CDCl_3$) 7.8 (1H, s, CH=N), 6.3 (1H, s, vinyl-H), 2.1 (3H, s, CH_3CO), 2.0 (3H, s, CH_3C=C), 1.5 (6H, s, $2CH_3$); δ_C ($CDCl_3$) 167.9 (C=O), 162.0 (C=N), 156.0 (*C*H=C), 118.0 (CH=*C*), 108.0 (C≡N), 39.8 (quaternary carbon), 25.8 ($2CH_3$), 19.8 (*C*H_3CO), 16.2 (*C*H_3C=C), 13.9 (CH_3); *m/z* 152 (M^+-42, 100%), 135 (25), 122 (27), 107 (19), 92 (12), and 70 (12). (Found: M^+-42, 152.0950. $C_{10}H_{14}N_2O_2$ requires M^+-42, 152.0950). *Cyclopropanes* (**8a**) were obtained as an oily, inseparable mixture of diastereoisomers (**a** and **b**) (ratio 4.4:1); $\nu_{max.}$ (liq. film) 2 230, 1 760, 1 620 cm^{-1}; δ_H ($CDCl_3$) 7.6 (isomer **a**) and 7.5 (isomer **b**) (1H, d, *J* 9 Hz, CH=N), 2.5 (isomer **b**) and 1.9 (isomer **a**) (1H, d, *J* 9 Hz, ring CH), 2.1 (3H, s, CH_3CO), 1.5, 1.4, and 1.2 (9H, s, $3CH_3$); δ_C ($CDCl_3$) 168.0 (C=O), 155.8 (C=N, isomer **a**), 153.9 (C=N, isomer **b**), 121.5 (C≡N, isomer **b**), 120.1 (C≡N, isomer **a**), 35.2, 33.1, 29.8, 28.7, 22.6, 22.3 (ring C), 21.3, 21.1, 19.8, 16.9, 16.7, 14.3, 14.1 (CH_3); *m/z* 135 (M^+-59, 4%), 119 (100), 107 (35), and 92 (34). (Found: M^+-59, 135.0911. $C_8H_{11}N_2$ requires M^+-59, 135.0912).

Irradiation of oxime acetate (**6c**). Compound (**6c**) (400 mg, 1.66 mmol) was irradiated for 150 min. Chromatography of the crude photolysate using ethyl acetate-hexane (7:93) afforded a mixture of the (*Z*)- and (*E*)-isomers (254 mg, 63%) (ratio 1:2) and a mixture of the cyclopropanes (**8c**) (84 mg, 21%). The spectroscopic data of the (*Z*)-isomer (**6c**) in the mixture were identical to those of a pure sample synthesized independently.[13] *Cyclopropanes* (**8c**) were obtained as an oily, inseparable mixture of diastereoisomers (**a** and **b**) (ratio 1:1.3); $\nu_{max.}$ (liq. film) 1 750, 1 730, 1 610 cm^{-1}; δ_H ($CDCl_3$) 7.51 (isomer **a**) and 7.50 (isomer **b**) (1H, d, *J* 9 Hz, CH=N), 4.1 (2H, m, CH_2), 2.10 and 2.05 (3H, s, $2CH_3CO$), 1.64 (isomer **b**) and 1.57 (isomer **a**) (1H, d, *J* 9 Hz, ring CH), 1.2 (9H, s, $3CH_3$); δ_C ($CDCl_3$) 171.3 and 168.5 (C=O), 158.2 (C=N), 69.8 and 66.2 (CH_2), 33.7 and 31.1 (CH), 29.9, 28.7, 28.3, and 27.1 (ring C), 23.2, 22.8, 20.9, 19.4, 18.8, and 17.6 (CH_3); *m/z* 185 (M^+-56, 3%), 124 (33), 109 (65), 99 (52), 82 (36), 73 (11), 59 (14), and 43 (100). (Found: M^+-56, 185.1174. $C_{10}H_{17}O_3$ requires M^+-56, 185.1178).

Irradiation of Oxime Acetate.(**6c***Z*). Compound (**6c***Z*) (300mg, 1.24 mmol) was irradiated for 150 min. Chromatography of the crude photolysate using a mixture of ethyl acetate-hexane (7:93) afforded a mixture of the (*Z*)- and (*E*)-isomers (216 mg, 72%) (ratio 1:2) and the cyclopropanes (**8c**) (50 mg, 17%).

Direct Irradiation of Oxime Acetate (**5a***E*).Compound (**5a***E*) (200mg, 0.88 mmol) was irradiated in anhydrous methylene dichloride (350 ml) for 3 h. in a quartz immersion-well apparatus using 16 W a low pressure Hg lamp. Chromatography of the crude photolysate using a mixture of ethyl acetate-

hexane (1:9) afforded a mixture of the (*Z*)- and (*E*)-isomers (**5a**) (150 mg, 75%) (ratio 1:1.25) and unidentified polar products (70 mg).

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