

tatively the photochemical behavior of  $\text{COT}^{2-}$  as well as that of previously observed types of compounds (phenols, ketones, amines, hydrocarbons).<sup>8</sup> The acidity of the cyclooctatrienes is predicted not to be greatly enhanced in the excited state, again in accord with experimental observations. It is to be expected that this simple theory will work in many cases since, although quantitative correlations of spectra are fairly poor, qualitative results have significance and one can often predict the direction of the spectral shift on going to the corresponding conjugate acid (or base). Since the electronic differences are large and may be responsible for  $pK$  changes of the order of 5–30,<sup>7–10</sup> it is clear that even a crude estimate is likely to give at least the correct direction of the change.

Hückel calculations suggest that carbanions probably cannot be treated as a general class. In contrast to  $\text{COT}^{2-}$ , anions of the benzylic type are predicted to be less basic when irradiated, which is also expected from the typical bathochromic shift of these anions relative to their conjugate acids.<sup>14</sup>

The limitations of this approach should be recognized. When calculated differences are small, they should be considered judiciously, and special care should be taken with highly symmetrical systems and those with nonbonding electrons. Nevertheless in many cases the predictions will be unambiguous, and the ease with which these calculations can be carried out makes this an attractive method for approaching new systems.<sup>15</sup>

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state should be proportional to the  $\pi$ -energy change on protonation of the excited state.

(13) Reference 11, Chapter 14.

(14) A. Streitwieser, Jr., and J. I. Brauman, *J. Am. Chem. Soc.*, **85**, 2633 (1963); R. Grinter and S. F. Mason, *Trans. Faraday Soc.*, **60**, 264 (1964).

(15) The same reasoning should be applicable to carbonium ion behavior as well.

(16) National Science Foundation Predoctoral Fellow, 1966–present.

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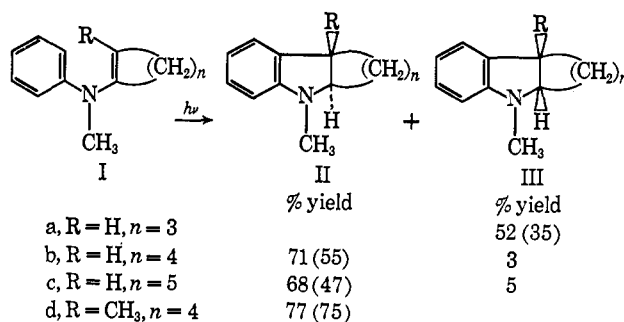
## Photochemical Synthesis of 2,3-Dihydroindoles from N-Aryl Enamines<sup>1</sup>

Sir:

Oxidative photocyclizations of *cis*-stilbenes to phenanthrenes are well known.<sup>2</sup> Closely related and noteworthy in the present context are the oxidative cyclizations of diphenylamines to carbazoles and phenylthioethenes to benzothiophenes.<sup>3</sup> Nonoxidative cyclizations, in contrast, are quite rare. Available examples are limited to stilbenes bearing strongly electron-withdrawing substituents in the  $\alpha, \beta$  positions,<sup>4</sup> 2-biphenyl-

isocyanate,<sup>5</sup> and certain acrylic acid anilides.<sup>6</sup> We now report a nonoxidative cyclization of N-aryl enamines which provides a useful two-step synthesis of 2,3-dihydroindoles from ketones and N-alkylanilines.<sup>7</sup> The cyclization proceeds under mild conditions (irradiation in ether solution at room temperature) and should be excellent for labile compounds. The method is suitable for N-aryl enamines derived from cyclic or acyclic ketones and can be used to prepare indole derivatives in which ring C is five, six, or seven membered and offers an entry into the difficultly available *trans*-hexahydrocarbazole series. The method provides a direct means for introduction of angular substituents at C-3 and should find significant application in the synthesis of dihydroindole alkaloids.

Photochemical cyclization of 1-(N-methylanilino)-cycloalkenes (I) gives primarily the *trans* tricyclic product II except for Ia which gives only the *cis* product III.



Degassed ether solutions of the enamine ( $2.3 \times 10^{-2} M$ ) were irradiated with a Pyrex-jacketed immersion lamp. Products were isolated by chromatography or distillation after removal of the ether. Minor products were separated by vpc. Yields given above are based on vpc analysis using known thermal conductivity ratios and an internal standard. Isolated yields are given in parentheses. Products IIb, IIIa, IIIb, and IIIc were identified by comparison with authentic samples. Product IIc was identified by oxidation to 1-methylcycloheptindole and by its spectroscopic properties.<sup>8,9</sup> The stereochemistry is tentatively considered to be *trans* because the product differs from the isomer available by reduction of the corresponding indole.<sup>10</sup> Product IIc shows the expected spectral properties<sup>11</sup> and is not identical with the known *cis* isomer.

(4) M. V. Sargent and C. J. Timmons, *J. Amer. Chem. Soc.*, **85**, 2186 (1963); *J. Chem. Soc.*, 5544 (1964).

(5) J. S. Swenton, *Tetrahedron Lett.*, 2855 (1967).

