

The Aza-di- π -methane Rearrangement of Stable Derivatives of 2,2-Dimethyl-4,4-diphenylbut-3-enal

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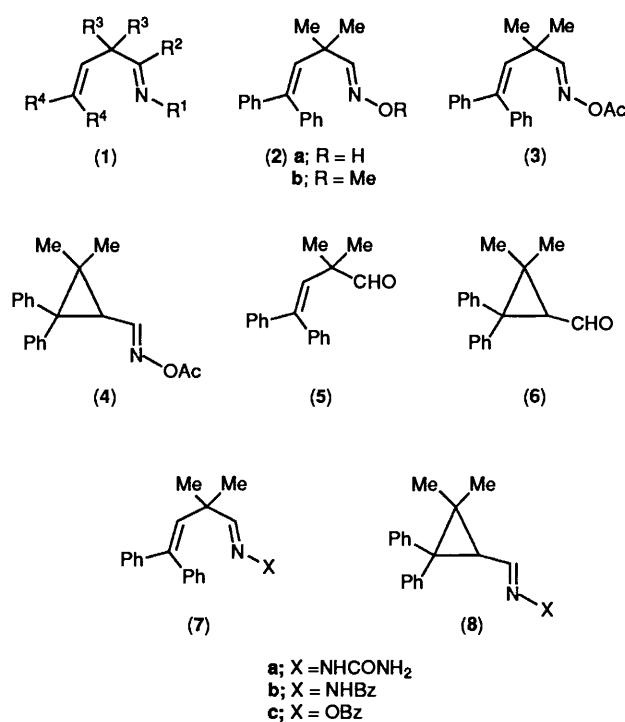
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The sensitised irradiations of the semicarbazone (**7a**), the benzoylhydrazone (**7b**), and the oxime benzoate (**7c**) of 2,2-dimethyl-4,4-diphenylbut-3-enal afford the corresponding derivatives of 2,2-dimethylcyclopropanecarbaldehyde (**8a–c**) in good yield by an aza-di- π -methane rearrangement.

The discovery of the aza-di- π -methane (ADPM) rearrangement has been the major prize arising from our study of the photochemical reactivity of β,γ -unsaturated imines (**1**).¹ Our research has shown that the success of the rearrangement is dependent upon the suppression of electron transfer from the nitrogen lone pair of the imine moiety to the alkene component.² Thus, the success of the reaction depends upon the ionization potential of the nitrogen lone pair and, as a consequence, the oxime (**2a**)³ with a relatively low ionization potential, is unreactive as is the corresponding oxime ether (**2b**).⁴ Conversion of the oxime into the acetate introduces an electron-withdrawing group which results in a raising of the ionization potential. This compound (**3**) was shown to be photochemically reactive in the ADPM rearrangement and affords the cyclopropane (**4**) in high yield.⁵ This *modus operandi* allows for the transformation of the aldehyde (**5**), which does not undergo the photochemical oxa-di- π -methane rearrangement,⁶ into the cyclopropane (**6**) via a stable C=N derivative. The present report details our search for other stable derivatives

and the success with the semicarbazone (**7a**), the benzoyl hydrazone (**7b**), and the oxime benzoate (**7c**).

The crystalline derivatives (**7**) were prepared readily by conventional methods and afforded the desired compounds in high yield. The structures of these products were readily confirmed by conventional spectroscopy and microanalysis. The irradiations were carried out in an immersion well apparatus using acetophenone as sensitiser. The irradiation of the semicarbazone (**7a**) for 2 h afforded, after work-up by flash chromatography, a mixture of starting material (60%) and a new product (40%). Spectroscopic evidence and microanalysis showed that this compound was isomeric with starting material. The ¹H NMR spectrum showed a doublet corresponding to one hydrogen at the correct resonance position for hydrogens in a three-membered ring. The presence of a cyclopropyl moiety was confirmed by the ¹³C spectrum. Thus the compound was conclusively identified as the cyclopropane (**8a**). Similar photochemical reactivity was shown by the other two derivatives (**7b**) and (**7c**). In the case of the benzoyl hydrazone



(7b) the qualitative rate of conversion was much faster than for (7a) and transformation to the cyclopropane (8b) (20%) was achieved in 30 min. The identity of this product was also verified readily by spectroscopic and microanalyses. Further proof of the formation of a cyclopropane was achieved by the hydrolysis, using $\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ (15%), of the benzoyl hydrazone derivative (8b) into the aldehyde (6). A similar result was obtained for the oxime benzoate (7c), the efficiency of the reaction in this case being the highest and yielding the cyclopropane derivative (8c) (90%) after irradiation for 20 min.

