

A NOVEL AZA-DI- $\pi$ -METHANE REARRANGEMENT  
THE PHOTOREACTION OF 4,4-DIMETHYL-1,6,6-TRIPHENYL-2-AZA-HEXA-2,5-DIENE

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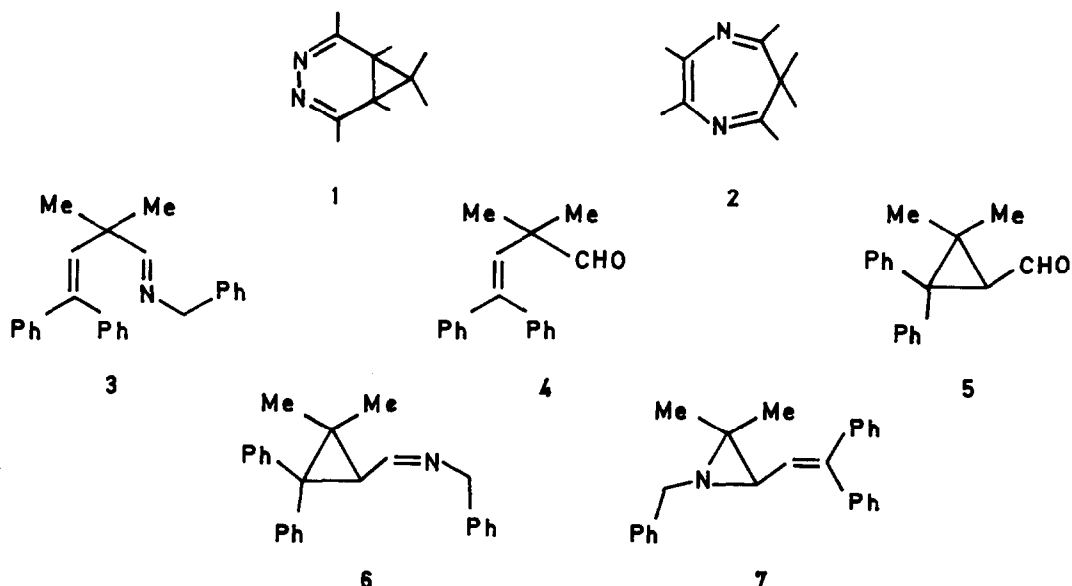
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Summary: The synthesis and the novel photochemical aza-di- $\pi$ -methane reaction of 4,4-dimethyl-1,6,6-triphenyl-2-aza-hexa-2,5-diene are described.

The photochemical reaction of 1,4-dienes, known as the di- $\pi$ -methane (Zimmerman) rearrangement, has been the subject of exhaustive studies<sup>1</sup>. The extension of this work to other 1,4-unsaturated systems such as  $\beta,\gamma$ -unsaturated ketones shows that these undergo an analogous photoreaction known as the oxa-di- $\pi$ -methane rearrangement<sup>2</sup>.

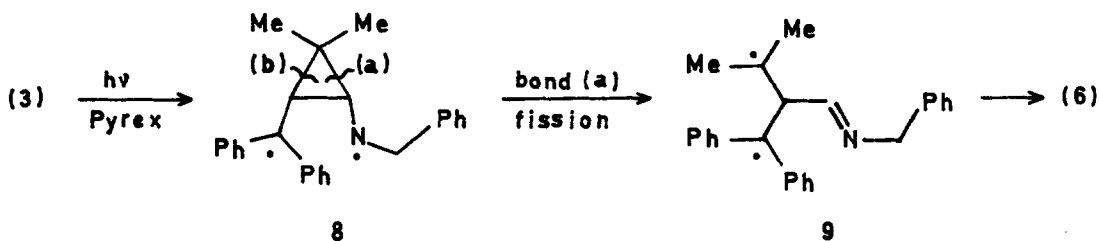
In principle it might be expected that the di- $\pi$ -methane rearrangement would be general for molecules in which two  $\pi$ -moieties are attached to an  $sp^3$  hybridized carbon. However, little is known about the influence of the introduction of a hetero-atom other than oxygen<sup>3</sup>. In particular there are few examples of the reactivity of 1,4-di- $\pi$ -systems in which one of the  $\pi$ -moieties is an imine group<sup>4</sup>. Reissenweber and Sauer<sup>5</sup> reported what could be the first case of an aza-di- $\pi$ -methane rearrangement in the photochemical transformation of the 3,4-diazanorcaradiene (1) into the 6H-1,4-diazepine (2). Proof of the proposed mechanism was not obtained, however, and the photoproduct could be formed by an alternative path such as 1,3-migration followed by ring-opening of a cyclobutene. We wish to report our studies on the photochemistry of acyclic  $\beta,\gamma$ -unsaturated imines. The imine (3) was synthesized from aldehyde (4)<sup>6</sup> and benzylamine by reflux in toluene for one hour under conditions for azeotropic removal of water. Concentration of the resultant solution in vacuo afforded a yellow oil, the n.m.r. spectrum of which showed 100% conversion to imine (3). Crystallization of the compound from

hexane at 0°C gave white crystals of the imine (3)<sup>7</sup>.



