



This assignment was confirmed by spin decoupling experiments and by other spectroscopic and analytical data.<sup>6</sup>

Comparison of the nmr spectrum of 5 with that of the nonfluxional 9-methylene-barbaralane<sup>7</sup> revealed a close resemblance, thus indicating that there is no interaction between the nonbonding orbitals on the nitrogens and the vinylcyclopropane moiety, at room temperature.

Interestingly, the direct irradiation of 5 (253.7nm, quartz) took another course affording diazahomosemibullvalene 6 as the only isolable photoisomer. No 5 could be detected by either tlc or nmr analysis. Since both 5 and 6 represent the two possible di- $\pi$ -methane rearrangement products of the bridged methylenecycloheptadiene system 4, we note here an unprecedented example of multiplicity dependent regiospecificity of the di- $\pi$ -methane rearrangement.<sup>7,8,9</sup>

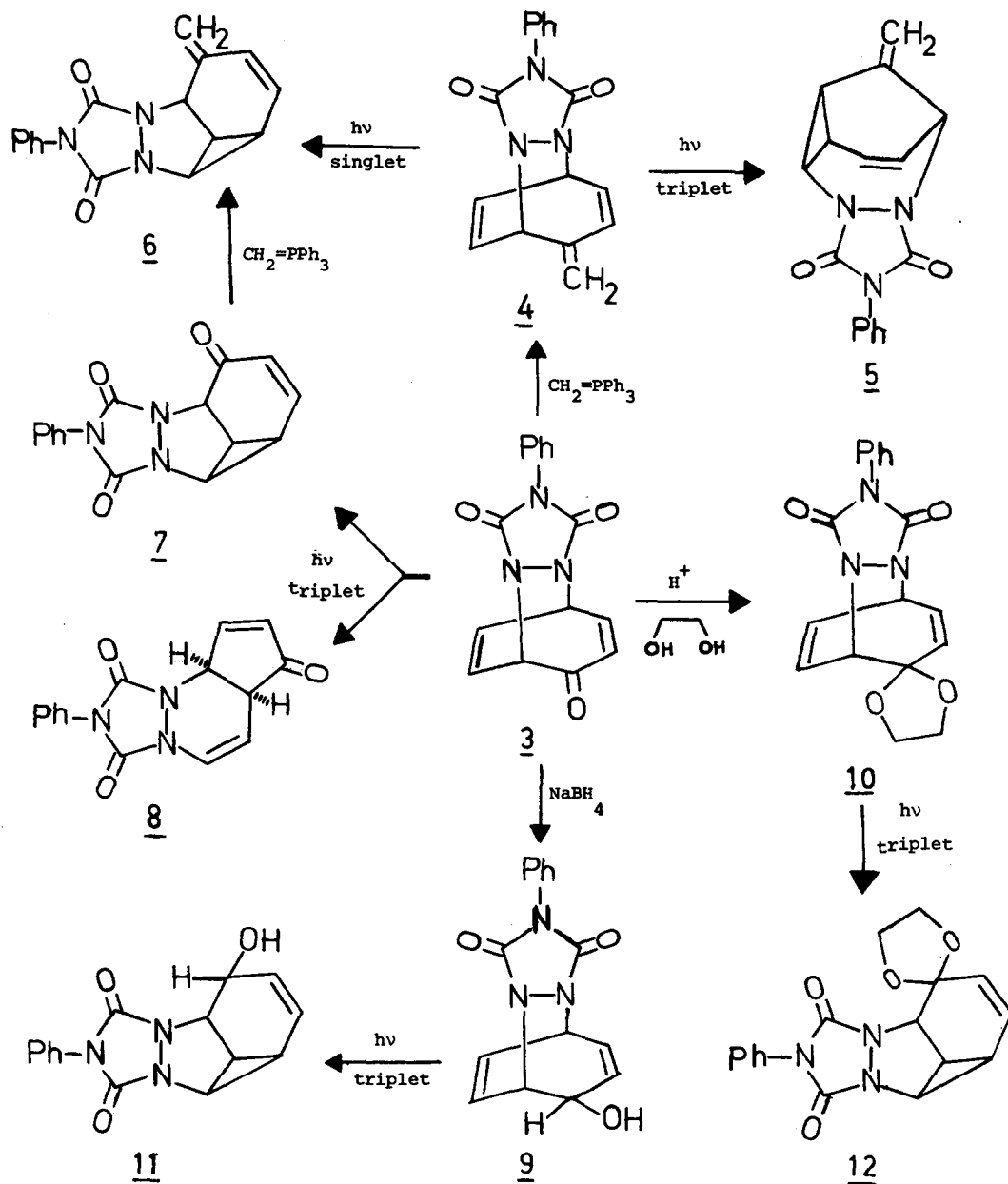
In further attempts to explore the diazahomobarrelene-barbaralane rearrangement we have studied other derivatives of the parent [3.2.2] system. Turning first to ketone 3 we found that while direct irradiation, first recorded by Sasaki *et al.*,<sup>5</sup> gave only [3,3] sigmatropic rearrangement products, the benzophenone sensitized photolysis of 3 afforded two new isomers, the expected<sup>8,10</sup> homosemibullvalone 7 and the [1,3] sigmatropic rearrangement product 8, usually formed from a singlet  $n, \pi^*$  excited state.<sup>11</sup> Ketone 7 could be transformed to 6 by a Wittig reaction, thus confirming its structural assignment.

In addition,  $\text{NaBH}_4$  reduction of 3 and the acid catalyzed ketalization of 3 gave alcohol 9 and ketal 10 respectively.

Irradiation of 9 and 10 in dilute acetone solutions resulted in the formation of 11 and 12 respectively as the only photoproducts with none of the corresponding barbaralanes. On the other hand the direct irradiation of either 9 or 10 did not afford any of the di- $\pi$ -methane rearrangement products.

Further studies of this and the related azo system are now in progress.

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