

Nonoxidative Photocyclization of *N*-Aryl Enamines. A Facile Synthetic Entry to *trans*-Hexahydrocarbazoles¹

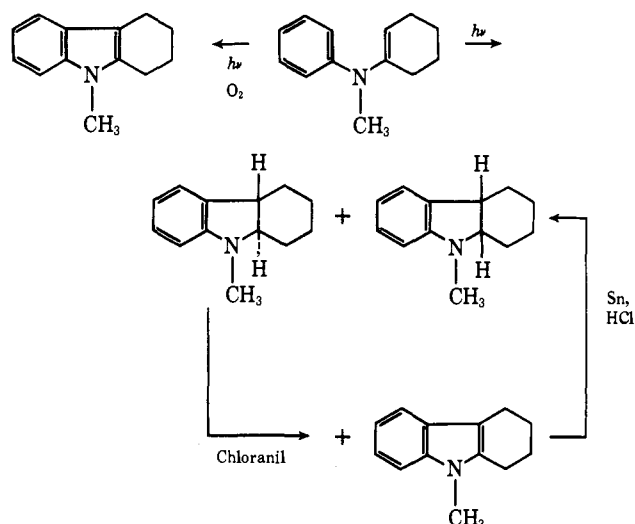
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Abstract: Nonoxidative photocyclization of *N*-arylenamines gives indolines in good yield. The reaction provides the first useful synthetic entry to *trans*-hexahydrocarbazoles and is useful for introduction of angular substituents in hexahydrocarbazoles. Acyclic as well as cyclic enamines undergo the reaction. The *trans* stereochemistry of the hexahydrocarbazole system is established by X-ray crystallography. The cyclization of α -(*N*-methylanilino)styrene proceeds *via* a triplet excited state. The *trans* stereochemistry of the reaction observed with *N*-methylanilino-cyclohexenes and *N*-methylanilino-cycloheptene is reasonable in terms of qualitative molecular orbital arguments. The hydrogen migrations observed are shown by deuterium-labeling experiments to involve two competing processes, a 1,4-shift and a sequence of 1,2-shifts.

Oxidative photocyclization of *cis*-stilbene and related systems has been known and studied for some time.² Nonoxidative photocyclization has been rather generally ignored as a synthetic process although a few examples of such reactions are known.³ Our work with the nonoxidative cyclization of acrylanilides⁴ led us to examine other systems of potential interest. Our attention turned first to *N*-aryl enamines because they held potential as synthetic precursors for indolines (2,3-dihydroindoles) and indoles and because they are readily synthesized in high yield.⁵

Irradiation of *N*-methylanilino-cyclohexene in degassed ether gave one major and two minor products. Analysis by vpc indicated yields of 71, 3, and 3%. The major product was isolated in 55% yield (together with small amounts of the two minor products). Oxidation of the major product gave *N*-methyltetrahydrocarbazole. Reduction of *N*-methyltetrahydrocarbazole with tin and hydrochloric acid gave *N*-methyl-*cis*-hexahydrocarbazole⁷ which proved to be identical with one of the minor products. The other minor product was identical with *N*-methyltetrahydrocarbazole. The major product of the reaction was identical with authentic *N*-methyl-*trans*-hexahydrocarbazole obtained in trace quantities in the reduction of *N*-methyltetrahydrocarbazole. The melting points of the picrate and methiodide of the major product agreed with the literature values for the derivatives of *N*-methyl-*trans*-hexahydrocarbazole. An attempt to cyclize *N*-methylanilino-cyclohexene thermally was unsuccessful.



Control experiments showed that the *cis*- and *trans*-hexahydrocarbazole derivatives were stable to irradiation under the conditions of the experiment in the absence of oxygen. Irradiation of either the *cis* or *trans* isomer of *N*-methylhexahydrocarbazole in the presence of oxygen gave a low yield of *N*-methyltetrahydrocarbazole. The *trans*- and *cis*-*N*-methylhexahydrocarbazoles were not interconverted on irradiation in the presence or absence of oxygen.

Assignment of the *cis* structure to the major reduction product of tetrahydrocarbazoles is generally accepted.^{8,9} The assignment is based ultimately on the assumption that *cis*-hexahydrocarbazoles are more stable than *trans*-hexahydrocarbazoles. This assignment, though plausible, is not rigorous. The *trans* stereochemical assignment rests in turn on the *cis* assignment, since the quantities of the *trans* isomer available in the past have been very limited. One might expect on the basis of conformational arguments similar to those applied to *cis*- and *trans*-decalin that the *cis*-hexahydrocarbazoles would show temperature-dependent nmr spectra due to conformational mobility while the *trans* isomers should not. In fact, the nmr spectra of *cis*- and *trans*-*N*-methylhexahydrocarbazoles showed

(1) Photochemical Transformations, XXXVIII. Preliminary communications of portions of this work have been published: O. L. Chapman and G. L. Eian, *J. Amer. Chem. Soc.*, **90**, 5329 (1968); and A. Bloom and J. C. Clardy, *Chem. Commun.*, 531 (1970).

(2) E. V. Blackburn and C. J. Timmons, *Quart. Rev., Chem. Soc.*, **23**, 482 (1969); F. R. Stermitz, *Org. Photochem.*, **1**, 247 (1967); H. Stegemeyer, *Naturwissenschaften*, **53**, 582 (1966).

(3) M. V. Sargent and C. J. Timmons, *J. Amer. Chem. Soc.*, **85**, 2186 (1963); *J. Chem. Soc.*, 5544 (1964); J. S. Swenton, *Tetrahedron Lett.*, 2855 (1967); I. Ninomiya, T. Naito, and T. Mori, *ibid.*, 2259, 3643 (1969).

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

(5) We have used Hoch's method⁶ for the preparation of the enamines.

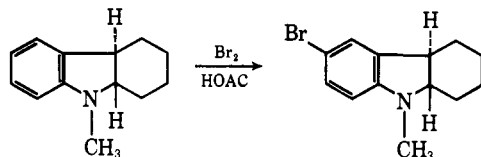
(6) J. Hoch, *C. R. Acad. Sci., Paris*, **200**, 938 (1935).

(7) W. H. Perkin and S. G. P. Plant, *J. Chem. Soc.*, 125, 1512 (1924). The *N*-methyl-*trans*-hexahydrocarbazole is stable to the conditions of the reduction (see Experimental Section).

(8) H. Booth, F. E. King, and J. Parrick, *J. Chem. Soc.*, 2302 (1958).

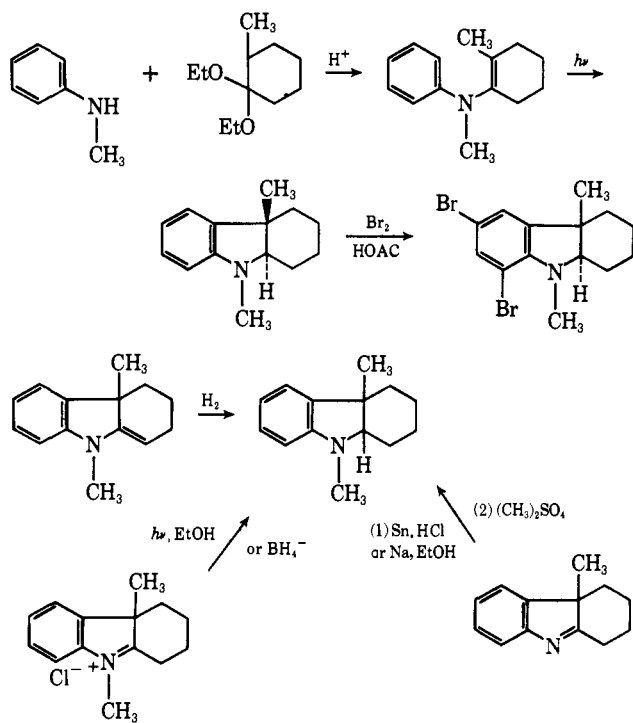
(9) J. Gurney, W. H. Perkin, and S. G. P. Plant, *ibid.*, 2627 (1927).

no temperature dependence in the range -50 to $+40^\circ$. X-Ray crystallography seemed a promising solution to the problem of rigorous stereochemical assignment. With this goal in mind *N*-methyl-*trans*-hexahydrocarbazole was brominated. In the end, crystals of another



derivative proved more suitable for X-ray crystallographic analysis (see below).

Synthesis of 1-(*N*-methylanilino)-2-methylcyclohexene is readily accomplished by reaction of *N*-methylaniline and the diethyl ketal of 2-methylcyclohexanone. Irradiation of the enamine in degassed ether gave *trans*-4a,9-dimethyl-1,2,3,4,4a,9a-carbazole (75%, isolated as the picrate). Two other minor products were detected but not isolated. The photoproduct is not identi-



cal with *cis*-4a,9-dimethyl-1,2,3,4,4a,9a-hexahydrocarbazole which is available by a variety of reductive procedures.¹⁰⁻¹² Crystals of the readily obtained dibromide of the photoproduct proved suitable for X-ray crystallographic analysis, and the structure was established by this means.

The crystals of *trans*-6,8-dibromo-4a,9-dimethyl-1,2,3,4,4a,9a-hexahydrocarbazole used for X-ray diffraction were monoclinic, space group $P2_1/n$. The unit cell parameters are $a = 12.53 \pm 0.02 \text{ \AA}$, $b = 15.88 \pm 0.02 \text{ \AA}$, $c = 7.22 \pm 0.02 \text{ \AA}$, and $\beta = 95.60 \pm 0.10^\circ$. The calculated density indicated four molecules per unit cell. A three-dimensional Patterson synthesis computed from the observed data (1444 reflections) gave the positions of the two independent bromine atoms. The remaining atoms (other than hydrogen) were found by

(10) M. F. Millson and R. Robinson, *J. Chem. Soc.*, 3362 (1955).

(11) H. Booth, F. E. King, and J. Parrick, *ibid.*, 2302 (1958).

(12) I. P. Ceratti and H. Schmidt, *Helv. Chim. Acta*, **45**, 1992 (1962).

