

## Novel Photorearrangements of 2-Aza-1,4-dienes To Produce Vinylaziridines and Cyclopropylimines

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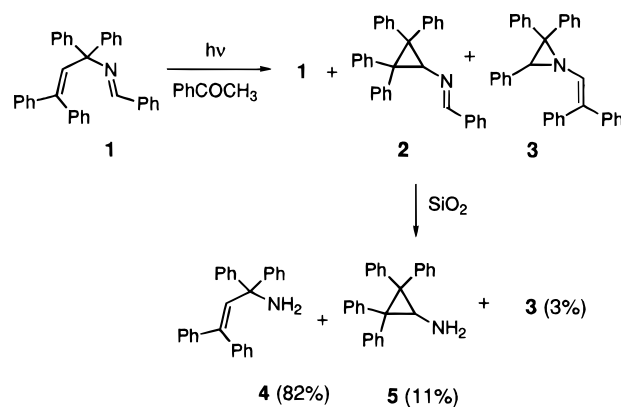
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Studies of 1,4-unsaturated systems comprise one of the most fruitful areas of organic photochemistry. Substances in this family typically undergo unique and synthetically useful photoreactions. Examples of this are found in di- $\pi$ -methane rearrangements of 1,4-dienes,<sup>1,2</sup> oxa-di- $\pi$ -methane photoreactions of  $\beta,\gamma$ -unsaturated ketones<sup>1,3</sup> and aldehydes,<sup>1</sup> 1,3-acyl migration processes of  $\beta,\gamma$ -unsaturated ketones,<sup>3a-c</sup> and aza-di- $\pi$ -methane rearrangements of 1-aza-1,4-dienes containing imines, oximes, and oxime esters.<sup>1,4</sup> Surprisingly, the photo-reactivity of closely related 2-aza-1,4-diene derivatives has yet to be described. Mariano and co-workers have previously documented the interesting single-electron-transfer (SET) promoted photocyclization reactions of iminium salts derived from 2-aza-1,4-dienes.<sup>5</sup> Our earlier efforts exploring the excited state chemistry of 1-aza-1,4-dienes<sup>1,4</sup> have recently been extended to studies of the potentially more interesting 2-aza-1,4-dienes. This expectation is due to the fact that di- $\pi$ -methane type rearrangements of 2-aza-1,4-dienes would lead to the production of vinylaziridines and/or cyclopropylimines, substances which have the capability of undergoing thermal transformation to five-membered *N*-heterocyclic products.<sup>6</sup> Our initial exploration of 2-aza-1,4-diene systems have demonstrated that these substances participate in unprecedented photorearrangement reactions under SET- and triplet-sensitized conditions to produce vinylaziridine and cyclopropylimine products.

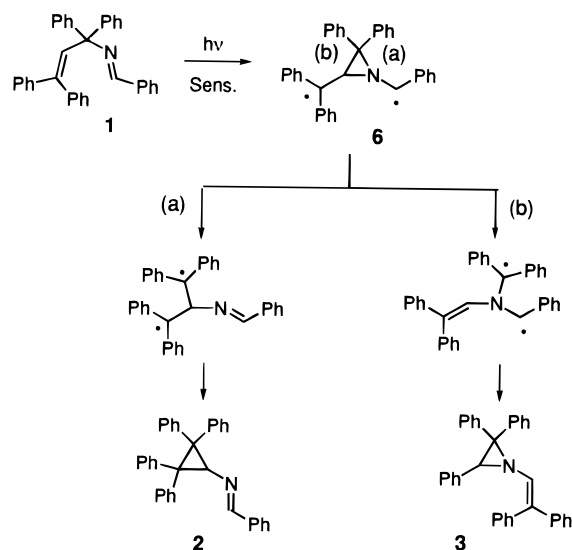
The reactivity profile was first revealed in our studies with the pentaphenyl-2-aza-1,4-diene **1**, a substance which was synthesized from 1,1,3,3-tetraphenyl-2-propen-1-ol<sup>7</sup> by standard procedures. Acetophenone, triplet-sensitized irradiation of azadiene **1** in CH<sub>2</sub>Cl<sub>2</sub> afforded after column chromatography on silica gel the propenylamine **4** (82%) and two new products that were identified as the cyclopropylamine **5** (11%) and the vinylaziridine **3** (3%) (Scheme 1). The former substance most likely arises by hydrolysis of the cyclopropylimine **2** during chromatography.

