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# THE PHOTOISOMERIZATION OF A CYCLIC DIENAMINE (1)

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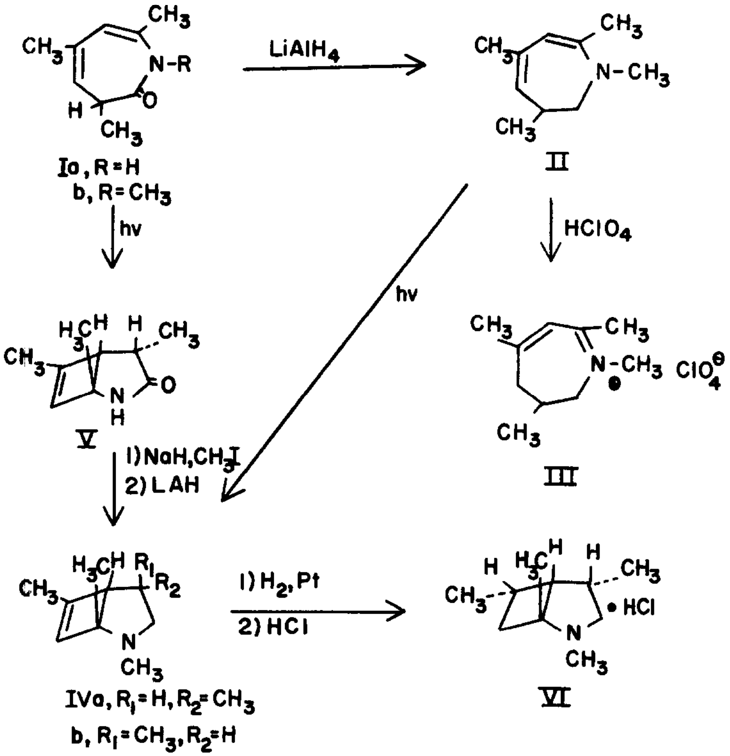
The prediction advanced by Barton in 1959 (3) that rings containing (2$\underline{n}$+1) members and $\underline{n}$ conjugated double bonds should, under conditions of irradiation, be observed to undergo bridging rather than ring cleavage reactions has proven generally reliable in the area of cycloheptadienes (2$\underline{n}$+3 members) (4). Despite the fact that photoisomerization of such seven-membered carbocyclic systems has enjoyed a large degree of success, investigations of suitable heterocyclic rings has been limited to a single example: the oxygen heterocycle, muconic anhydride (7). We wish now to report that 2,3-dihydro-1,3,5,7-tetramethyl-1H-azepine (II), a cyclic dienamine (8), conforms to this generalization and, when irradiated, readily affords the photoisomer IV.

Recently, 1,3-dihydro-2H-azepin-2-ones were reported to result in good yield by the ring expansion of sodio 2,6-disubstituted phenoxides with chloramine (10). Methylation of 1,3-dihydro-3,5,7-trimethyl-2H-azepin-2-one (Ia) with sodium hydride and methyl iodide in dimethylformamide readily gave rise to the methyl homolog Ib (11). Reduction of Ib with lithium aluminum hydride in ether afforded in excellent yield the cyclic dienamine II b.p. 50-54° (1.0 mm.); $\nu^{CCl_4}$ 1635 and 1595 cm.$^{-1}$



(C=C); $\lambda_{max}^{Et_2O}$ 301 mμ (7,050). The dienamine II was a colorless liquid which rapidly yellowed on exposure to the atmosphere, but which could be preserved for prolonged periods in a nitrogen atmosphere at -10°. The n.m.r. spectrum ($CDCl_3$) of II was fully compatible with the assigned structure. Treatment of II with perchloric acid yielded a perchlorate salt as white prisms from acetone, m.p. 106-106.5° (12), $\nu^{Nujol}$ 1680 ($C=N^{\oplus}$) and 1605 cm.$^{-1}$ (C=C); $\lambda_{max}^{EtOH}$ 272 mμ (4,950), which has been assigned structure III on the basis of spectral evidence.