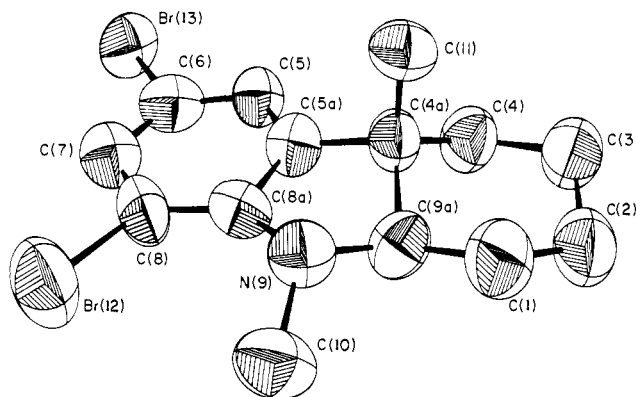
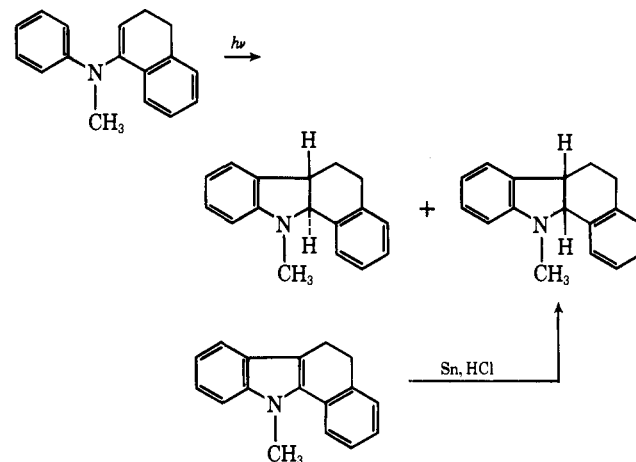


Figure 1. Computer drawing of *trans*-6,8-dibromo-4a,9-dimethyl-1,2,3,4,4a,9a-hexahydrocarbazole including anisotropic thermal motion.

successive structure factor calculations and electron density syntheses. These positions were refined by full matrix least-squares techniques with anisotropic thermal parameters for all atoms to a conventional discrepancy index [R] of 0.089. The structure is shown in Figure 1 and bond distances and angles are tabulated in the Experimental Section. The *trans* stereochemistry at positions 4a and 9 is unambiguously established.

The enamine of α -tetralone provides an example of the utility of the photocyclization in the synthesis of tetracyclic indolines. Two isomeric products are formed in 56 and 39% yield.



The *trans* isomer (major product) showed a larger value for the coupling constant of the bridgehead protons (12.5 Hz) than the *cis* isomer (9 Hz). The *cis* isomer was identified by comparison with an authentic sample prepared by reduction of the corresponding indole.

The effect of para substituents in the aniline ring of *N*-methylanilino-cyclohexene was examined briefly. The *p*-bromo derivative did not give any indoline derivative presumably because of photochemical cleavage of the carbon-bromine bond. The *p*-methoxy derivative gave *trans*-6-methoxy-9-methyl-1,2,3,4,4a,9a-hexahydrocarbazole (12% yield). No attempt was made to maximize the yield in this system.

The effect of ring size on the system was explored with the enamines of cycloheptanone and cyclopentanone. Irradiation of the enamine of cycloheptanone gave *trans*-2,3-dihydro-1-methyl-2,3-cycloheptindole as

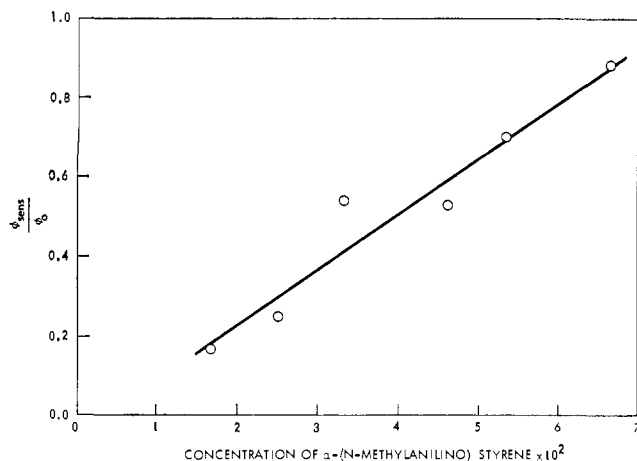
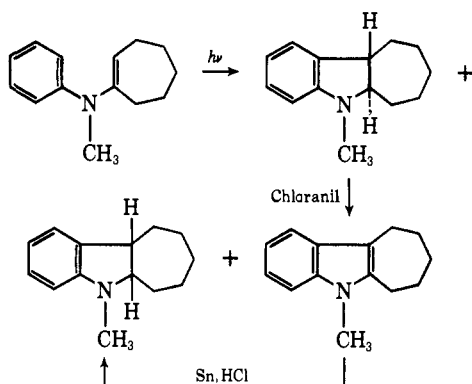
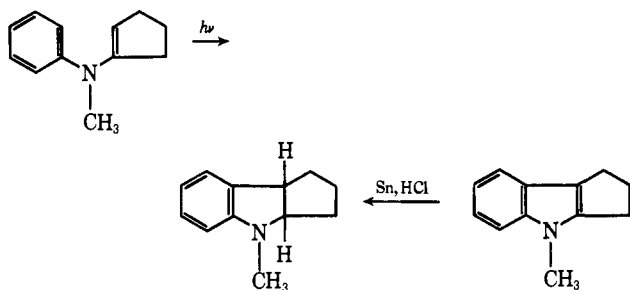


Figure 2. Plot of $\phi_{\text{sens}}/\phi_0$ vs. concentration of α -(*N*-methylanilino)-styrene.

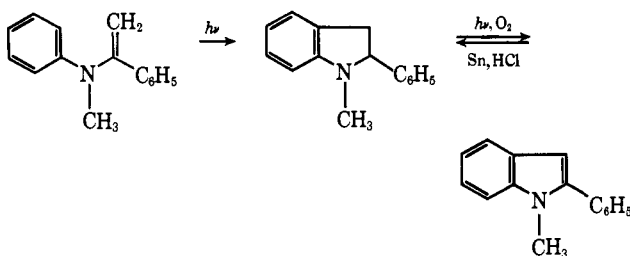
the major product (75%) and minor amounts of the *cis* isomer and the indole. The *cis* isomer and the indole were identified by comparison with authentic samples.



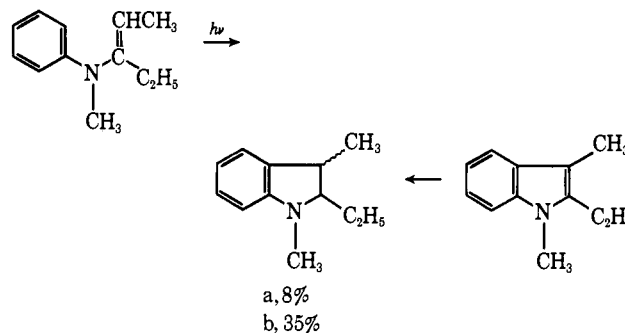
The *trans* isomer was oxidized to the indole. Similar irradiation of the enamine of cyclopentanone gave only the *cis*-indoline (52%) which was identical with the authentic material prepared by reduction of the indole.



The photocyclization is satisfactory for certain enamines of acyclic ketones. Irradiation of α -(*N*-methylanilino)styrene, for example, gives 1-methyl-2-phenyl-2,3-dihydroindole in 73% isolated yield. Irradiation of the product in the presence of oxygen gives



the indole. Irradiation of the enamine of 3-pentanone gives two isomeric indolines in a 4.7:1 ratio. The same two isomers are obtained in a 2.1:1 ratio by reduction of 1,3-dimethyl-2-ethylindole. In contrast, irradiation of the β -(*N*-methylanilino)styrene and ethyl



3-(*N*-methylanilino)acrylate did not give indoline products.

Attempts to make the oxidative cyclization of *N*-aryl enamines to indoles a preparatively useful reaction met with little success. Oxidants employed were oxygen and iodine.¹³ In both cases the indoline was formed under the oxidative conditions. The indolines were converted slowly on irradiation in the presence of oxygen to the indoles.

The photocyclization of α -(*N*-methylanilino)styrene was selected for study because it is a very clean reaction and the product is not a mixture of stereoisomers. The quantum yield for formation of 2-phenyl-1-methyl-2,3-dihydroindole is 0.2 at 340 ± 15 nm at room temperature. The addition of 1,3-cyclohexadiene (up to 0.1 *M*) did not quench product formation. The reaction is sensitized by sensitizers with triplet energies as low as 61 kcal/mol but not by fluorenone ($E_T = 53$ kcal/mol). The $\phi_{\text{sens}}/\phi_0$ ratios are low because the concentration of enamine must be kept low in order for the sensitizer to absorb the light. A study of the effect of enamine con-

Table I. Sensitization of Photocyclization of α -(*N*-Methylanilino)styrene

Sensitizer	E_T	$\phi_{1,sc}$	[En-amine] $\times 10^2$	[Sens] $\times 10^2$	$\phi_{\text{sens}}/\phi_0$	λ
Xanthone	74		5.12	1.05	0.45	334
Michler's ketone	61	1.0	5.12	1.15	0.60	334
Fluorenone	53	0.93	4.60	8.15	0.01	336

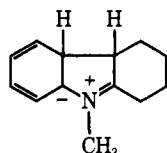
centration on the ratio $\phi_{\text{sens}}/\phi_0$ with Michler's ketone is shown in Figure 2. The sensitizer is absorbing essentially all of the light in these experiments. As the enamine concentration is increased, the fraction of the sensitizer triplets quenched by enamine increases. The $\phi_{\text{sens}}/\phi_0$ ratios show minor dependence on the concentration of the sensitizer for thioxanthone and Michler's ketone.¹⁴ The ratios rise slightly as the sensitizer concentration is lowered with >99% of the light absorbed by the sensitizer. It seems reasonable to conclude that

(13) Attempts to use cupric chloride led to a dark reaction with the enamine.

(14) This is probably due to self-quenching of the sensitizer. See, for example, O. L. Chapman and G. Wampfler, *J. Amer. Chem. Soc.*, **91**, 5390 (1969).

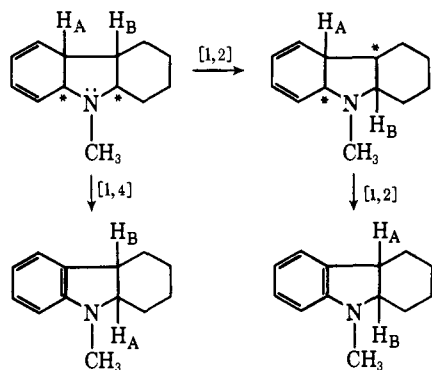
the photocyclization α -(*N*-methylanilino)styrene can proceed by way of the low-lying triplet excited state. In the direct irradiation, reaction may occur *via* the low-lying singlet excited state as well as the triplet. The observation that 1,3-cyclohexadiene does not quench the triplet cyclization requires that cyclization be rapid with respect to diffusion controlled quenching; *i.e.*, the rate constant for triplet cyclization must be greater than $1 \times 10^9 \text{ sec}^{-1}$ for the experiment with 0.1 *M* quencher.

Attempts to detect ground-state intermediates in the photocyclizations of enamines were unsuccessful. Irradiation of 1-(*N*-methylanilino)cyclohexene as a neat film in an infrared cell at -190° gave *trans*-9-methyl-1,2,3,4,4a,9a-hexahydrocarbazole with no sign of an intermediate. This is important because the *trans* isomer of the enamine double bond is a conceivable intermediate in the cyclization. Attempts to trap a dipolar ion intermediate analogous to that observed in the oxida-



tive photocyclization of diphenylamine¹⁵ with furan and maleic anhydride failed. In the presence of furan, the usual photochemical products from 1-(*N*-methylanilino)cyclohexene were observed. Maleic anhydride reacted with 1-(*N*-methylanilino)cyclohexene in a dark reaction.