The identities of **4** and **5** were established by use of spectroscopy while unambiguous structure assignment of **3** was made by X-ray diffraction analysis.<sup>8</sup> The production of **3** and **5** in this photoreaction is in accord with the operation of mechanistic pathways involving the generation and competitive

### Scheme 1



### Scheme 2



cleavage of aziridinyldicarbonyl biradical **6** (Scheme 2). Thus, the major photoproduct **2** is formed by C–N bond cleavage in **6** (path a), and **3** results from C–C bond fragmentation in this intermediate (path b). As such, this represents the first example of a 2-aza-di- $\pi$ -methane rearrangement which occurs *via* a three-membered ring heterocyclic biradical and brings about the formation of a heterocyclic product.<sup>9</sup>

Direct irradiation of **1** in CH<sub>2</sub>Cl<sub>2</sub> by use of Pyrex-filtered light ( $\lambda > 290$  nm) also afforded, after column chromatography on silica gel, **4** (82%) and **5** (4%). Qualitatively, the direct irradiation reaction is less efficient than the triplet-sensitized process. In addition, the direct irradiation photoreaction of **1** is quenched by 1,3-cyclooctadiene, suggesting that it occurs *via* the triplet state.

In order to gain a more complete picture of the photoreactivity of azadiene **1**, an acetonitrile solution of this compound containing the SET-sensitizer 9,10-dicyanoanthracene (DCA) was irradiated. Three products were produced following silica gel chromatography and were identified as the propenylamine **4**, the vinylaziridine **3** (11%), and a new cyclopropylamine (**12**, 19%) resulting from hydrolysis of imine **11** (Scheme 3). The products generated in this process appear consistent with a

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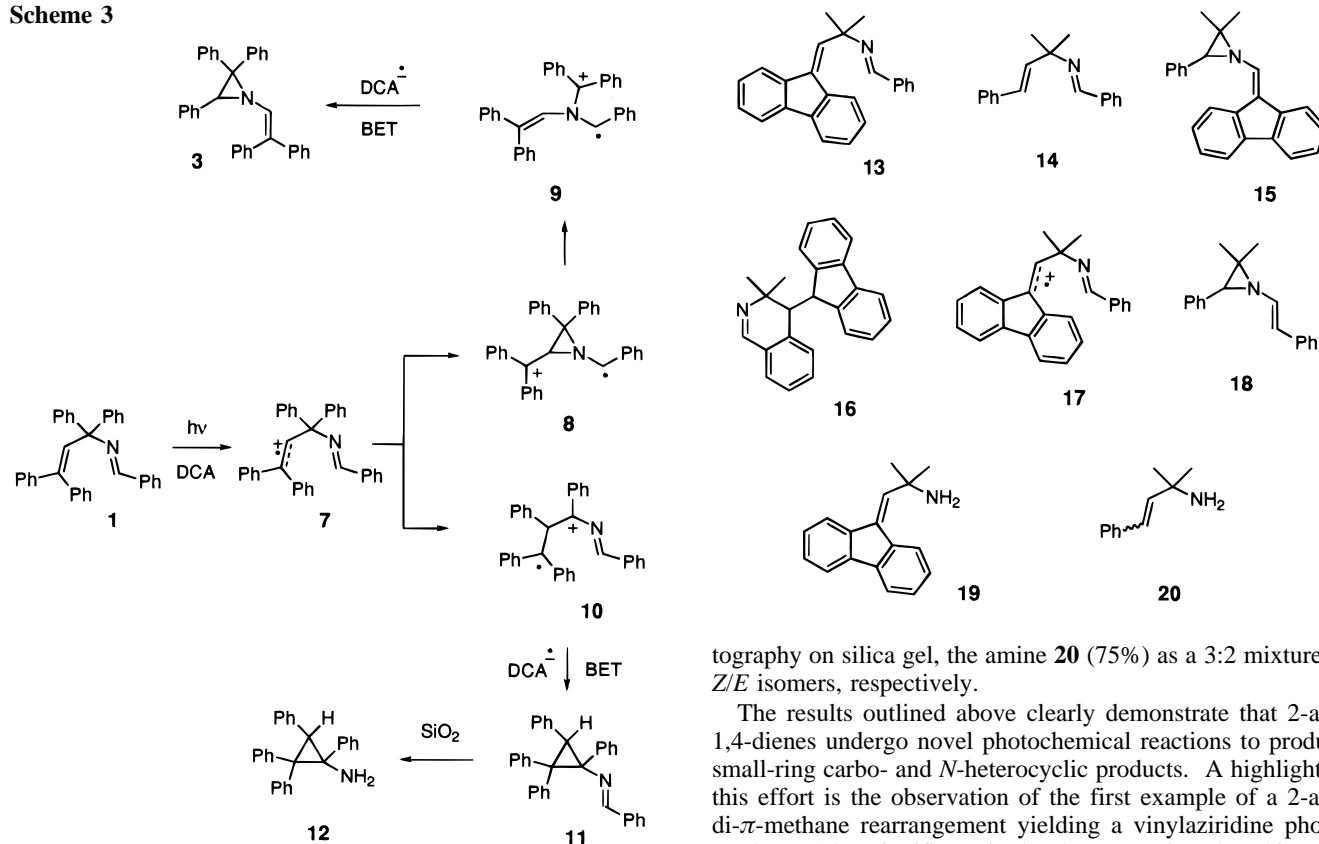
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(8) Crystallographic data for vinylaziridine **3**: crystal system, triclinic; space group, P1 (No. 2); color of crystal, colorless; unit cell parameters,  $a = 10.843(2)$  Å,  $b = 11.223(5)$  Å,  $c = 11.654(3)$  Å  $\alpha = 99.64(2)^\circ$ ;  $\beta = 96.75(2)^\circ$ ;  $\gamma = 111.05(3)^\circ$ ; Z value = 2; R value = 0.042; GOF (*F*) value = 0.47.

