

The Aza-di- π -methane Rearrangement of *O*-Acetyl 2,2-Dimethyl-4,4-diphenylbut-3-enal Oxime

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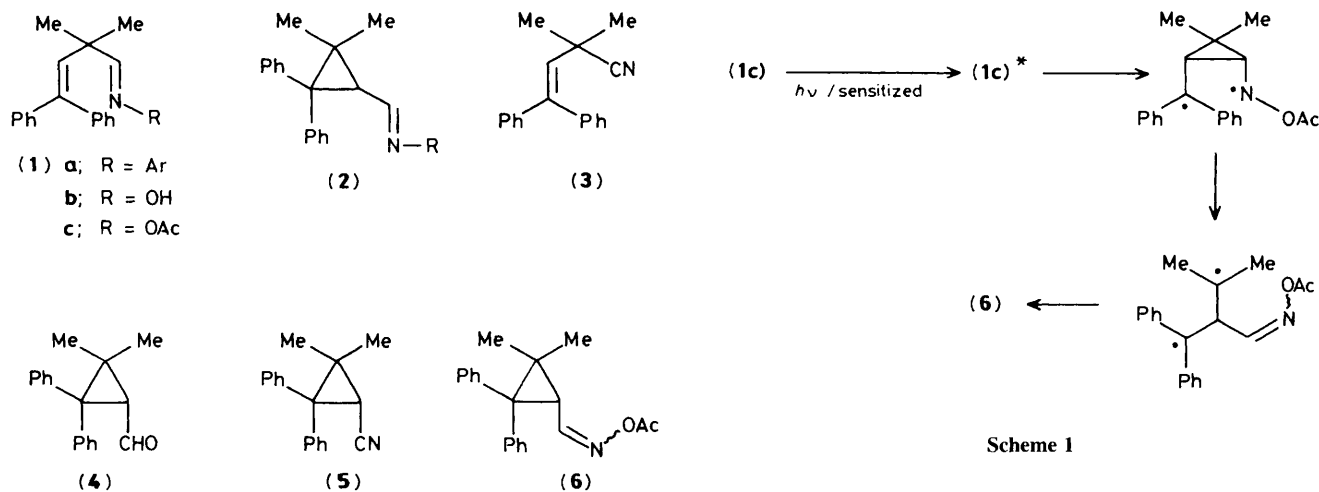
The photochemical reaction of *O*-acetyl 2,2-dimethyl-4,4-diphenylbut-3-enal oxime is described: the reaction yields two cyclopropane derivatives, *O*-acetyl 3,3-dimethyl-2,2-diphenylcyclopropane carboxaldehyde oxime as the primary photoproduct, formed by an aza-di- π -methane reaction previously unobserved in such compounds, and 1-cyano-3,3-dimethyl-2,2-diphenylcyclopropane formed by thermal elimination of acetic acid from the primary product.

A number of years ago we reported the first example of the aza-di- π -methane reaction in which the acyclic imines (**1**; R = alkyl or benzyl) were converted into the cyclic imines (**2**).^{1,2} This filled a gap in our knowledge of compounds known to undergo the di- π -methane reaction.^{3,4} In our earlier studies we established that the aza-di- π -methane reaction of imines was dependent on the type of substitution on the nitrogen and quantitatively confirmed that the ease with which the rearrangement occurred was related to the conjugation between the aryl substituent on nitrogen and the nitrogen lone pair in (**1a**).⁵ Thus we were convinced that the success of the cyclization of the acyclic imines was dependent upon the ionization potential of the imine nitrogen. We also noted the failure of the oxime (**1b**) and of the nitrile (**3**) to undergo rearrangement.⁶ Research has shown that oxime ethers⁷ fail to undergo an aza-di- π -methane rearrangement and only isomerize around the N=C or C=C double bond. While others⁸ have reported an aza-di- π -methane rearrangement in a cyclic

imine, in only one case has an oxime, contained in a constrained ring system, been observed to undergo this reaction.⁹ From these results we postulated that oximes, in general, could be made to rearrange if it were possible to increase the ionization potential of the oxime group thus minimising the possibility of an intramolecular electron transfer. This can be done readily using the acetate derivative of the oxime and herein we report our observations on the reactivity of *O*-acetyl 2,2-dimethyl-4,4-diphenylbut-3-enal oxime.