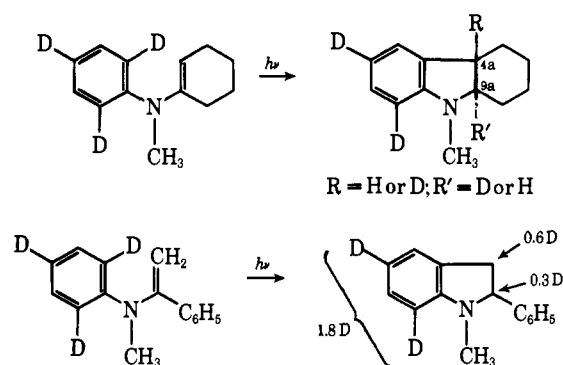
In the nonoxidative photocyclizations hydrogen shifts must occur. It is likely (see below) that these shifts occur after carbon-carbon bond formation. Two basic mechanisms must be considered. In the



first mechanism, two [1,2] hydrogen shifts are required. The second mechanism involves a [1,4] hydrogen shift. Deuterium labeling experiments offer a direct means for distinguishing these two processes. Satisfactory quantitative deuterium analysis of both enamines and products by mass spectrometry was frustrated by the loss of one and two mass units from the parent ion of the unlabeled compounds even at low ionizing voltages. Consequently, a less satisfactory nmr method was used. The relevant regions of the spectrum, aromatic protons, olefinic protons, and methine or methylene protons were integrated relative to an internal standard (the *N*-methyl group or added nitromethane). Minor deuterium incorporation in the enamine double bond

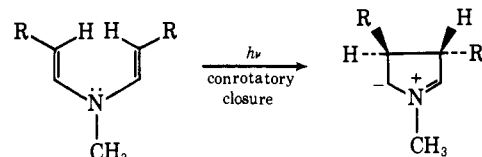
(15) H. Linschitz and K. H. Grellman, *J. Amer. Chem. Soc.*, **86**, 303 (1964); K. H. Grellman, G. M. Sherman, and H. Linschitz, *ibid.*, **85**, 1881 (1963).

was noted and appropriate corrections for this incorporation were made. The labeled enamines prepared were 1-(*N*-methylanilino-2,4,6-*d*₃)cyclohexene and α -(*N*-methylanilino-2,4,6-*d*₃)styrene. Irradiation of the

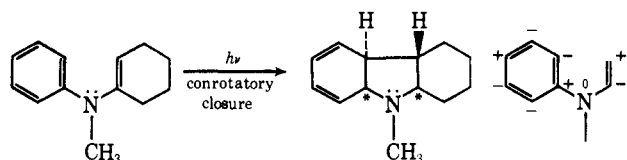


cyclohexene derivative gave *trans*-9-methyl-1,2,3,4,4a,9a-hexahydrocarbazole with a minimum of 89% retention of total deuterium. It was not possible to determine accurately the deuterium content at positions 4a and 9a. Irradiation of the styrene derivative gave 2-phenyl-1-methyl-2,3-dihydroindole with 90% retention of total deuterium. The deuterium was distributed over the 2 (30%) and 3 positions (60%). This result suggests that both mechanisms operate.

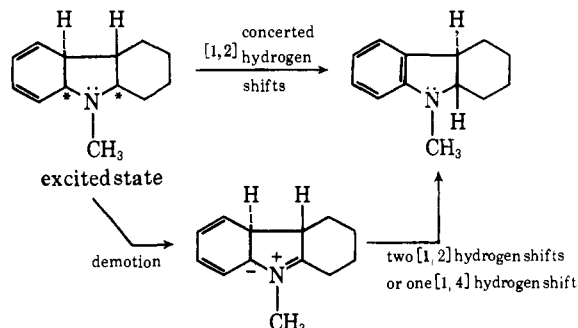
Qualitative molecular orbital arguments suggest that photochemical electrocyclic reaction of a divinylamine should occur in a conrotatory fashion.¹⁶ The divinylamine is analogous to a pentadienyl anion. The signs of the highest occupied molecular orbital (ψ_6) in the



lowest excited state of the *N*-methylaniline enamines are such that conrotatory cyclization is expected. Once

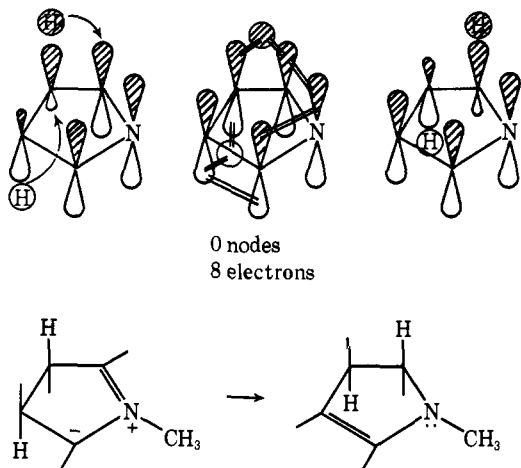


the carbon-carbon bond is formed, the stereochemistry of the product is fixed since the hydrogen atoms must stay on the same face of the molecule as they shift. The selective formation of *trans* products is a logical consequence of the initial carbon-carbon bond formation regardless of the details of the hydrogen shifts. In the



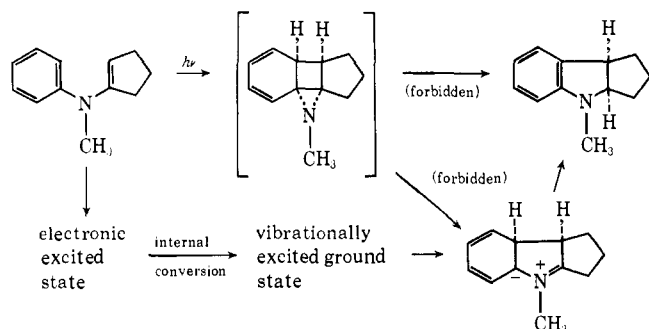
(16) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969), and references cited.

excited state after cyclization both [1,2] and [1,4] suprafacial hydrogen shifts are forbidden. It is interesting to note, however, that a concerted process in which two 1,2-hydrogen shifts occur simultaneously in the excited state is allowed.¹⁷ In this process a cyclic array of atomic orbitals with zero nodes may be considered.



The system contains eight electrons and the photochemical process is allowed.¹⁸ Alternatively, this process can be viewed as a $\pi_4s + \sigma_2a + \sigma_2a$ cycloaddition. Demotion of the excited state would lead to a dipolar species in which two successive (but not concerted) 1,2-hydrogen shifts and a 1,4-hydrogen shift are allowed processes. The deuterium labeling results show that [1,2] and [1,4] shifts compete, but it is not known whether they occur in ground state or excited state processes. Experiments designed to trap the dipolar intermediate have not been successful, but this cannot be taken as compelling evidence against the presence of such an intermediate. This is particularly true in view of the evidence presented by Linschitz and coworkers that a dipolar intermediate is formed in the oxidative photocyclization of diphenylamines.¹⁵

The cis products observed in the cyclization of *N*-methylanilino-cyclopentene and as minor products in other cyclizations must arise from a competing slower cyclization mechanism. One possibility is $\pi_2s + \pi_2s$ cycloaddition. An analogous cycloaddition is observed in the photochemistry of divinyl sulfides.¹⁹ The intermediate formed by such a cycloaddition would



have the requisite cis hydrogens and might go on to cis product. Alternatively, the electronically excited enamine may undergo internal conversion to a vibrationally excited ground state which cyclizes to the cis di-

(17) This view uses the Zimmerman formalism.¹⁸

(18) H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969).

(19) E. Block and E. J. Corey, *J. Org. Chem.*, **34**, 896 (1969).

polar intermediate. Rapid loss of vibrational excitation in solution makes this possibility less appealing. Hydrogen shifts analogous to those described above for the trans, dipolar intermediate would then lead to the *cis*-indoline.

The nonoxidative photocyclization of enamines is a useful synthetic reaction which proceeds under very mild conditions. It provides the only satisfactory synthetic route to *trans*-hexahydrocarbazoles.

Experimental Section

All melting points were taken on a Kofler hot stage. Melting and boiling points are uncorrected. Ultraviolet spectra were recorded on a Beckman Model DK-2A or a Cary 14 recording spectrophotometer. Nuclear magnetic resonance spectra were measured on a Varian Associates Model A-60 spectrometer. Chemical shifts were measured relative to TMS and are reported as δ values. All infrared spectra were recorded on a Perkin-Elmer Model 21 spectrometer. Mass spectra were measured on an Atlas CH-4 instrument at 70 eV. Element analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Quantitative Analysis. Quantitative vpc analyses were performed on a Varian Aerograph, Model 1520 instrument. Peak areas were measured by disk integration. Internal standards were added after irradiation and corrections were made for differences in thermal conductivity. The data reported are the average of at least two analyses. One of four columns was used. Column A (5 ft \times 0.25 in.) was packed with 5% potassium hydroxide, 10% polyethylene glycol (Carbowax 20M), and 85% 60–80 mesh Chromosorb W. Column B (8 ft \times 0.25 in.) was packed with 5% polyalkylene glycol (Ucon water soluble, HB, or polar) and 95% 60–80 mesh Chromosorb W. Column C (7.5 ft \times 0.25 in.) was packed with 5% Fluorosilicon fluid (FS-1265 or QF-1) and 95% 80–100 mesh Diatoport S. Column D (10 ft \times 0.25 in.) contained 7% Fluorosilicon fluid (FS-1265 or QF-1) and 93% 80–100 mesh Diatoport S.

Preparation of Enamines. The enamines were prepared according to the general procedure of Hoch⁶ from *N*-methylaniline and the diethyl ketal or by a parallel procedure using the enol ether.

1-(*N*-Methylanilino)cycloheptene. *N*-Methylaniline (15.5 g, 0.143 mol) and cycloheptanone diethyl ketal (31.7 g, 0.170 mol) were heated for 18 hr to 200°. The product, 1-(*N*-methylanilino)cycloheptene (22.5 g, 79%), was isolated by vacuum distillation: bp 108–110° (0.5 mm); uv max (cyclohexane) 278 (ϵ 8360) and 242 nm (ϵ 6750); ir (cap film) 1641, 1598, 1498, 749, and 695 cm^{-1} ; nmr (CCl_4) δ 6.5–7.3 (m, 5 H, aromatic), 5.36 (t, 1 H, $J = 7$ Hz, vinyl), 2.90 (s, 3 H, NCH_3), 1.85–2.35 (m, 4 H, allylic), and 1.20–1.85 (m, 6 H, methylene).

Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{N}$: C, 83.53; H, 9.51; N, 6.95. Found: C, 83.26; H, 9.61; N, 6.94.