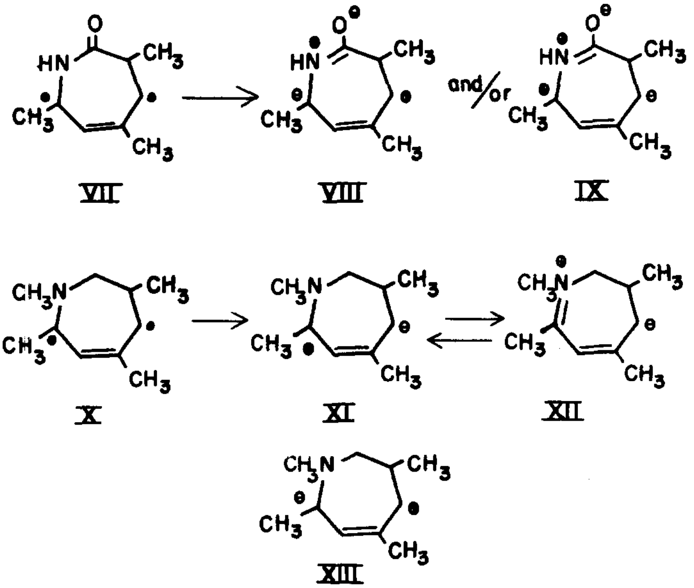
Irradiation of a dry, purified tetrahydrofuran solution of II in an atmosphere of nitrogen with an unfiltered 200W Hanovia lamp for three days afforded the colorless amine IV in 81% yield, b.p. 53° (15 mm.) (12), $n_D^{24}$ 1.4568, $\nu^{CCl_4}$ 3020 and 1635 cm.$^{-1}$ (C=C), no UV absorption above 236 mμ. The stable photoproduct IV actually consisted of a mixture of the isomers a and b in a ration of about 6:1 as determined by gas chromatography and n.m.r. techniques. Treatment of the mixture with ethanolic picric acid gave the picrate of IVa, m.p. 212-214° (12).

In an ancillary experiment, irradiation of a tetrahydrofuran solution of Ia under similar conditions gave rise to the single isomer V, m.p. 73-74° (12), in 77.5% yield. The stereochemical structure of V was likewise readily derived from its n.m.r. spectrum (13). Methylation and lithium aluminum hydride reduction of V readily afforded IVa, identified by comparison of the free bases and picrate salts.

It is obvious that the photochemical behavior of Ia and II parallel each other. An important aspect of this similarity is the role of the nitrogen atom in the photoexcited states of these molecules, for an amide nitrogen and a basic enamine nitrogen should not be expected to exert their influence in similar fashions.

In considering first the photochemical rearrangement of amide Ia, we find that the reaction proceeds only to the extent of 35-40% and that sizeable quantities of Ia are recovered unchanged, even after prolonged exposure to ultraviolet light. On the other hand, the cyclic dienamine II rearranges under similar conditions in excellent yield to IV.

Initial excitation of Ia and II must almost certainly lead to the singlet states depicted as VII and X, respectively. Species VII may then undergo an electron demotion process and give rise to VIII and IX. Most interestingly, VIII would receive little, if any, stabilization from the



amide nitrogen (written in its polarized form), while IX would probably resist formation because of the proximity, and resulting repulsion, of like charges.

On the contrary, X can, by a similar process, be converted to XI, a dipolar structure which is capable of considerable stabilization due to the proximity of the basic nitrogen (XI → XII). Structure XIII (incapable of stabilization) could also be formed from X by the electron demotion pathway, but conceivably could also, under the conditions of photochemical excitation, be reconverted to its singlet state (X) and then to XI.

The stabilization of the photoexcited state by a proximately located nitrogen atom should lower the energy for its formation and render more facile the photoisomerization process. This concept agrees with the observed data.

## REFERENCES

(1) Dihydroazepinone Chemistry. V. For paper IV, see L. A. Paquette and J. K. Reed, *J. Med. Chem.*, in press.

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(3) D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1959).

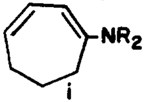
(4) To the author's knowledge, 3,5-cycloheptadienone and 2-methyl-3,5-cycloheptadienone are the sole examples to date of 1,3-cycloheptadienes which have yielded ring cleavage products rather than valence tautomers on irradiation.

(5) O. L. Chapman and G. W. Borden, *J. Org. Chem.*, **26**, 4185 (1961).

(6) O. L. Chapman, D. J. Pasto, G. W. Borden and A. A. Griswold, *J. Am. Chem. Soc.*, **84**, 1220 (1962).

(7) G. J. Fonken, *Chem. and Ind.*, 1575 (1961).

(8) In keeping with the nomenclature of enamines (9), II is termed a "cyclic dienamine" while *i* would simply be a "dienamine".



*i*

(9) J. Szmuszkovicz, "*Advances in Organic Chemistry, Methods and Results*," eds. R. A. Raphael, E. C. Taylor and H. Wynberg, Interscience Publishers, Inc., New York, 1963.

(10) L. A. Paquette, *J. Am. Chem. Soc.*, **84**, 4987 (1962); see also W. Theilacker, K. Ebke, L. Seidl and S. Schwerin, *Angew. Chem.*, **75**, 208 (1963).

(11) L. A. Paquette, *J. Am. Chem. Soc.*, in press.

(12) Satisfactory carbon, hydrogen and nitrogen analyses were obtained for all the new compounds described herein.

(13) A thorough discussion of these spectra will soon be published; see, L. A. Paquette, *J. Am. Chem. Soc.*, in press; see also, O. L. Chapman and E. D. Hoganson, *ibid.*, in press.