(6) P. G. Cleveland and O. L. Chapman, *Chem. Commun.*, 1064 (1967).

(7) The N-aryl enamines were prepared by an established method (J. Hoch, *C. R. Acad. Sci., Paris*, **200**, 938 (1935)). Previously unknown enamines gave satisfactory element analyses and spectra.

(8) IIc: bp 119–120° (0.5 mm); mol wt 201 (mass spectrometry);  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  296 ( $\epsilon$  2550), 251 m $\mu$  ( $\epsilon$  8090); aromatic protons ( $\delta$  6.1–7.1, m, 4 H), methine protons ( $\delta$  2.6–3.0, m, 2 H), N-methyl protons ( $\delta$  2.55, s, 3 H), and methylene protons ( $\delta$  1.2–2.4, m, 10 H); 13.36, 13.47 (sh), and 13.78  $\mu$ .

(9) All new compounds gave satisfactory elemental analyses.

(10) The isomer obtained by reduction is presumed to be *cis* because reduction of tetrahydrocarbazole and cyclopent[b]indole give *cis*-dihydro compounds. In these cases, however, there is a clear thermodynamic preference for the *cis* isomer. The relative thermodynamic stabilities of *cis*- and *trans*-dihydrocyclohept[b]indole are not clear.

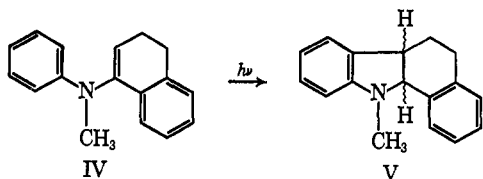
(11) IIc: bp 140° (5 mm); mol wt 201 (mass spectrometry); aromatic protons ( $\delta$  6.3–7.2, m, 4 H), N-methyl protons ( $\delta$  2.47, s, 3 H), methylene and methine protons ( $\delta$  0.9–2.7, m, 9 H), and C-methyl protons ( $\delta$  0.95, s, 3 H); 13.48 and 13.96  $\mu$ .

(1) Photochemical Transformations. XXVIII.

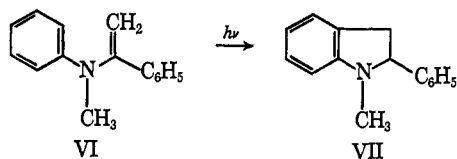
(2) F. R. Stermitz in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 247.

(3) (a) H. Linschitz and K. H. Grellman, *J. Amer. Chem. Soc.*, **86**, 303 (1964); K. H. Grellman, G. M. Sherman, and H. Linschitz, *ibid.*, **85**, 1881 (1963); (b) S. H. Groen, R. M. Kellogg, J. Buter, and H. Wynberg, *J. Org. Chem.*, **33**, 2218 (1968).

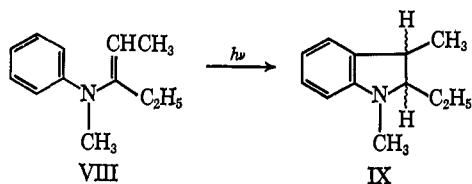
Similar irradiation of the enamine IV derived from N-methylaniline and 1-tetralone gave two isomers of V<sup>12</sup> in a combined isolated yield of 60%. The same two stereoisomers are obtained by reduction of the corresponding indole.



The cyclization is not limited to enamines derived from cyclic ketones. Irradiation of  $\alpha$ -(N-methylanilino)styrene (VI) gives VII<sup>13</sup> in 66% isolated yield, and irradiation of a mixture of *cis* and *trans* isomers of



VIII gives two stereoisomers of IX (43%).<sup>14</sup> Reduction of 1,3-dimethyl-2-ethylindole gives the same two isomers of IX.



The cyclizations illustrated above may be considered as an electrocyclic reaction of divinylamines which, if it is a photochemical process, should occur in a conrotatory manner.<sup>15-19</sup> Ejection demotion should then produce a dipolar species<sup>20</sup> which can undergo a thermal, suprafacial [1,4] sigmatropic shift of a hydrogen atom giving the *trans*-2,3-disubstituted product.<sup>16, 21, 22</sup>

(12) Va: mp 135–136°; mol wt 235 (mass spectrometry); aromatic protons ( $\delta$  6.1–7.2, m, 8 H), methine protons ( $\delta$  4.29, d, 1 H;  $\delta$  3.35–3.75, m, 1 H), methylene protons ( $\delta$  2.5–2.8, m, 2 H;  $\delta$  1.7–2.1, m, 2 H), N-methyl protons ( $\delta$  2.57, s, 3 H);  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  257 ( $\epsilon$  9720), 302 m $\mu$  ( $\epsilon$  2910); 13.27, 13.50  $\mu$ ; Vb: liquid; mol wt 235 (mass spectrometry); aromatic protons ( $\delta$  6.4–7.4, m, 8 H), methine proton ( $\delta$  3.52, d, 1 H), N-methyl protons ( $\delta$  2.85, s, 3 H), methylene and methine protons ( $\delta$  1.5–3.0, m, 5 H); 13.3 (sh) and 13.5  $\mu$ .

