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# THE PHOTOCHEMICAL SYNTHESIS OF POTENTIAL PYRETHROID COMPONENTS BY THE AZA-DI-π-METHANE REARRANGEMENT OF β,γ-UNSATURATED OXIME ACETATES.

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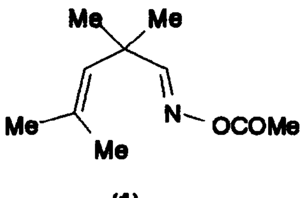
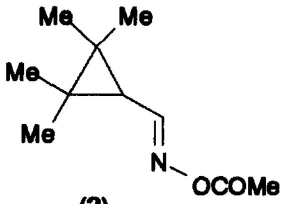
**Summary:** The syntheses and photochemical reactions of oxime acetates of ethyl 4,4-dimethyl-5-oxopent-2-enoate and ethyl 2,4,4-trimethyl-5-oxo-2-enoate are described. The former compound undergoes *E-Z*-isomerisation of the C=C bond while the latter rearranges by the aza-di-π-methane reaction to afford a cyclopropane derivative.

The oxa-di-π-methane rearrangement of β,γ-unsaturated ketones has been shown to have considerable value in the synthesis of cyclopropane derivatives.[1] However, the analogous reaction of aldehydes is not well exemplified and does have a major drawback in that aldehydes undergo facile photodecarbonylation and, therefore, fail to yield cyclopropane derivatives. Our discovery of the acyclic aza-di-π-methane rearrangement of imines[2] and oxime acetates[3] of β,γ-unsaturated aldehydes has overcome this problem and these compounds readily undergo photorearrangement into cyclopropanes derivatives with quantum efficiency as high as 0.8.[4] Since the early observations we have identified a variety of features which help to control the efficiency of the reaction and have demonstrated that electron transfer from the nitrogen of the 1-aza-1,4-diene to the alkene component has an adverse effect on the efficiency.[5,6] Our present research is aimed at the development of the aza-di-π-methane rearrangement as a synthetic path to cyclopropane derivatives which would be of use as the cyclic component of pyrethroid insecticides, which are important in agriculture due to low mammalian toxicity and biodegradability.[7] In a simple example of this we have shown that the azadiene (1) can be converted photochemically into the cyclopropane oxime acetate (2). This also affords the nitrile (3) by the thermal elimination of acetic acid from (2).[8] Both of these are readily converted into 1,1,2,2-tetramethylcyclopropane carboxylic acid, the acid component of the pyrethroid *terallethrin*.[9] The present paper reports our study of changes of functionalisation around the azadiene skeleton and the successful photochemical synthesis of a novel cyclopropane of potential value in the synthesis of pyrethroid insecticides.



(1)



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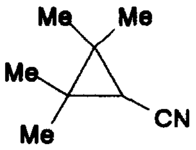
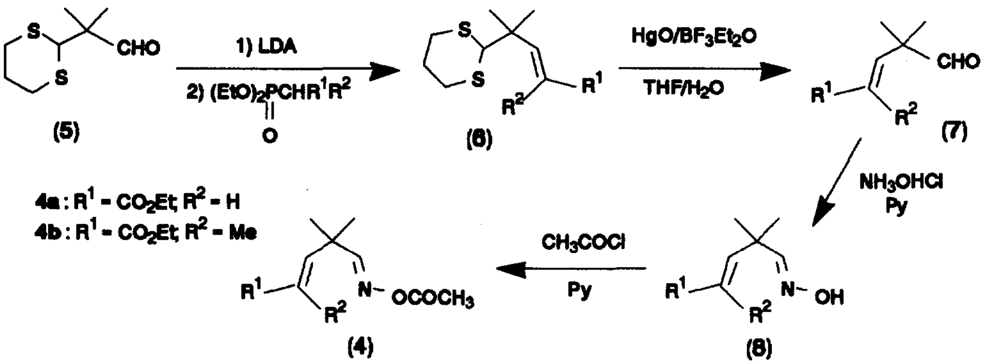


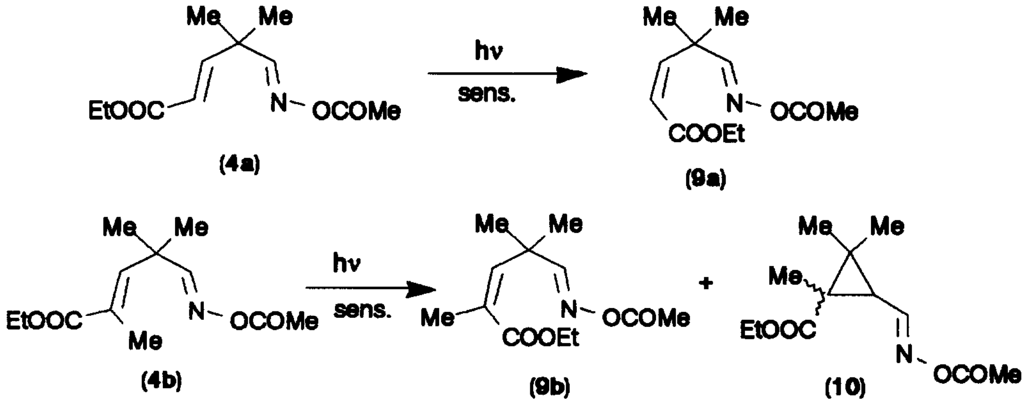
(3)

