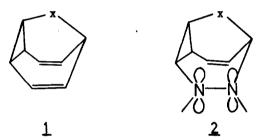
PHOTOCHEMISTRY OF BRIDGED CYCLOHEPTADIENES.¹ PHOTOCHEMICAL ENTRY TO THE DIAZABARBARALANE SYSTEM.

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While much interest has been devoted in recent years to the fluxional properties of carbocyclic bridged homotropylidene systems (1),² very few examples of the heterocyclic analogues are recorded in the literature.³

In light of recent evidence for the sp^2 character of the nitrogen atoms in condensed triazolidinediones (e.g. 3) and the potential ability of the nonbonding orbitals to participate in a Cope type rearrangement, 4,5 we have been intrigued, by the possible behaviour of the heterocyclic diaza-vinylcyclopropane system 2.



In this communication we wish to describe a photochemical access to the diazabarbaralane system $(2, X + CH_2)$, utilizing a characteristic photorearrangement of bicyclo-[3.2.2]nonatrienes.

N-Phenyl-6,7-dicarboxamide of 2-methylene-6,7-diazabicyclo[3.2.2]nona-3,8-diene (<u>4</u>), m.p. 151° , was prepared in moderate yield by the Wittig reaction of methylenetriphenylphosphorane with the readily available Diels-Alder adduct of tropone and 4-phenyl-1,2,4-triazolidine-3,5-dione (<u>3</u>).⁶

Irradiation of a 0.1% acetone solution of <u>4</u>, using a 300nm light source (Rayonet Reactor), through pyrex, resulted in smooth conversion of <u>4</u> to a single photoisomer, in 60%, which was assigned structure <u>5</u> based on its nmr spectrum (CDCl₃) which displayed signals at δ 2.13 (H₂,m, J = 8,6,6, \sim 2), 2.59 (H₁,dt,8,8, \sim 2), 4.17 (H₈,dd,8,6), 4.98 (H₅,dd,6, \sim 2), 5.22, 5.33 (2H methylene,s,s), 6.18 (H₄,H₅,m,9,6, \sim 2), 7.4 (5H aromatic,m).

This assignment was confirmed by spin decoupling experiments and by other spectroscopic and analytical data. 6

Comparison of the nmr spectrum of 5 with that of the nonfluxional 9-methylenebenzobarbaralane⁷ revealed a close resemblance, thus indicating that there is no interaction between the nonbonding orbitals on the nitrogens and the vinylcyclopropane moeity, at room temperature.

Interestingly, the direct irradiation of $\frac{5}{2}$ (253.7nm, quartz) took another course affording diazahomosemibullvalene <u>6</u> as the only isolable photoisomer. No <u>5</u> could be detected by either tlc or nmr analysis. Since both <u>5</u> and <u>6</u> represent the two possible di- π -methane rearrangement products of the bridged methylenecycloheptadiene system <u>4</u>, we note here <u>an unprecedented example of multiplicity dependent regiospecificity of the</u> di- π -methane rearrangement.^{7,8,9}

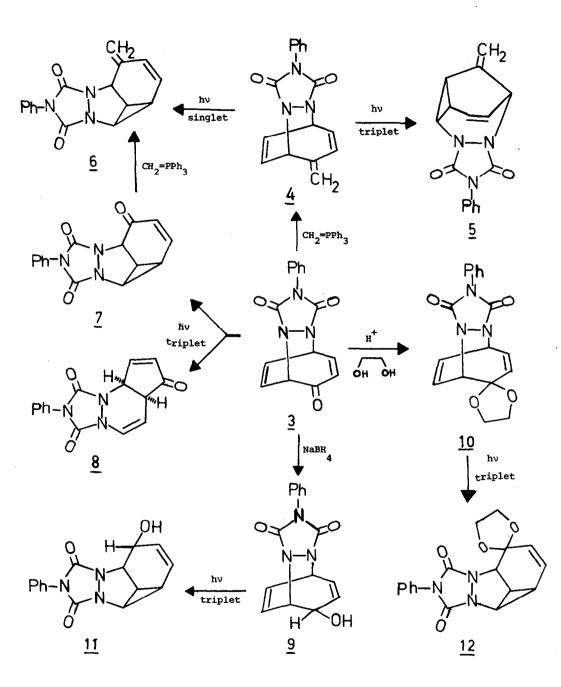
In further attempts to explore the diazahomobarrelene-barbaralane rearrangement we have studied other derivatives of the parent [3.2.2] system. Turning first to ketone <u>3</u> we found that while direct irradiation, first recorded by Sasaki <u>et al.</u>,⁵ gave only [3,3] sigmatropic rearrangement products,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

In addition, NaBH₄ reduction of $\underline{3}$ and the acid catalyzed ketalization of $\underline{3}$ gave alcohol $\underline{9}$ and ketal $\underline{10}$ 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- π -methane rearrangement products.

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

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