The oxime acetate (**1c**)[†] was readily synthesized in 95% yield by the conversion of the oxime (**1b**)⁶ using standard

[†] All new products gave satisfactory microanalytical results. Oxime acetate (**1c**) was obtained in 95% yield as white crystals from hexane, m.p. 82–84 °C; i.r.: ν_{max} 1760 (C=O), 1625 (C=N), 1210 cm^{-1} (C–O); ¹H n.m.r. (CDCl₃): δ 1.33 (6H, s, Me), 1.93 (3H, s, Me), 5.90 (1H, s, vinyl), 6.95–7.33 (11H, m, aryl H and CH=N).



Scheme 1

procedures. The irradiation of (1c) was carried out in a conventional apparatus[‡] using acetophenone sensitization. After conventional work-up, the reaction mixture was separated by flash column chromatography to afford two products in 11 and 79% yields after 25 min irradiation. The first product was readily shown to be a nitrile by the absorption at 2230 cm^{-1} . The second retained the acetate group and exhibited an absorption at 1765 cm^{-1} . The n.m.r. spectra of both products 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. Both compounds exhibited absorptions in their n.m.r. spectra in the δ 2–2.5 region. From previous studies² with the aldehyde (4) it was clear that the two products from the irradiation of (1c) were cyclopropyl derivatives, the nitrile (5) and the oxime acetate (6). § Final proof of structure was obtained by the hydrolysis of the oxime acetate (6) in H_2O – EtOH – HCl , which afforded the aldehyde (4) in high yield.

In line with our previous observations of the photochemical rearrangement of imines, we suggest that the formation of cyclopropyl derivatives from the sensitized reaction of the oxime acetate (1c) in benzene follows the aza-di- π -methane path shown in Scheme 1. The reaction clearly arises from the triplet state since direct irradiation fails to bring about the rearrangement. The route shown in Scheme 1 readily accounts

for the formation of the oxime acetate (6) but does not provide a reasonable explanation for the formation of the nitrile (5). Indeed, (5) is not a photochemical product but is produced by the thermal elimination of acetic acid from the oxime acetate (6). Proof of this was obtained when (6) was warmed to 80 °C *in vacuo* under conditions identical to those used for the removal of acetophenone from the photolysate, to give the nitrile (5) as a major product.

This novel aza-di- π -methane photoreactivity of an oxime acetate may provide a general, easily applicable method for the preparation of cyclopropyl derivatives of β,γ -unsaturated aldehydes or ketones which do not normally undergo such a reaction. The use of the oxime acetate has advantages over the imines used in our previous study, the oxime acetates being considerably more stable and not prone to hydrolysis and, in qualitative terms, the aza-di- π -methane rearrangement of the oxime acetates appears to be a faster and more efficient reaction.

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[‡] Irradiations of the oxime acetate (316 mg) with acetophenone (2.00 g) in benzene (320 ml) were carried out in a conventional immersion well apparatus with a Pyrex filter and a 400 W medium pressure Hg arc lamp. The solutions were deaerated with nitrogen prior to and during irradiation.

§ Nitrile (5) was obtained as colourless crystals from hexane, m.p. 124–125 °C; i.r.: ν_{max} 2230 cm^{-1} (CN); ^1H n.m.r. (CDCl_3): δ 1.08 (3H, s, Me), 1.33 (3H, s, Me), 2.00 (1H, s, cyclopropyl H), 6.98–7.35 (10H, m, aryl).

Oxime acetate (6) was obtained as colourless crystals from hexane, m.p. 130–132 °C; i.r.: ν_{max} 1765 (C=N), 1195 cm^{-1} (C–O); ^1H n.m.r. (CDCl_3 , 90 MHz): δ 1.10 (3H, s, Me), 1.28 (3H, s, Me), 2.10 (3H, s, Me), 2.48 (1H, d, J 10 Hz, cyclopropyl H), 6.91–7.35 (11H, m, aryl and CH=N); ^{13}C n.m.r. (CDCl_3 , 75 MHz): δ 168.46 (C=O), 159.74 (CH=N), 143.60, 140.33, 130.46, 128.73, 128.53, 126.70, 126.47 (aryl C), 48.23 (cyclopropyl C-2), 33.17 (Me), 29.68 (cyclopropyl C-3), 25.32 (cyclopropyl C-1), 20.66 (Me), 19.39 (Me).