The dienes (4) required for this study were unknown. Therefore, it was necessary to design a route to this class of compound. The synthetic path devised is outlined in Scheme 1. This involves Wittig reaction of the protected dialdehyde (5)[10] affording the alkenes (6, 85%), deprotection[11] to (7, 70-85%), oximation to (8, 72-79%) and acetylation, by standard procedures, to give the dienes (4, 75-98%). All of these new compounds (4, and 6-8) are well characterised and give satisfactory microanalytical and spectroscopic data in accord with the proposed structures.[12]



Scheme 1

Acetone-sensitized (λ > 280 nm) or direct irradiation at 254 nm[13] of oxime acetate (4a) for periods up to 7 h exclusively brings about *trans-cis*-isomerisation to afford a mixture of starting material (4a, 70%) and the isomer (9a, 30%).(Scheme 2) The *Z*-isomer (9a) was readily identified by the reduction in the coupling constant from 16Hz in the *E*-isomer to 13.7Hz as well as the shift in resonance position. No evidence for the expected cyclopropane was obtained. The failure of this compound to undergo cyclisation could be due to an adverse intramolecular electron transfer from the oxime nitrogen to the alkene moiety as discussed by us previously.[3] An alternative explanation could be deactivation of the triplet excited state by a free rotor effect.[14] In an effort to substantiate the foregoing the irradiation of (4b) was carried out. Under similar conditions acetone-sensitised irradiation of (4b) also afforded *trans-cis* isomerisation (64%) but in addition a new product was isolated in 28% yield. The mass spectrum of this showed it to be isomeric with starting material. The $^1H$ and $^{13}C$ n.m.r. spectra confirmed that the products was the cyclopropane (10).[15] The major difference between the two examples cited here is the different substitution at C-4. It is clear that two substituents at this position minimize the possibility of free rotor deactivation while mono-substitution permits the excited state deactivation path to take place. This successful cyclisation arises only from the C-4 disubstituted compounds. Clearly the success with (4b) suggests that an adverse electron transfer is not operative.



**Scheme 2**

In spite of the lack of reactivity of the oxime (4a) the success of the cyclisation of (4b) opens a new photochemical route to pyrethroids which could compete with earlier photochemical paths to these compounds.[16]

## Acknowledgements.

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12.- Spectroscopic data for 1-aza-1,4-dienes (**4**):

Compound (**4a**): $\nu_{max}$ (film) 1760, 1720, 1650, 1630 cm$^{-1}$; $\delta_H$ ($CDCl_3$) 7.5 (1H, s, CH=N), 6.8 (1H, d, J = 16Hz, vinyl H), 5.7 (1H, d, J = 16Hz, vinyl H), 4.1 (2H, q, $CH_2$), 2.1 (3H, s, $CH_3CO$), 1.3 (9H, m, $3CH_3$); $\delta_C$ ($CDCl_3$) 170.0 (CO), 162.0 (CN), 156.0, 151.0, 120.0, 60.7, 39.8, 24.5, 24.4, 19.0, 14.0; *m/z* 227 ($M^+$, 1%), 185 (99), 170 (20), 142 (100), 122 (65), 117 (36), 114 (28), 112 (48), 99 (13), 96 (30), 94 (170).

Compound (**4b**): $\nu_{max}$ (film) 1760, 1705, 1640, 1625 cm$^{-1}$; $\delta_H$ ($CDCl_3$) 7.8 (1H, s, CH=N), 6.8 (1H, s, vinyl H), 4.2 (2H, q, $CH_2$), 2.1 (3H, s, $CH_3CO$), 1.9 (3H, s, $CH_3$), 1.4 (6H, s, $2CH_3$), 1.3 (3H, t, $CH_3$); $\delta_C$ ($CDCl_3$) 168.3 (CO), 163.3 (CN), 144.2, 130.0, 60.8, 39.0, 26.0, 19.4, 14.2, 13.3; *m/z* 241 ($M^+$, 4%), 199 (82), 184 (29), 153 (78), 136 (27), 126 (96), 108 (46), 83 (16), 70 (32), 43 (100).

13.- The photolyses were carried out in an immersion well apparatus with a Pyrex filter and a 400 watt medium pressure Hg arc lamp. a solution of (**4**, 300 mg) in anhydrous methylene chloride (380 ml) was purged for 1 h with nitrogen and irradiated under a positive pressure of nitrogen.

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15.- Cyclopropanes (**10**) were obtained as an oil and as an inseparable mixture of isomers (**a** and **b**) in a ratio 1:1, $\nu_{max}$ (film) 1760, 1715, 1610 cm$^{-1}$; $\delta_H$ ($CDCl_3$) 8.00 (d, J = 9Hz) (isomer **a**) and 7.49 (d, J = 9Hz) (isomer **b**) (1H, CH=N), 4.15 (2H, q, $CH_2$), 2.55 (d, J = 9Hz) (isomer **b**) and 1.78 (d, J = 9Hz) (isomer **a**) (1H, ring CH), 2.14 and 2.12 (3H, s, $CH_3CO$), 1.39 (3H, s, $CH_3$), 1.23 (9H, m, $3CH_3$); $\delta_C$ ($CDCl_3$) 168.5 (CO), 158.8 (CN), 156.8 (CN), 61.1 ($CH_2$), 36.9, 36.1, 35.5, 30.9, 29.9, 29.6 (ring carbons), 22.2 ($2CH_3$ on C3), 19.4, 18.3, 17.6, 17.2 ($CH_3$ on C2 and $CH_3CO$), 14.3 ($C\underline{H}_3CH_2O$).

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