1-(*N*-Methylanilino)-2-methylcyclohexene. 2-Methylcyclohexanone diethyl ketal (6.41 g, 0.034 mol) and *N*-methylaniline (3.7 g, 0.034 mol) were heated in the presence of *p*-toluenesulfonic acid for 4 hr to 200°. Vacuum distillation of the crude product gave 3.90 g (56.5%) of the pure enamine: bp 90–95° (0.25 mm); uv max (cyclohexane) 253 (ϵ 13,700) and 301 nm (ϵ 2720); ir (cap film) 1675, 1600, 1502, 745, and 690 cm^{-1} ; nmr (CCl_4) δ 6.35–7.30 (m, 5 H, aromatic), 2.81 (s, 3 H, NCH_3), 1.75–2.20 (m, 4 H, allylic), 1.50 (s, 3 H, CCH_3), and 1.30–1.75 (m, 4 H, methylene); mass spectrum m/e 201 (44), 200 (40), 186 (100), 158 (29), 144 (41), 143 (34), and 91 (29).

Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{N}$: C, 83.54; H, 9.51; N, 6.96. Found: C, 83.47; H, 9.47; N, 6.82.

3-(*N*-Methylanilino)-2-pentene. The diethyl ketal of 3-pentanone (16.0 g, 0.10 mol) and *N*-methylaniline (10.7 g, 0.10 mol) were heated to 180° in the presence of *p*-toluenesulfonic acid for 4 hr. The residue was distilled under vacuum to give 11.9 g (68%) of the enamine: bp 54–60° (0.25 mm); uv max (cyclohexane) 245 (ϵ 11,240) and 269 (s) nm (ϵ 7020); mass spectrometric mol wt 175. The nmr spectrum showed the product to be a mixture of *cis* and *trans* isomers.

Anal. Calcd for $\text{C}_{12}\text{H}_{17}\text{N}$: C, 82.23; H, 9.77; N, 7.99. Found: C, 82.01; H, 9.98; N, 8.12.

4-(*N*-Methylanilino)-1,2-dihydronaphthalene. *N*-Methylaniline (4.70 g, 0.044 mol) and 4-ethoxy-1,2-dihydronaphthalene (7.65 g, 0.044 mol) were heated for 4 hr to 180°. No acid catalyst was used. Ethanol distilled over as the reaction proceeded. The residue was

distilled under vacuum affording 5.61 g (54%) of the enamine: bp 148–150° (0.10 mm); ν max (cyclohexane) 252 (ϵ 20,200) and 298 nm (ϵ 5140); ir (cap film) 1600, 1502, 767, 740, and 692 cm^{-1} ; nmr (CCl_4) δ 6.25–7.30 (m, 9 H, aromatic), 5.70 (t, 1 H, $J = 4.5$ Hz, vinyl), 3.06 (s, 3 H, NCH_3), and 2.0–3.0 (m, 4 H, methylene); mass spectrum m/e 235 (19), 234 (100), 233 (97), 143 (20), 130 (22), 105 (18), and 76 (17).

Anal. Calcd for $\text{C}_{17}\text{H}_{17}\text{N}$: C, 86.77; H, 7.28; N, 5.95. Found: C, 86.49; H, 7.39; N, 5.93.

Irradiation of Enamines. Preparative irradiations were done in a Pyrex immersion well with a capacity of 300 ml. Freshly opened absolute ether was the solvent. The light source was a Hanovia Type A 550-W mercury lamp. The arms of the immersion well were closed with rubber septa, and the solutions were purged with argon for 30 min before irradiation. The solution was agitated with a magnetic stirring bar during irradiation. Aliquots were removed at regular intervals with a syringe and the progress of the reaction was monitored by tlc.

Irradiation of 1-(*N*-Methylanilino)cyclopentene. A solution of the enamine (0.81 g, 4.68×10^{-3} mol) was irradiated in 300 ml of ether (1.56×10^{-2} M) for 6.5 hr. Evaporation of the solvent left an oily residue. Analysis of this material by vpc on column A using benzophenone as an internal standard showed no starting material and a 52% yield of the indoline photoproduct. The crude product (0.70 g) was chromatographed over silica gel. Fraction 1 (100 ml of Skelly B) contained no eluate. Fractions 2 (50 ml of 2% ethyl acetate in Skelly B) and 3 (75 ml of 4% ethyl acetate–Skelly B) contained 0.40 g (57%) of material which showed only one spot on tlc. The indoline was isolated as the picrate (0.66 g, 35%); mp 122–123° (lit.⁸ mp 121–122°). Other runs on more concentrated solutions and with longer irradiation times gave lower yields of product and large amounts of yellow high boiling material. The indoline could also be isolated by distillation of the reaction mixture: bp 77° (0.3 mm) (lit.⁸ bp 127–128° (10 mm)); methiodide mp 189–190° (lit.⁸ mp 187–189°). The uv spectrum of the indoline in 95% ethanol showed maxima at 260 (ϵ 8950) and 308 nm (ϵ 2320). The mass spectrum showed ions at m/e 173 (30), 145 (16), 144 (100), 108 (25), and 91 (25).

Irradiation of 1-(*N*-Methylanilino)cyclohexene. The enamine⁸ (4.20 g, 2.36×10^{-2} mol) was dissolved in 300 ml of ether (7.87×10^{-2} M) and irradiated for 6 hr. Evaporation of the solvent left an oil which was analyzed by vpc on column A using benzophenone as an internal standard, and found to contain 71% *trans*-9-methyl-1,2,3,4,4a,9a-hexahydrocarbazole, 3% of the *cis* isomer, and 3% 9-methyl-1,2,3,4-tetrahydrocarbazole. The major product was isolated by recrystallization of the crude residue from 95% ethanol giving 2.32 g (55%) of *trans*-9-methyl-1,2,3,4,4a,9a-hexahydrocarbazole: mp 58–60° (lit.²⁰ mp 59–61°); picrate mp 125–126° (lit.²⁰ mp 122–124°); methiodide mp 233–234° (lit.²⁰ mp 233–234°); uv max (95% ethanol) 246 (ϵ 7760) and 288 nm (ϵ 2400); mass spectrum m/e 187 (33), 186 (24), 145 (17), 144 (100), 131 (17), and 130 (15).

Irradiation of 1-(*N*-Methylanilino)cycloheptene. The enamine (6.08 g, 3.02×10^{-2} mol) was irradiated in 300 ml of ether (1.01×10^{-1} M) for 9 hr. The residue was distilled, bp 119–120° (0.5 mm), giving 2.67 g (44%) of a mixture of two products. Pure samples of the major and minor products were obtained by preparative vpc on a 10 ft \times $\frac{3}{8}$ in. column packed with 5% potassium hydroxide, 10% Carbowax 20M, and 85% Chromosorb W. The major product, *trans*-*N*-methyl-5,5a,6,7,8,9,10,10a-octahydrocyclohept[*b*]indole, showed uv maxima at 251 (ϵ 8090) and 296 nm (ϵ 2550) and formed a picrate 115–116° and a methiodide derivative, mp 215–217°. The mass spectrum of the major product showed the molecular ion at m/e 201 (18%) with fragment ions at m/e 159 (47), 155 (84), 144 (100), 125 (24), 81 (25), and 77 (87).

Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{N}$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.59; H, 9.51; N, 7.01.

The ir spectrum of the minor product was identical with that of *cis*-*N*-methyl-5,5a,6,7,8,9,10,10a-octahydrocyclohept[*b*]indole obtained by reduction of the corresponding indole.^{7,20}

In another run a solution of the enamine (3.4×10^{-1} M) was irradiated for 7 hr. Analysis of the crude reaction mixture by vpc on column A using diphenylamine as a standard for integration showed 12% of the starting material remained while 65.5% of the *trans* product and 4% of the *cis* product were present along with a trace of the indole. Correcting for the presence of starting material, the yield is 75% *trans*- and 5% *cis*-*N*-methyl-5,5a,6,7,8,9,10,10a-octahydrocyclohept[*b*]indole.

After irradiation of a 1.41×10^{-2} M solution of the enamine for 7 hr the major photoproduct was isolated as the methiodide in 47% yield.

Irradiation of 1-(*N*-Methylanilino)-2-methylcyclohexene. The enamine (3.90 g, 1.94×10^{-2} mol) was irradiated in 300 ml of ether (6.48×10^{-2} M) for 6 hr. One major photoproduct was detected by tlc accompanied by two minor products. The product was extracted into 10% hydrochloric acid and recovered by treatment of the acidic solution with sodium hydroxide and extraction into ether. After drying (MgSO_4), the organic layer was concentrated and distilled to give 2.73 g (70%) of *trans*-4a,9-dimethyl-1,2,3,4,4a,9a-hexahydrocarbazole, bp 135–140° (5 mm). An analytical sample was obtained by preparative vpc (FS-1265). The product showed uv maxima at 248 (ϵ 7280) and 295 nm (ϵ 2360). The mass spectrum gave the molecular ion at m/e 201 (42) and fragment ions at m/e 200 (12), 187 (18), 186 (100), 158 (27), 144 (37), and 121 (28). The product formed a picrate melting at 177–178°.

Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{N}$: C, 83.54; H, 9.51; N, 6.96. Found: C, 83.67; H, 9.54; N, 7.07.

Another mixture of photoproducts, obtained by irradiation of a 8.45×10^{-2} M solution for 9 hr, was analyzed by vpc using benzophenone as a standard for integration on column C and found to contain 5% unreacted starting material along with the photoproducts. After correction for unreacted enamine, the yield of *trans*-4a,9-dimethyl-1,2,3,4,4a,9a-hexahydrocarbazole was 79% and the two minor products were each formed in about 1% yield. These were not isolated or identified.

The major product was isolated in 75% yield as the picrate after irradiation of a 1.50×10^{-2} M solution for 7 hr.

Irradiation of α -(*N*-Methylanilino)styrene. A solution of the enamine²⁰ (1.16 g, 5.56×10^{-3} mol) in 300 ml of ether (1.85×10^{-2} M) was irradiated for 5 hr. Evaporation of solvent gave an oil which crystallized on standing. The crude product was recrystallized from 95% ethanol to yield 0.84 g (73%) of *N*-methyl-2-phenyl-2,3-dihydroindole: mp 92–93°. Chromatography over silica gel eluting with 2% ethyl acetate in Skelly B or vacuum sublimation raised the mp to 94–95°. The product showed uv maxima at 252 (ϵ 8960) and 297 nm (ϵ 2870). The mass spectrum gave the molecular ion at m/e 209 (50) and fragment ions at m/e 208 (15), 132 (100), 117 (19), and 91 (16).

Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{N}$: C, 86.02; H, 7.22; N, 6.69. Found: C, 86.16; H, 7.34; N, 6.64.

Irradiation of 4-(*N*-Methylanilino)-1,2-dihydronaphthalene. A solution of the enamine (1.88 g, 8.0×10^{-2} mol) in 300 ml of ether (2.67×10^{-2} M) was irradiated for 10 hr. Complete destruction of starting material occurred, and two photoproducts were detected by tlc. The solvent was evaporated, and a portion of the residue (1.48 g) was chromatographed over 45 g of silica gel. Fraction 1 (80 ml of benzene) contained no photoproducts. Fraction 2 (50 ml of benzene) contained 0.19 g of the *cis*-indoline. Fraction 3 (65 ml of benzene) contained 0.72 g of a mixture of the *cis*- and *trans*-indolines. Fraction 4 (45 ml of benzene) contained 0.15 g of the *trans*-indoline. The total weight of photoproducts collected was 1.06 g (72%). Fraction 2 was recrystallized from ethanol to give the *cis*-indoline: mp 135–136°; picrate mp 144–145°; uv max (95% ethanol) 257 (ϵ 9720) and 302 nm (ϵ 2910). The ir spectrum of the *cis*-indole was identical with that of the product obtained on reduction of the corresponding indole. Element analysis was carried out on the reduction product.