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## Scheme 3



pathway in which an initially formed olefin-localized cation radical intermediate **7** bridges by C–N bond formation to give aziridinyl cation radical **8**. Ring opening in **8** generates **9** that by back electron transfer and biradical cyclization yields **3**. A competitive route involving phenyl migration in **7** generates cation radical **10**, the precursor of **11**. To our knowledge, these reactions represent the first examples of SET-promoted rearrangements in 1,4-unsaturated systems that afford three-membered ring products. Of equal interest is the fact that vinylaziridine **3** is obtained in both the triplet- and SET-sensitized photoreactions of **1**.

Additional examples of these novel photorearrangement reactions were uncovered in our investigations with the 2-azadienes **13** and **14**. Upon DCA SET-sensitized irradiation, **13** reacts to afford the vinylaziridine **15** (24%) and a new product that was identified as the dihydroisoquinoline **16** (16%). The latter compound is formed by an alternative cyclization of the radical cation **17** in a reaction similar to that reported by Zimmerman *et al.* in the DCA-sensitized irradiation of aryl-substituted 1,4-pentadienes.<sup>10</sup> DCA-sensitized irradiation of azadiene **14** gives the corresponding vinylaziridine **18** in low yield (3%).<sup>11</sup>

The *m*-methoxyacetophenone triplet-sensitized reactions of these substances have also been probed. Under these conditions, azadiene **13** afforded, after column chromatography on silica gel, the amine **19** (66%), resulting from hydrolysis of the starting imine, and a complex mixture of products in which the corresponding vinylaziridine and cyclopropylamines were not present, as shown by <sup>1</sup>H NMR. Irradiation of compound **14** under these conditions brought about *cis*–*trans* isomerization around the C–C double bond, yielding, after column chroma-

tography on silica gel, the amine **20** (75%) as a 3:2 mixture of *Z/E* isomers, respectively.

The results outlined above clearly demonstrate that 2-aza-1,4-dienes undergo novel photochemical reactions to produce small-ring carbo- and *N*-heterocyclic products. A highlight of this effort is the observation of the first example of a 2-azadi- $\pi$ -methane rearrangement yielding a vinylaziridine photoproduct. Also significant is the demonstration that this rearrangement process can take place under both SET- and triplet-sensitized irradiation conditions. It is our belief that these results have opened a new area of research in organic photochemistry. Further studies are in progress to determine the scope and synthetic applications of these reactions.

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**Supporting Information Available:** Experimental procedures for the syntheses of the starting materials and for the irradiations, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for all the starting materials and photoproducts, and X-ray crystallographic data for **3** (21 pages). An X-ray crystallographic file, in CIF format, is available through the Internet only. See any current masthead page for ordering and Internet access instructions.

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(11) The yields of photoproducts have not been optimized. However, it is worth noting that although the isolated yields of products in some of these reactions are low, the yields based on recovered starting material are very high. Attempts made at this preliminary stage to increase the conversion resulted in a decrease in the yield of recovered starting material without increasing the yields of products. The possibility that the low yields of products would be due to a photoequilibrium between the reactants and the products was taken into account. To clarify this point, vinylaziridine **15** was irradiated under DCA- and *m*-methoxyacetophenone-sensitization. Under these two conditions, aziridine **15** was reactive yielding a complex mixture of products in which the corresponding 2-azadiene **13** or the amine **19** were not present. These results show that the low isolated yields of photoproducts are not due to a photoequilibrium between the reactants and the products.

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