Direct irradiation<sup>8</sup> (in *t*-butanol) or acetophenone-sensitized irradiation (in benzene) of imine (3) through Pyrex brought about its conversion to a single photoproduct (c.a. 40%) exhibiting n.m.r. resonances at 2.35 (doublet) and 4.5 (broad)  $\delta$ . Chromatography of the resultant concentrated photolysates on silica gel afforded two aldehydes identified as (4) and (5) by comparison of their spectra with those previously reported<sup>6,9</sup>. Aldehyde (4) is formed by hydrolysis of starting material. Aldehyde (5), however, is clearly produced by hydrolysis of a new imine (6) formed during the irradiation. This imine (6), synthesized by reaction of aldehyde (5) with benzylamine, exhibits the n.m.r. resonances<sup>10</sup> at 2.35 and 4.5  $\delta$  which had been recorded from the crude photolysates prior to chromatography.

We believe that the formation of imine (6) is the result of a novel aza-di- $\pi$ -methane reaction a simple interpretation (Scheme) of which envisages the formation of imine (6) by fission of bond (a) in (8). Careful examination of the photolysates fails to show the presence of the aziridine (7) which might have been produced by fission of bond (b)<sup>11</sup> in (8) (Scheme). An alternative route to product via photochemical conversion of aldehyde (4) can be discounted since this aldehyde was also absent from the photolysates and furthermore an earlier study<sup>12</sup> of (4) reported the absence of oxa-di- $\pi$ -methane reactivity.



SCHEME

The photoreaction described for the imine (3) has features which differentiates it from the photoreactions encountered with 1,4-dienes and  $\beta,\gamma$ -unsaturated ketones. Most noteworthy is the fact that the imine (3) apparently undergoes photorearrangement from the triplet state. The product (6) is formed by both sensitized and direct irradiation and in the direct case preliminary studies with triplet quenchers suggest that this too is a triplet state process. This is different from acyclic 1,4-dienes photochemistry where the formation of the normal di- $\pi$ -methane product is mainly a singlet state reaction<sup>1</sup>. Furthermore there is no evidence for a 1,3-migration product (a singlet state reaction) which often typifies the photoreactivity of  $\beta,\gamma$ -unsaturated ketones<sup>2</sup>. It should also be pointed out that as far as we are aware this reaction is one of the very few cases in which an acyclic imine undergoes photochemical intramolecular rearrangement<sup>13,14</sup>.

We believe that the reaction described herein may have synthetic potential. The procedure adopted, namely that of conversion of the aldehyde (4) to its imine (3), permits the operation of the di- $\pi$ -methane transformation in a molecule, e.g. aldehyde (4), which does not normally exhibit such reactivity. The photoconversion of imine (3) is not unique and preliminary studies have shown the applicability of the method to other molecules. Present work is aimed at identifying the excited state involved and studying the scope of the process.

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#### REFERENCES AND NOTES

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5. G. Reissenweber and J. Sauer, Tetrahedron Letters, 4389 (1977).
6. H. E. Zimmerman and A. C. Pratt, J. Am. Chem. Soc., 92, 6259 (1970).
7. Imine (3) is poorly stable and was purified by crystallization only and not by chromatography since it decomposes very easily to give the aldehyde (4). Identification of the structure is based on the non ambiguity of the n.m.r. and i.r. data: n.m.r. ( $\text{Cl}_4\text{C}$ )  $\delta$  1.2 (6H, s,  $2\text{CH}_3$ ), 4.05 (2H, broad s,  $\text{CH}_2$ ), 6.0 (1H, s,  $\text{CH}=\text{CPh}_2$ ), 7.0-7.1 (15H, m, aromatic), 7.3 (1H, broad s,  $\text{CH}=\text{N}$ ); i.r. ( $\text{Cl}_4\text{C}$ ) 1660 ( $\text{C}=\text{N}$ )  $\text{cm}^{-1}$ .
8. Irradiations were carried out in an immersion well apparatus with a Pyrex filter and a 400 watt medium pressure Hg lamp, under nitrogen. Direct irradiations used solutions  $8.8 \times 10^{-3}$  M while the sensitized experiments used  $1.5 \times 10^{-3}$  M.
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10. The imine (6) had the following characteristic spectral data: n.m.r. ( $\text{Cl}_4\text{C}$ )  $\delta$  1.05 (3H, s,  $\text{CH}_3$ ), 1.35 (3H, s,  $\text{CH}_3$ ), 2.35 (1H, d, cyclopropyl), 4.5 (2H, broad s,  $\text{CH}_2$ ), 6.9-7.4 (16H, m, aromatic and  $\text{CH}=\text{N}$ ); i.r. ( $\text{Cl}_4\text{C}$ ) 1650 ( $\text{C}=\text{N}$ )  $\text{cm}^{-1}$ .
11. The absence of the aziridine (7) by rupture of bond (b) in (8) could be predicted since fission to (9), bond (a) rupture, would be the preferred electronic path affording the better biradical.
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