An analytical sample of the *trans*-indoline was obtained by preparative vpc (FS-1265). The *trans*-indoline showed uv maxima (95% ethanol) at 247 (ϵ 8060), 294 (ϵ 2650), 314 (ϵ 2020), and 335 nm (ϵ 1780). The mass spectrum gave the molecular ion at m/e 235 (100) and fragment ions at m/e 234 (98), 233 (12), 219 (18), 218 (20), 217 (15), 144 (18), and 106 (17). The *trans*-indoline formed a picrate, mp 163–164°.

Anal. Calcd for $\text{C}_{17}\text{H}_{17}\text{N}$: C, 86.77; H, 7.28; N, 5.95. Found: C, 86.24; H, 7.46; N, 6.26.

Another sample of the enamine was irradiated in ether (1.45×10^{-2} M) for 1 hr. The residue, after evaporation of solvent, was analyzed by vpc (column C) with benzophenone as a standard for integration and found to contain 35.4% unreacted starting material, 19% *cis*- and 36.4% *trans*-indoline. Correcting for the presence of unreacted starting material, the yields are 39.3% *cis*- and 56.5% *trans*-indoline.

Irradiation of 3-(*N*-Methylanilino)-2-pentene. A solution of the enamine (3.50 g, 2.0×10^{-2} mol) in 300 ml of ether (6.67×10^{-2} M) was irradiated for 10 hr. After evaporation of solvent the crude product was eluted over 15 g of silica gel with 10% ethyl acetate in Skelly B to remove polymeric material. A total of 2.36

(20) T. Masamune, *Bull. Chem. Soc. Jap.*, **30**, 491 (1957).

g of photoproducts and *N*-methylaniline was eluted. This mixture was chromatographed over 178 g of basic alumina (Woelm activity grade I). Fraction 1 (120 ml of Skelly B) contained no residue. Fractions 2 (160 ml of 2% ethyl acetate in Skelly B), 3 (125 ml of 2% ethyl acetate in Skelly B), and 4 (100 ml of 5% ethyl acetate in Skelly B) contained 1.76 g of a mixture of three photoproducts. This mixture was analyzed by vpc on column B using diphenyl ether as a standard for integration. The mixture consisted of *N*-methylaniline (10%), the two isomers of 1,3-dimethyl-2-ethyl-2,3-dihydroindole (16 and 69%), and 1,3-dimethyl-2-ethylindole (5%). The absolute yield of the dihydroindoles are 8 and 35% and of the indole 3%.

Analytical samples of the indoline products were obtained by preparative vpc (10% Ucon water soluble). The minor isomer of 1,3-dimethyl-2-ethyl-2,3-dihydroindole gave a mass spectrum with the parent ion at *m/e* 175 (20) and fragment ions at 147 (14), 146 (100), 144 (11), 131 (11), and 117 (15).

Anal. Calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.77; N, 7.99. Found: C, 81.99; H, 9.88; N, 7.85.

The major isomer showed a molecular ion at *m/e* 175 and the same fragmentation pattern as the minor isomer.

Anal. Calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.77; N, 7.99. Found: C, 81.97; H, 9.62; N, 8.04.

Irradiation of 1-(*N*-Methyl-4-anisidino)cyclohexene. Cyclohexanone diethyl ketal (9.21 g, 0.054 mol) and *N*-methyl-4-anisidine (6.48 g, 0.054 mol) were heated for 3 hr to 190° in the presence of *p*-toluenesulfonic acid. Ethanol (5 ml) distilled over during this period. Vacuum distillation of the residue gave 6.66 g (57%) of the enamine: bp 120–124° (0.5 mm); uv max (cyclohexane) 243 (ϵ 10,700) and 311 nm (ϵ 2670); ir (cap film) 1612, 1509, 1236, and 835 cm^{-1} ; nmr (CCl_4) δ 6.5–7.0 (m, 4 H, aromatic), 4.81 (broad s, 1 H, vinyl), 3.69 (s, 3 H, NCH_3), 2.97 (s, 3 H, OCH_3), and 1.40–2.40 (m, 8 H, methylene); mass spectrum *m/e* 217 (96), 216 (86), 213 (55), 198 (81), 188 (88), 160 (31), 122 (39), 121 (40), 77 (30), and 68 (100). A 3.09×10^{-2} M solution of the enamine (2.01 g, 9.25×10^{-3} mol) in ether was irradiated with a 450-W Hanovia Type L mercury lamp for 9 hr. The reaction seemed to stop after about 4 hr. The residue was chromatographed over 60 g of silica gel. Fraction 1 (175 ml of 20% ethyl acetate in Skelly B) contained no residue. Fraction 2 (115 ml of 20% ethyl acetate in Skelly B) contained the photoproduct. Further fractions contained mixtures of photoproduct and 4-anisidine. Fraction 2 was recrystallized from Skelly B and sublimed under vacuum to yield 0.24 g (12%) of *trans*-9-methyl-6-methoxy-1,2,3,4,4a,9a-hexahydrocarbazole: mp 76–77°; picrate mp 150–151°; uv max (95% ethanol) 243 (ϵ 9450) and 304 nm (ϵ 3050); mass spectrum *m/e* 217 (100), 216 (46), 214 (73), 202 (77), 195 (33), 187 (64), 174 (98), 172 (42), 107 (55), and 106 (67).

Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81. Found: C, 77.19; H, 8.73.

Irradiation of 1-(4-Bromo-*N*-methylanilino)cyclohexene. 4-Bromo-*N*-methylaniline (9.5 g, 0.05 mol) and cyclohexanone diethyl ketal (8.6 g, 0.05 mol) were heated in the presence of *p*-toluenesulfonic acid for 2 hr to 180° while 5 ml of ethanol distilled over. Vacuum distillation of the residue gave 8.42 g (63%) of the enamine: bp 126–130° (0.05 mm); uv max (cyclohexane) 252 nm (ϵ 10,300); ir (cap film) 1582, 1487, and 809 cm^{-1} ; nmr (CCl_4) δ 8.61 (d, 2 H, aromatic), 7.88 (d, 2 H, aromatic), 6.40 (broad t, 1 H, vinyl), 3.50 (s, 3 H, NCH_3), and 1.7–2.9 (m, 8 H, methylene); mass spectrum *m/e* 267 (41), 266 (42), 265 (49), 264 (44), 263 (44), 262 (20), 261 (40), and 68 (100). A solution of the enamine (1.20 g, 4.52×10^{-2} mol) in ether (1.51×10^{-2} M) was irradiated for 18 hr with a Hanovia Type L 450-W mercury lamp. A large amount of dark sticky material precipitated on the walls of the immersion well. The solution was analyzed by tlc and found to contain several products in small amounts, but none of these showed the same R_f value as authentic *trans*-6-bromo-9-methylhexahydrocarbazole (see below). None of the minor photoproducts were isolated or identified.

Irradiation of 2-(4-Chloroanilino)fumaric Acid Dimethyl Ester. The enamine was irradiated in ether (1.25×10^{-2} M) with the 450-W lamp for 13 hr. Analysis of the residue by nmr showed it to consist of starting material. This could be recovered by recrystallization from anhydrous methanol.

Irradiation of β -(*N*-Methylanilino)acrylic Acid Ethyl Ester. Irradiation of a 3.3×10^{-2} M solution of the enamine in ether for 8 hr with the 450-W lamp produced no detectable change. Evaporation of the solvent left an oil which was shown by nmr to be unreacted starting material. No isomerization to the cis compound

had occurred as evidenced by the 13-Hz coupling constant for the only observable vinyl proton.

Irradiation of β -(*N*-Methylanilino)styrene. The enamine⁶ was irradiated in ether (4.95×10^{-3} M) for 22 hr. The residue was analyzed by vpc (column C) and found to contain only hydrolysis products. Some apparently polymeric material precipitated on the walls of the immersion well during the irradiation.

Bromination of *trans*-9-Methyl-1,2,3,4,4a,9a-hexahydrocarbazole. Bromine (0.80 g, 5×10^{-3} mol) in 5 ml of glacial acetic acid was added to a stirred solution of *trans*-9-methyl-1,2,3,4,4a,9a-hexahydrocarbazole (0.93 g, 5×10^{-3} mol) in 10 ml of acetic acid over a 30-min period. The bromine color was rapidly discharged, and a light yellow precipitate appeared. About 50 ml of acetic acid was added to keep the suspension mobile. The mixture was stirred at room temperature for 30 min after addition of bromine was complete. The precipitate was collected on a filter and treated with excess aqueous sodium hydroxide, and the basic solution was extracted with ether. After drying, the ether was evaporated leaving an oil which was crystallized from ethanol affording 0.80 g (60%) of *trans*-9-methyl-6-bromo-1,2,3,4,4a,9a-hexahydrocarbazole: mp 68–69°; uv max (95% ethanol) 257 (ϵ 12,000) and 303 nm (ϵ 2530); ir (KBr) 1602, 1471, 1455, 805, and 731 cm^{-1} ; nmr (CCl_4) δ 6.9–7.2 (m, 2 H, aromatic), 6.30 (d, 1 H, $J = 8$ Hz, aromatic), 2.58 (s, 3 H, NCH_3), 1.1–2.5 (m, 10 H, methylene and methine); mass spectrum *m/e* 267 (58), 265 (62), 224 (97), 222 (100), 187 (20), 186 (24), 185 (30), and 144 (54).

Anal. Calcd for $C_{13}H_{16}NBr$: C, 58.66; H, 6.06; N, 5.26. Found: C, 58.96; H, 6.20; N, 5.30.

Bromination of *trans*-4a,9-Dimethyl-1,2,3,4,4a,9a-hexahydrocarbazole. To a stirred solution of *trans*-4a,9-dimethyl-1,2,3,4,4a,9a-hexahydrocarbazole (1.13 g, 5.6×10^{-3} mol) in 5 ml of glacial acetic acid was added a solution of bromine (0.90 g, 5.6×10^{-3} mol) in 5 ml of acetic acid. A precipitate appeared as each drop of bromine was added but dissolved on stirring. When addition was complete, a red-brown precipitate remained, and the solution was stirred at room temperature for another 30 min. The mixture was made basic with sodium hydroxide and extracted with ether. The oil left after evaporation of the ether was chromatographed over silica gel (45 g). Fractions 1 (50 ml of Skelly B) and 2 (50 ml of 2% ethyl acetate in Skelly B) contained no residue. Fraction 3 (125 ml of 5% ethyl acetate in Skelly B) contained the dibromo compound which was recrystallized from ethanol to give 0.24 g (12%) of *trans*-4a,9-dimethyl-6,8-dibromo-1,2,3,4,4a,9a-hexahydrocarbazole: mp 8–91°; uv max (95% ethanol) 263 (ϵ 10,400) and 308 nm (ϵ 2910); ir (KBr) 1558, 1440, 1414, 1050, 861, 744, and 665 cm^{-1} ; nmr (CCl_4) δ 7.30 (d, 1 H, $J = 2$ Hz, aromatic), 6.90 (d, 1 H, $J = 2$ Hz, aromatic), 2.98 (s, 3 H, NCH_3), 1.35–2.70 (m, 9 H, methylene and methine), and 0.95 (s, 3 H, CCH_3); mass spectrum *m/e* 361 (55), 359 (100), 357 (56), 345 (20), 343 (38), 341 (21), 265 (54), and 263 (19).