The formation of the cyclopropane derivatives (8a) and (8b) arises by the now well established triplet-sensitised aza-di- π -methane rearrangement. It is clear from these results that the ADPM rearrangement is not restricted to imines and oxime acetates but can be readily extended to other common derivatives of carbonyl compounds. An advantage of the derivatives used in this study is that they, and the cyclopropanes obtained from them, are stable and crystalline. The success of the photocyclisation of the derivatives (7) indicates that there is no adverse effect in incorporating a nitrogen adjacent to the imine nitrogen.

It is worthy of note that in qualitative terms the rearrangement of the oxime benzoate (7c) is much more efficient than the corresponding reaction of the oxime acetate (3). This is of importance since we have demonstrated that the ADPM reaction of oxime acetates is more efficient in some cases than the di- π -methane rearrangement of related 1,4-dienes.⁷ Therefore, the extension of the ADPM reaction to other stable derivatives of β,γ -unsaturated carbonyl compounds would allow us to determine which functional group would be the best for the photochemical transformation of such compounds into the corresponding cyclopropyl derivatives.

Experimental

Preparative Photolyses.—All 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 (7) (250 mg) and acetophenone (7 g) in anhydrous benzene (280 ml) were purged for 1 h with oxygen-free nitrogen and irradiated under a positive pressure of nitrogen for the times shown. After completion of the irradiation the solvent was removed under reduced pressure and the products were separated by flash chromatography.

Irradiation of the Semicarbazone (7a).—This compound was irradiated for 2 h. Work-up afforded starting material (7a) and the semicarbazone (8a) as a colourless crystalline compound from hexane–ethanol in 40% yield, m.p. 122–124 °C; $\nu_{\text{max}}(\text{KBr})$ 3 550–3 380 (NH and NH_2), 1 700 (C=O), and 1 620 (C=N) cm^{-1} ; $\delta_{\text{C}}(\text{CDCl}_3)$ 15.1 (CH_3), 20.5 (CH_3), 29.5 (cyclopropyl C-2), 36.2 (cyclopropyl C-1), 47.0 (cyclopropyl C-3), 126.1–144.2 (aryl C), 144.8 (C=N), and 157.2 (C=O) (Found: C, 74.6; H, 7.0; N, 13.8. $\text{C}_{19}\text{H}_{21}\text{N}_3\text{O}$ requires C, 74.30; H, 6.80; N, 13.60%).

Irradiation of the Benzoyl Hydrazone (7b).—This compound was irradiated for 2 h. Work-up afforded starting material (7b) and the benzoyl hydrazone (8b) as a colourless crystalline compound from hexane–ethanol in 20% yield, m.p. 98–100 °C; $\nu_{\text{max}}(\text{KBr})$ 3 220 (NH), 1 645 (C=O), and 1 610 cm^{-1} (C=N); $\delta_{\text{C}}(\text{CDCl}_3)$ 20.6 (CH_3), 25.4 (CH_3), 29.4 (cyclopropyl C-2), 36.0 (cyclopropyl C-1), 47.8 (cyclopropyl C-3), 126.2–143.8 (aryl and vinyl C), 152.1 (C=N), and 163.5 (C=O) (Found C, 81.7; H, 6.8; N, 7.5. $\text{C}_{25}\text{H}_{24}\text{N}_2\text{O}$ requires C, 81.50; H, 6.65; N, 7.60%).

Irradiation of the Oxime Benzoate (7c).—This compound was irradiated for 20 min. Work-up afforded starting material (7c) and the oxime benzoate (8c) as a colourless crystalline compound from hexane in 90% yield, m.p. 110–112 °C; $\nu_{\text{max}}(\text{KBr})$ 1 745 (C=O) and 1 620 cm^{-1} (C=N); $\delta_{\text{C}}(\text{CDCl}_3)$ 20.6 (CH_3), 25.3 (CH_3), 29.8 (cyclopropyl C-2), 33.3 (cyclopropyl C-1), 48.3 (cyclopropyl C-3), 126.4–143.6 (aryl and vinyl C), 160.4 (C=O), and 164.1 (C=N) (Found C, 81.5; H, 6.5; N, 7.8. $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}$ requires C, 81.30; H, 6.20; N, 7.60%).

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