(13) VII: mp 94–95°; mol wt 209 (mass spectrometry); aromatic protons ( $\delta$  6.2–7.5, m, 9 H), methine proton ( $\delta$  4.1–4.5, q, 1 H), methylene protons ( $\delta$  2.7–3.5, m, 2 H), N-methyl protons ( $\delta$  2.57, s, 3 H);  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  252 ( $\epsilon$  8960), 297 m $\mu$  ( $\epsilon$  2870); 13.06, 13.33, 13.47, 14.02, and 14.25  $\mu$ .

(14) IXa: liquid; mol wt 175 (mass spectrometry); aromatic protons ( $\delta$  6.2–7.1, m, 4 H), methine protons ( $\delta$  2.8–3.3, m, 2 H), N-methyl protons ( $\delta$  2.64, s, 3 H), methylene protons ( $\delta$  1.4–1.9, m, 2 H), C-methyl protons ( $\delta$  1.07, d, 3 H;  $\delta$  1.0, t, 3 H); 13.31 and 13.60  $\mu$ ; IXb: liquid; mol wt 175 (mass spectrometry); aromatic protons ( $\delta$  6.2–7.0, m, 4 H), methine protons ( $\delta$  2.7–3.0, m, 2 H), N-methyl protons ( $\delta$  2.68, s, 3 H), methylene protons ( $\delta$  1.4–1.9, m, 2 H), C-methyl protons ( $\delta$  1.30, d, 3 H;  $\delta$  0.98, t, 3 H); 13.38 and 13.72  $\mu$ .

(15) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

(16) R. Hoffmann and R. B. Woodward, *Accounts Chem. Research*, **1**, 17 (1968); R. B. Woodward, "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, pp 217–249.

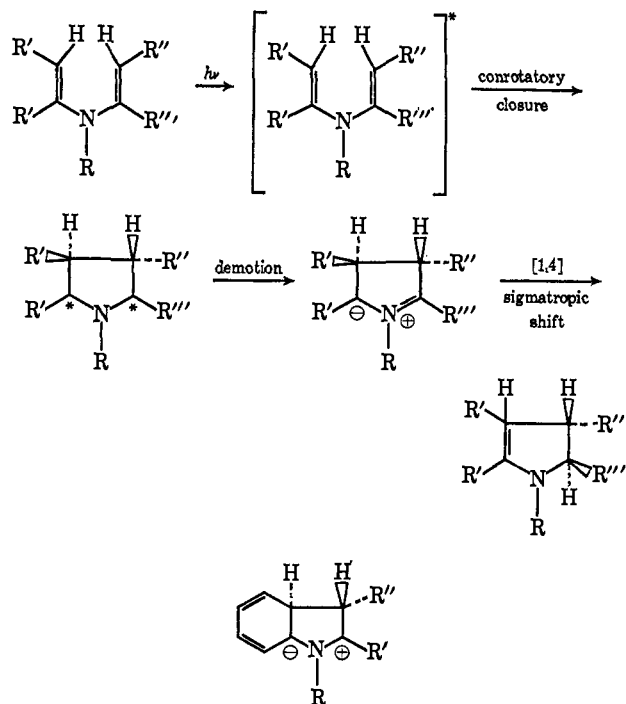
(17) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965).

(18) K. Fukui, *Tetrahedron Lett.*, 2009 (1965).

(19) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564, 1566 (1966).

(20) An intermediate has been detected in the oxidative cyclization of N-substituted diphenylamines to N-substituted carbazoles which has been assigned a dipolar structure.<sup>20</sup>

(21) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965).



If this is the path by which the *trans* products are formed, it is not clear how the *cis* products are formed. Deuterium labeling experiments with 1-(N-methyl-2,4,6-trideuterioanilino)cyclohexene showed that at least the major portion of the hydrogen transfer is intramolecular. Satisfactory quantitative data are difficult to obtain because both starting material and product fragment even at low ionizing potential.

Irradiation of the N-aryl enamines cited above in the presence of oxygen or iodine, conditions known to favor oxidative cyclization,<sup>1</sup> gives small amounts of the corresponding indoles, but the 2,3-dihydroindoles are still the major products.

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(22) In the dihydroindole system the hydrogen shift could also be considered a [1,8] sigmatropic shift. The thermal reaction in this case should also be suprafacial. Antarafacial shifts are excluded by the ring system.

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## Diels–Alder Reactions of Diazadienes and Chemistry of the Adducts

Sir:

Despite the wealth of mechanistic and synthetic information on the Diels–Alder reaction, little is known about the behavior of heterodienes in this reaction. This communication describes our results with 2,3-diazadienes which are reactive four-electron components and yield interesting and otherwise inaccessible products.

Cyclic azines such as the isopyrazoles Ia and Ib<sup>1</sup>

(1) Prepared by Mrs. V. Abraitys of these laboratories by reaction of the corresponding 1,3-dione with hydrazine according to the method of I. I. Grandberg, A. P. Krasnoshechek, A. N. Kost, and G. K. Faizova, *J. Gen. Chem. USSR*, **33**, 2521 (1963). The compound Ia was reported; Ib is a new composition.