Anal. Calcd for $C_{14}H_{17}NBr_2$: C, 46.82; H, 4.77; N, 3.90. Found: C, 46.51; H, 4.75; N, 3.80.

Oxidation of *trans*-9-Methyl-1,2,3,4,4a,9a-hexahydrocarbazole. The *trans*-9-methyl-1,2,3,4,4a,9a-hexahydrocarbazole (0.058 g, 3.1×10^{-4} mol) and chloranil (0.229 g, 9.3×10^{-4} mol) were dissolved in 3 ml of xylene and heated for 6 hr on the steam bath. Greenish yellow crystals separated on cooling and were removed by filtration. The filtrate was diluted with ether, washed twice with 5% sodium hydroxide and twice with water, then dried, and evaporated leaving a purple solid, mp 75–83°. Recrystallization from ethanol gave 9-methylcarbazole: mp 81–84° (lit.²¹ mp 87°). The ir spectrum of the product was identical with that of the product obtained by a similar procedure for the oxidation of 9-methyl-1,2,3,4-tetrahydrocarbazole.²²

Oxidation of *trans*-5-Methyl-5a,6,7,8,9,10,10a-octahydrocyclohept[*b*]indole. A solution of *trans*-5-methyl-5a,6,7,8,9,10,10a-octahydrocyclohept[*b*]indole (0.92 g, 4.5×10^{-3} mol) and chloranil (1.12 g, 4.5×10^{-3} mol) in toluene (20 ml) was heated on the steam bath for 30 min. On cooling, a precipitate appeared which was removed by filtration. The filtrate was diluted with ether, then washed with 5% sodium hydroxide and water. Analysis by tlc showed that some indoline starting material remained. This was removed by extraction with 10% hydrochloric acid. Evaporation of the dried ether left an oil which was crystallized from 95%

(21) I. Heilbron, Ed., "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1965, p 552.

(22) R. Huisgen, K. Herbig, A. Siegel, and A. Huber, *Chem. Ber.*, **99** 2526 (1966).

ethanol and shown by ir and nmr to be the indole, mp 51–52° (lit.²³ mp 50°).

Irradiation of *cis*- and *trans*-9-Methyl-1,2,3,4,4a,9a-hexahydrocarbazole. Three samples of each isomer in ether (about 5.3×10^{-2} M) were prepared in cells constructed from 13-mm Pyrex culture tubes joined to a standard taper 10–30 joint. Two samples of each isomer were purged with oxygen for 3 min and sealed with rubber septa. One sample of each isomer was degassed by four freeze–pump–thaw cycles and sealed under vacuum. One sample of each isomer which had been purged with oxygen was set aside in the dark while the other four samples were irradiated for 6 hr on the merry-go-round apparatus (see below). All samples were analyzed by vpc (column C). The samples kept in the dark and the degassed, irradiated samples contained only the indoline products. The samples which were irradiated in the presence of oxygen contained both indoline starting material and 9-methyl-1,2,3,4-tetrahydrocarbazole. No isomerization of the indolines was observed in any of the samples.

Treatment of *trans*-9-Methyl-1,2,3,4,4a,9a-hexahydrocarbazole with Tin and Hydrochloric Acid. The *trans*-indoline (0.90 g, 5×10^{-3} mol) obtained in the photocyclization reaction was dissolved in 7.5 ml of 95% ethanol and 4 ml of concentrated hydrochloric acid. Granulated tin (1.64 g, 1.5×10^{-2} mol) was added, and the solution was heated for 3 hr on the steam bath. The reaction was worked up as described for the reduction of 9-methyl-1,2,3,4-tetrahydrocarbazole. The steam distillate was extracted with ether, and the dried organic layer evaporated giving 0.72 g (80%) of recovered starting material, mp 58–60°.

Pyrolysis of 1-(*N*-Methylanilino)cyclohexene. A solution of the enamine in spectrograde cyclohexane was injected into a vertical 11 in. \times 0.88 in. column packed with glass helices and heated to 500°. The column was washed with cyclohexane, and the washings and condensate were concentrated on the steam bath. Analysis of these solutions by vpc showed only *N*-methylaniline and cyclohexanone to be present.

Reduction of 5-Methyl-5,6,7,8,9,10-hexahydrocyclohept[*b*]indole. To a solution of the indole (1.99 g, 0.010 mol) in 15 ml of 95% ethanol was added granulated tin (3.38 g, 0.030 mol) and 8 ml of concentrated hydrochloric acid. The mixture was heated on the steam bath for 3 hr. The hot solution was filtered, and the unreacted tin was washed with 5 ml of hydrochloric acid and 5 ml of ethanol. The washings and filtrate were combined, made basic with 40% sodium hydroxide, and extracted with ether. Evaporation of the dried organic layer left an oil which was distilled to yield *cis*-5-methyl-5,5a,6,7,8,9,10,10a-octahydrocarbazole (1.05 g, 52%); bp 106–108° (0.5 mm); picrate mp 134–135°; mass spectrum *m/e* 201 (11), 158 (9), 144 (100), and 131 (9). The distillate contained a small amount of the *trans* isomer (<2% by vpc).

Anal. Calcd for C₁₄H₁₃N: C, 83.54; H, 9.51; N, 6.96. Found: C, 83.46; H, 9.55; N, 7.02.

Reduction of 1-Methyl-2-phenylindole. Granulated tin (1.78 g, 0.015 mol) was added to a mixture of the indole (1.04 g, 0.005 mol), 8 ml of 95% ethanol, and 4 ml of concentrated hydrochloric acid, and the mixture was heated on the steam bath for 3 hr. The initially yellow solution became colorless after 1 hr. The unreacted metal was removed by filtration and washed with hot ethanol. The filtrate and washings were combined, treated with excess 40% sodium hydroxide, and extracted with ether. After drying, the ether layer was evaporated leaving 0.98 g (94%) of the crude product, mp 86–90°, which was recrystallized from ethanol affording 0.80 g (77%) of pure 1-methyl-2-phenyl-2,3-dihydroindole, mp 93–94°. The ir and nmr spectra were identical with those of the product from irradiation of α -(*N*-methylanilino)styrene.

Reduction of 11-Methyl-5,6-dihydro-11*H*-benzo[*b*]carbazole. The indole (2.33 g, 0.010 mol) and granulated tin (3.38 g, 0.030 mol) were slurried in a mixture of 8 ml of concentrated hydrochloric acid and 15 ml of 95% ethanol and refluxed for 3 hr on the steam bath. Unreacted metal was filtered off and washed with hot ethanol. The combined filtrate and washings were made basic with excess concentrated sodium hydroxide and extracted with ether. Evaporation of the dried ether left a residue which was recrystallized from ethanol to give 1.70 g (73%) of *cis*-11-methyl-5,6,6a,11a-tetrahydro-11*H*-benzo[*b*]carbazole, mp 135–136°.

Anal. Calcd for C₁₇H₁₃N: C, 86.77; H, 7.28; N, 5.95. Found: C, 86.92; H, 7.57; N, 5.82.

Concentration of the mother liquor left an oil which contained the *trans* isomer identified by the nmr spectrum.

Reduction of 1,3-Dimethyl-2-ethylindole. The indole (4.10 g, 0.024 mol) and granulated tin (8.45 g, 0.024 mol) were added to 35 ml of 95% ethanol and 20 ml of concentrated hydrochloric acid and refluxed on a steam bath. The initial yellow color had completely faded after 30 min. Heating was continued for a total of 3 hr. The mixture was made basic with 40% sodium hydroxide and steam distilled. The distillate was treated with 10% sodium hydroxide and extracted with ether. The dried ether layer was evaporated leaving an oil (1.53 g, 36%) which was analyzed by vpc (column B) using diphenyl ether as a standard for integration and found to contain the isomeric 1,3-dimethyl-2-ethyl-2,3-dihydroindoles (29 and 61%) and the indole (5%).

1-(*N*-Methylanilino-2,4,6-*d*₃)cyclohexene. *N*-Methylaniline-*d*₃²⁴ (5.5 g, 0.05 mol) and 1-ethoxycyclohexene (6.3 g, 0.05 mol) were heated in the presence of a trace of *p*-toluenesulfonic acid for 4 hr to 220°. Distillation of the residue gave the enamine, bp 113–115° (2.0 mm). Deuterium content was measured by nmr. Two integrations of each peak were made. The *N*-methyl protons were used as a standard and integrated to 46.5 ± 2 units or 15.5 units per proton. The aromatic proton resonance integrated to 40 ± 2 units or 2.6 protons. The vinyl resonance integrated to 11 ± 1 units or 0.7 proton. The methylene resonance integrated to 124 ± 4 units or 8.0 protons. Since the undeuterated material contained 17.0 protons, the deuterium content of the enamine was 2.7 deuterium atoms per molecule.

Irradiation of the deuterated enamine in ether as described for the protio compound gave the *trans*-indoline which was isolated by recrystallization of the crude residue from 95% ethanol. Since the methyl resonance of this compound overlaps with the methine absorption, another standard was necessary. The methyl protons of nitromethane absorb at about δ 4.0, well separated from any of the indoline peaks. The spectrum of a mixture of the indoline (0.0800 g, 4.22×10^{-4} mol, assuming *d*₃) and nitromethane (0.0364 g, 5.96×10^{-2} mol) was taken and four integrations were made. The nitromethane methyl protons integrated to 53 ± 1 units or 17.7 units per proton. Correcting for the molar excess of nitromethane, the number of units expected for each proton of the indoline is 12.5. The aromatic peaks of the indoline integrated to 28 ± 1 units or 2.2 protons. The remaining proton resonances (*N*-methyl, methine, and methylene) integrated to 155 ± 2 units or 12.4 protons. Thus the deuterium content of the photoproduct was 2.4 deuterium atoms per molecule and 89% of the total deuterium was retained.

α -(*N*-Methylanilino)styrene-*d*₃. Acetophenone diethyl ketal (9.7 g, 0.05 mol) and *N*-methylaniline-*d*₃²⁴ (5.5 g, 0.05 mol) were heated together for 15 hr to 200°. No acid catalyst was used in the preparation. The enamine was isolated by distillation of the residue, bp 125–130° (1.5 mm). Deuterium assay was made by nmr. Only one integration was made. The *N*-methyl proton resonance, used as the standard, integrated to 52 units or 17 units per proton. The aromatic resonance integrated to 121 units or 7.1 protons and the vinyl peak integrated to 32 units or 1.9 protons. Thus, the enamine contained 3.0 deuterium atoms per molecule.

Irradiation of the enamine was carried out in benzene and the product was isolated by crystallization of the crude residue from 95% ethanol. Analysis by nmr was based on two integrations. The *N*-methyl resonance was used as the standard and integrated to 37.5 ± 1 units or 12.5 units per proton. The aromatic resonance integrated to 90 ± 2 units or 7.2 protons. The proton α to the nitrogen appeared as the X portion of an ABX pattern and integrated to 8.5 ± 1 units or 0.7 proton. The AB portion integrated to 17.5 ± 2 units or 1.4 protons. Thus, the indoline contains 2.7 deuterium atoms and 90% of the total label was retained.

Quantum Yield Apparatus. Samples used in quantum yield determinations were irradiated in cells constructed from 13-mm Pyrex culture tubes joined to a standard taper 10–30 joint. Samples were degassed by four freeze–pump–thaw cycles (10^{-6} mm) before irradiation and sealed under vacuum. Either of two assemblies was used. One was a commercial "merry-go-round" apparatus^{25,26} immersed in a water bath at 25° and equipped with a Pyrex immersion well containing a Hanovia Type A 550-W lamp and four Corning 7-60 filters. Under these conditions nearly all of the light output was at 366 nm. The other apparatus was a linear mono-

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chromator equipped with a Bausch and Lomb 33-86-07 grating and an Osram HBO 200-W super pressure mercury lamp. The cells in this assembly were cooled by passing water at 25° through the cell housing. Irradiations were done with the monochromator set at 340 nm and the slits at position 4. Under these conditions the band pass was ± 15 nm and nearly all of the light output was at 334 nm.

Sensitized quantum yields were corrected for light absorption by the enamine. In all cases the sensitizer absorbed at least 90% of the light and usually absorbed more than 95%. Quantum yields vary slightly due to the nonuniformity of the cells. Over several runs the quantum yield for formation of the 2-phenylindoline (99) in benzene was 0.21 ± 0.04 . Light intensity was measured by ferrioxalate actinometry.

Sensitization by Xanthone. Four cells were charged with 1.00 ml of a 1.53×10^{-1} M solution of α -(*N*-methylanilino)styrene in benzene. Xanthone (1.00 ml of a 3.24×10^{-2} M solution in benzene) was added to two of the cells and each sample was diluted to 3.00 ml with benzene. The solutions were degassed, sealed, and irradiated for 30 min on the linear apparatus at 340 nm with the slit at position 4. Under these conditions the band pass is ± 15 nm and essentially all of the light output is at 334 nm. The light intensity was 2.22×10^{16} quanta/sec. Results are given in Table II. The average value of $\phi_{\text{sens}}/\phi_0$ was 0.45.

Table II. Sensitization of Photocyclization by Xanthone

[Enamine] $\times 10^2$	[Sens] $\times 10^2$	Moles of product $\times 10^5$	ϕ_{product}
5.12	0	1.61	0.243
5.12	0	1.42	0.214
5.12	1.05	0.613	0.093
5.12	1.05	0.758	0.114

Sensitization with Michler's Ketone. Each of four cells was charged with 1.00 ml of a 1.53×10^{-1} solution of α -(*N*-methylanilino)styrene in benzene. Two of the cells also contained 1.00 ml of a 3.45×10^{-2} M solution of Michler's ketone in benzene. Each cell was diluted to 3.00 ml with benzene, degassed, sealed, and irradiated for 30 min on the linear apparatus (334 nm). Light output was 2.22×10^{16} quanta/sec. Results are shown in Table III. The average value of $\phi_{\text{sens}}/\phi_0$ was 0.60.

Table III. Sensitization of Photocyclization by Michler's Ketone

[Enamine] $\times 10^2$	[Sens] $\times 10^2$	Moles of product $\times 10^5$	ϕ_{product}
5.12	0	1.61	0.243
5.12	0	1.42	0.214
5.12	1.15	0.799	0.120
5.12	1.15	1.02	0.154

Sensitization with Fluorenone. Two samples were prepared. Each contained 1.00 ml of a 1.37×10^{-1} M solution of α -(*N*-methylanilino)styrene in benzene. One also contained 1.00 ml of a 2.44×10^{-1} M solution of fluorenone in benzene. Both samples were diluted to 3.00 ml with benzene, degassed, sealed, and irradiated for 45 min on the merry-go-round fitted with the Corning 7-60 filters. The quantum yield in the direct irradiation was 0.209 and in the sensitized irradiation was 0.009 which is negligible.

Effect of Sensitizer Concentration on Photocyclization. The concentrations of two sensitizers were varied at constant enamine concentration (Table IV). Eight cells were charged with 1.00 ml of a 2.95×10^{-2} M solution of enamine in benzene. Aliquots (0.60, 0.80, and 2.00 ml) of a 3.28×10^{-2} M solution of xanthone in benzene were added to three cells and to three others were added aliquots (0.20, 0.60, and 2.00 ml) of a 3.16×10^{-2} M solution of Michler's ketone in benzene. Each sample was irradiated for 30 min on the linear apparatus under the conditions described earlier. The light output at 334 nm was 2.06×10^{16} quanta/sec. Samples were concentrated by blowing prepurified nitrogen over the solution before analysis.

Effect of Enamine Concentration on Sensitized Photocyclization. The concentration of α -(*N*-methylanilino)styrene was varied and

Table IV. Effect of Sensitizer Concentration on Photocyclization

[Enamine] $\times 10^2$	[Sens] ^a $\times 10^2$	Moles of product $\times 10^5$	ϕ_{product}	$\phi_{\text{sens}}/\phi_0$
1.09	0	0.924	0.150	
1.09	0	1.32	0.214	
1.09	0.656 Xan	0.233	0.038	0.208
1.09	0.875 Xan	0.234	0.038	0.208
1.09	2.18 Xan	0.128	0.021	0.115
1.09	0.211 MK	0.574	0.093	0.508
1.09	0.633 MK	0.479	0.078	0.423
1.09	2.11 MK	0.307	0.050	0.272

^a Xan = xanthone, MK = Michler's ketone.

the concentration of Michler's ketone sensitizer was kept constant. Eight samples were prepared. Six contained 1.00 ml of a 5.82×10^{-2} M solution of Michler's ketone in benzene. All contained between 0.50 and 2.00 ml of a 9.96×10^{-2} M solution of the enamine. Irradiations were carried out on the linear apparatus for 30 min. Light intensity was 2.28×10^{16} quanta/sec. Samples were concentrated by blowing nitrogen over the solution before analysis. The results are shown in Table V.

Table V. Effect of Enamine Concentration on Sensitized Photocyclization

[Enamine] $\times 10^2$	[Sens] $\times 10^2$	Moles of product $\times 10^5$	ϕ_{prod}	$\phi_{\text{sens}}/\phi_0$
3.32	0	1.19	0.204	
3.32	0	0.928	0.160	
6.64	1.94	0.925	0.159	0.875
5.32	1.94	0.733	0.126	0.694
4.66	1.94	0.554	0.095	0.523
3.32	1.94	0.568	0.097	0.534
2.50	1.94	0.258	0.044	0.242
1.66	1.94	0.181	0.031	0.171

Attempted Quenching with 1,3-Cyclohexadiene. Commercial 1,3-cyclohexadiene was distilled before use. Six samples were prepared. Each contained 1.00 ml of a 1.37×10^{-1} M solution of the enamine in benzene. Five samples contained between 0.10 and 2.00 ml aliquots of a 1.75×10^{-1} M solution of 1,3-cyclohexadiene (Q) in benzene. Samples were irradiated for 45 min on the merry-go-round apparatus with the Corning 7-60 filters. Enamine absorbed 100% of the light in all cases, and light intensity in quanta per second is tabulated for each position. Results are given in Table VI.

Table VI. Effect of 1,3-Cyclohexadiene on Photocyclization

[Enamine] $\times 10^2$	[Q] $\times 10^2$	1×10^{16}	Moles of product $\times 10^5$	ϕ_{prod}	ϕ_q/ϕ_0
4.57	0	3.05	2.87	0.210	1.00
4.57	0.583	3.03	2.78	0.205	0.98
4.57	1.16	2.95	2.76	0.208	0.99
4.57	2.92	3.14	2.68	0.191	0.91
4.57	5.83	2.96	2.73	0.206	0.98
4.57	11.6	2.91	2.64	0.202	0.96

X-Ray Crystal Structure. A sample of *trans*-6,8-dibromo-1,2,3,4-4a,9a-hexahydro-4a,9-dimethylcarbazole was recrystallized from absolute ethanol and dried in a vacuum pistol. Microscopic examination revealed that the clear, white crystals were platelike with sharply defined faces. Crystals were selected and mounted in thin-walled Lindemann glass capillaries to prevent decomposition. Preliminary Weissenberg and precession photographs exhibited 2/m Laue symmetry indicating a monoclinic space group. The following systematic absences were observed: $h0l$, when $h +$

Table VII. Final Fractional Coordinates

Atom	x	y	z
C(1)	0.2361 (4)	-0.2104 (6)	0.8538 (6)
C(2)	0.1735 (6)	-0.1629 (8)	0.0063 (4)
C(3)	0.0845 (5)	-0.1005 (2)	0.9328 (8)
C(4)	0.1269 (4)	-0.0364 (2)	0.7874 (2)
C(4a)	0.1797 (7)	-0.0875 (7)	0.6379 (9)
C(5)	0.2126 (1)	0.0355 (0)	0.4033 (7)
C(5a)	0.2418 (7)	-0.0373 (0)	0.5004 (4)
C(6)	0.2765 (5)	0.0591 (1)	0.2678 (8)
C(7)	0.3673 (2)	0.0153 (8)	0.2222 (3)
C(8)	9.3966 (6)	-0.0587 (5)	0.3266 (2)
C(8a)	0.3359 (8)	-0.0871 (8)	0.4690 (0)
N(9)	0.3401 (7)	-0.1587 (6)	0.5834 (1)
C(9a)	0.2765 (9)	-0.1372 (8)	0.7358 (2)
C(11)	0.0989 (0)	-0.1462 (3)	0.5237 (8)
C(10)	0.4463 (9)	-0.1993 (7)	0.6391 (5)
Br(12)	0.5123 (4)	-0.1200 (1)	0.2448 (5)
Br(13)	0.2418 (3)	0.1601 (1)	0.1293 (1)

Table VIII. Final Thermal Parameters^a

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.0132 (2)	0.0067 (5)	0.0399 (2)	-0.0007 (6)	0.0041 (0)	0.0059 (9)
C(2)	0.0136 (9)	0.0095 (6)	0.0289 (2)	-0.0021 (4)	0.0048 (8)	-0.0003 (3)
C(3)	0.0128 (2)	0.0085 (7)	0.0318 (6)	0.0016 (2)	0.0044 (7)	0.0032 (5)
C(4)	0.0128 (9)	0.0079 (4)	0.0288 (2)	0.0010 (0)	0.0041 (4)	-0.0004 (8)
C(4a)	0.0092 (9)	0.0056 (6)	0.0251 (1)	0.0005 (8)	0.0037 (3)	0.0007 (3)
C(5)	0.0109 (3)	0.0045 (5)	0.0315 (9)	-0.0011 (2)	0.0037 (4)	0.0005 (0)
C(5a)	0.0103 (9)	0.0047 (8)	0.0276 (3)	-0.0000 (8)	0.0025 (2)	-0.0010 (0)
C(6)	0.0112 (7)	0.0044 (5)	0.0403 (5)	-0.0011 (3)	-0.0007 (8)	0.0005 (2)
C(7)	0.0113 (8)	0.0048 (4)	0.0370 (5)	-0.0018 (3)	0.0025 (1)	-0.0016 (5)
C(8)	0.0088 (7)	0.0068 (8)	0.0349 (9)	-0.0012 (3)	0.0072 (2)	-0.0036 (9)
C(8a)	0.0091 (8)	0.0049 (4)	0.0341 (9)	-0.0003 (0)	0.0007 (1)	-0.0015 (6)
N(9)	0.0107 (4)	0.0051 (3)	0.0321 (4)	0.0005 (6)	0.0022 (3)	0.0008 (2)
C(11)	0.0094 (8)	0.0060 (3)	0.0336 (8)	-0.0004 (8)	-0.0003 (4)	-0.0005 (5)
C(10)	0.0099 (5)	0.0079 (5)	0.0467 (3)	0.0012 (1)	-0.0009 (6)	0.0021 (8)
Br(12)	0.0132 (4)	0.0106 (7)	0.0531 (9)	0.0023 (9)	0.0102 (6)	0.0003 (4)
Br(13)	0.0154 (0)	0.0059 (9)	0.0430 (4)	-0.0011 (6)	0.0020 (2)	0.0033 (3)

^a The form of the anisotropic temperature factor is $\exp(-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl])$.

Table IX. Selected Bond Distances^a

Atom	Atom	Distance, Å
C(1)	C(2)	1.600 (0.021)
C(1)	C(9a)	1.554 (0.017)
C(2)	C(3)	1.547 (0.021)
C(3)	C(4)	1.590 (0.018)
C(4)	C(4a)	1.549 (0.016)
C(4a)	C(5a)	1.542 (0.015)
C(4a)	C(9a)	1.557 (0.016)
C(4a)	C(11)	1.552 (0.016)
C(5)	C(5a)	1.382 (0.015)
C(5)	C(6)	1.370 (0.017)
C(5a)	C(8a)	1.456 (0.016)
C(6)	C(7)	1.402 (0.017)
C(6)	Br(13)	1.920 (0.013)
C(7)	C(8)	1.425 (0.017)
C(8)	C(8a)	1.410 (0.017)
C(8)	Br(12)	1.887 (0.012)
C(8a)	N(9)	1.403 (0.015)
N(9)	C(9a)	1.460 (0.016)
N(9)	C(10)	1.498 (0.016)
C(10)	Br(12)	3.289 (0.017)

^a Standard deviations obtained from ORFFE in parentheses.

$l = 2n + 1, 0k0$, when $k = 2n + 1$. These absences indicate space group $P2_1/n(C_{2h}^2)$, alternate setting). The unit cell parameters at room temperature are $a = 12.53 \pm 0.02$ Å, $b = 15.88 \pm 0.02$ Å, $c = 7.22 \pm 0.02$ Å, $\beta = 95.60 \pm 0.10^\circ$. These parameters were obtained by a least-squares fit to ten independent reflection angles measured on a diffractometer. A calculated density of 1.670 g/cc indicated four molecules per unit cell or one molecule per

asymmetric unit. An accurate observed density was not obtained because of solubility and decomposition difficulties.

For data collection, a crystal having approximate dimensions 0.1 mm \times 0.1 mm \times 0.05 mm was selected.

Data were collected at room temperature utilizing a Hilger-Watts four circle diffractometer equipped with scintillation counter and using Ni-filtered Cu K α radiation [1.5418 Å]. Within a 2θ sphere of 110° all data in the hkl and $\bar{h}\bar{k}l$ octants were recorded using the θ - 2θ scan technique with a take-off angle of 8° .

As a general check on electronic and crystal stability, the intensities of three standard reflections were measured periodically during the data collection. No significant change in intensity was observed. The absorption coefficient for Cu radiation is 48 cm^{-1} , and an absorption correction was judged to be unnecessary. The standard deviations of the intensity, $\sigma[I]$, were estimated by use of $\sigma[I] = ([\text{total count}] + [\text{background}] + [5\% \text{ total count}]^2 + [5\% \text{ background}]^2)^{1/2}$. Of the 1806 reflections measured, 1444 had $I > 3\sigma[I]$ and these were considered observed and were used in the refinement. The intensities were corrected for Lorentz and polarization factors to give F_o^2 .

Table X. Selected Bond Angles^a

Atom	Atom	Atom	Angle, deg
C(1)	C(2)	C(3)	116.8 (1.1)
C(1)	C(9a)	C(4a)	110.2 (1.0)
C(1)	C(9a)	N(9)	117.9 (1.0)
C(2)	C(3)	C(4)	111.1 (1.1)
C(2)	C(1)	C(9a)	103.4 (1.0)
C(3)	C(4)	C(4a)	108.4 (1.0)
C(4)	C(4a)	C(5a)	109.6 (1.0)
C(4)	C(4a)	C(9a)	108.4 (0.9)
C(4)	C(4a)	C(11)	112.5 (1.0)
C(4a)	C(5a)	C(5)	129.2 (1.0)
C(4a)	C(5a)	C(8a)	106.6 (0.9)
C(4a)	C(9a)	N(9)	103.6 (0.8)
C(5)	C(5a)	C(8a)	123.6 (1.0)
C(5)	C(6)	C(7)	125.3 (1.1)
C(5)	C(6)	Br(13)	118.7 (1.0)
C(5a)	C(4a)	C(9a)	97.7 (0.8)
C(5a)	C(4a)	C(11)	108.2 (0.9)
C(5a)	C(5)	C(6)	116.3 (1.1)
C(5a)	C(8a)	C(8)	116.2 (1.0)
C(5a)	C(8a)	N(9)	112.2 (1.1)
C(6)	C(7)	C(8)	117.1 (1.1)
C(7)	C(6)	Br(13)	115.8 (1.0)
C(7)	C(8)	C(8a)	121.2 (1.1)
C(7)	C(8)	Br(12)	115.2 (0.8)
C(8)	C(8a)	N(9)	134.1 (1.1)
C(8a)	C(8)	Br(12)	123.2 (1.0)
C(8a)	N(9)	C(9a)	105.1 (0.9)
C(8a)	N(9)	C(10)	119.2 (1.0)
C(9a)	N(9)	C(10)	115.7 (1.0)

^a Standard deviations obtained from ORFFE in parentheses.

A three-dimensional Patterson synthesis was computed from the observed data.²⁷ The positions of the two independent bromine atoms were obtained from this synthesis. The remaining non-hydrogen atoms were found by successive structure factor calculations and electron density syntheses. The positions were refined by full matrix least-squares techniques with anisotropic thermal parameters for all atoms to a conventional discrepancy index [$R = \sum ||F_o| - |F_c|| / \sum |F_o|$] of 0.089 and a weighted R factor [$wR = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$] of 0.119.^{28,29} The scattering factors were those of Hanson, *et al.*³⁰

A final electron density difference map showed no peaks greater

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(30) H. P. Hanson, F. Merman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

than 0.4 e/Å³. No unusual trends in F_o and F_c values were found and the weighting scheme was judged to be a reasonable one.

In Tables VII and VIII we give the final values of the positional parameters and the anisotropic thermal parameters.

In Tables IX and X we give the final intramolecular bond distances and angles along with their standard deviations as derived from the inverse matrix.³¹

In Table XI³² are given the values of $10F_o$ and $10F_c$, respectively. A drawing of the molecule including anisotropic thermal motion is presented in Figure 1.³³

Acknowledgment. This research was supported by Grant G-6740 from the National Science Foundation.

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(32) Listings of the observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publication, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit \$3.00 for photocopy or \$2.00 for microfiche.

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Photochemical Transformations of Small Ring Carbonyl Compounds. XXX. Electron Transfer in the Photochemistry of Azetidiny Ketones¹

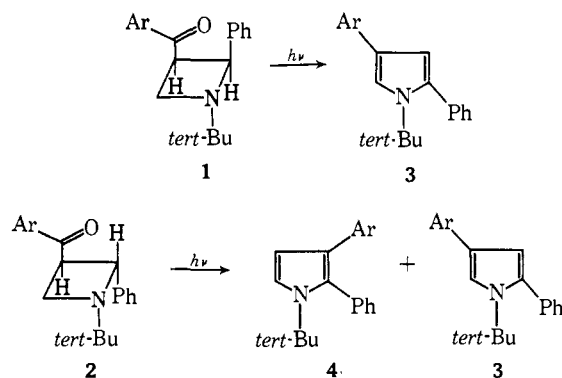
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Abstract: The photoinduced ring expansion of several azetidiny ketones has been examined. Upon irradiation with ultraviolet light in ethanolic solution, 3-arylazetidines **5** and **6** rearrange smoothly and in high yield to arylpyrroles **9** and **10**. Irradiation of 3-*N*-*tert*-butylazetidiny *n*-butyl ketone (**7**) gave two primary photoproducts. The ratio of the two products was found to vary with the nature of the solvent. A mechanism involving intramolecular electron transfer from nitrogen to the excited triplet state and subsequent formation of a charge transfer complex is proposed. While 3-arylazetidines undergo smooth rearrangement to arylpyrroles, the isomeric 2-azetidiny ketone system affords a complex mixture of photoproducts.

Recently, we described the photochemical rearrangement of 3-arylazetidines to diarylpyrroles.⁴ In our studies we showed that the photoreaction proceeds with low quantum efficiency and low sensitivity to diffusion-controlled quenchers. These properties led us to suggest initial rapid intramolecular electron transfer between the ketone triplet and the electron pair on nitrogen followed either by proton transfer or charge destruction and quenching.⁴ Further studies on the excited state behavior of azetidiny ketones seemed desirable for several reasons: (a) to determine whether the photorearrangement was a general phenomenon, (b) to explore the photobehavior of the isomeric 2-arylazetidiny ketone system, (c) to relate photobehavior to selected structural modifications, and (d) to assess the importance of electronic perturbations on the

electron-transfer route. The present paper describes the photochemical properties of several azetidiny ke-



(1) For part XXIX, see A. Padwa, *Accounts Chem. Res.*, **4**, 48 (1971).
(2) Alfred P. Sloan Foundation Research Fellow, 1968-1970.
(3) NDEA Predoctoral Fellow, 1968-1970.
(4) A. Padwa and R. Gruber, *J. Amer. Chem. Soc.*, **92**, 100, 107 (1970).

tones in which structural modifications have been made to provide further insight into the behavior of the excited state of these heterocyclic ketones.